Rb-Promoted Molybdenum Carbide Nano-Catalysts for Higher Alcohol Synthesis from Syngas

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Heng Shou

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Doctor of Philosophy (Chemical Engineering)

Heng Shou

Author

This dissertation has been read and approved by the examining committee

Robert J. Deen

Thesis advisor

Gregory L. ...

Philip ...

John T. Yallop
Matthew ...

Accepted for the School of Engineering and Applied Science

J. H. Aylor

Dean, School of Engineering
and Applied Science

May 2013

Abstract

The catalytic conversion of synthesis gas derived from coal, natural gas or renewable biomass is among the most promising routes to produce alternative energy carriers and chemical feedstocks. Although production of diesel fuel and methanol from syngas has been well-developed on a world scale, there is still a growing need for the direct synthesis of higher (C₂+) alcohols for use as fuel additives or chemical precursors. When properly promoted by alkali metals, molybdenum carbide is considered to be a promising catalyst for this process. In this study, molybdenum carbide nanoclusters (1-3 nm) were synthesized on various supports using wet impregnation. The selectivity of catalytic syngas conversion toward C₂ alcohols was enhanced with added Rb₂CO₃ promoter. Although the alcohol selectivity decreased with CO conversion, the loss can be partially recovered with addition of a cobalt promoter. *In situ* X-ray absorption spectroscopy (XAS) was conducted in a self-built high-pressure reactor cell operating at syngas reaction conditions (573 K, 30 bar syngas), which revealed the existence of surface oxygen on Mo₂C and the structural modification of Rb₂CO₃ promoter in CO hydrogenation. An air-free sample preparation method was developed for *ex situ* XAS analysis, which allowed direct evidence of surface oxidation of Mo₂C caused by passivation to be observed. The reduction of highly dispersed cobalt domains (< 2 nm) in co-existence with Mo₂C was also observed by XAS.

Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) was used to characterize the surface of Mo₂C nanoclusters at working conditions. With CO as a probe, DRIFTS unveiled the structure-function relationship between the Rb promoter and the catalyst for the first time. A strong correlation between the red-shifted band of

adsorbed CO and the elevated alcohol selectivity was observed. More importantly, experimental results from probe reactions and IR spectroscopy, combined with the first-principle theoretical calculations (performed in collaboration with Georgia institute of Technology), suggested that the basic Rb_2CO_3 promoter likely interacted with the Mo_2C catalyst by neutralizing the acidic hydroxyl groups on the catalyst surface.

Finally, an advanced multi-component system for steady-state isotopic transient kinetic analysis (SSITKA) was constructed to allow the measurement of fundamental kinetic parameters. The multi-product SSITKA revealed that the intrinsic turnover frequency (TOF) on the “slow” Mo_2C catalysts was in fact comparable to other active catalysts for CO hydrogenation such as those based on Fe and Rh. Consequently, the very small coverage of the reactive intermediates on Mo_2C surface was discovered to be the reason for its low apparent activity in CO hydrogenation.

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Chapter 1.

Introduction

1.1 Higher alcohol synthesis: A potential way to selectively convert syngas

Limited crude oil reserves and competition with the food industry associated with fermentation-based biofuel production inspire new research efforts on effective catalytic transformations of alternative carbon sources to produce energy carriers and chemical feedstocks. Syngas ($\text{CO} + \text{H}_2$) can be derived from gasification of coal [1], steam reforming of natural gas [2] and gasification [3] or aqueous-phase reforming [4] of renewable biomass, and is a platform for the synthesis of fuels and chemicals. Given the abundant reserves of coal and natural gas, especially the newly discovered shale gas, North America possesses vast potential resources of syngas, which provides a platform for producing of alternative fuels and chemicals and attracts new efforts in research and development.

Fuels and chemicals produced from syngas are shown in Figure 1.1, which include hydrogen, methanol, diesel, isobutanol, ethanol, etc. [5] Fischer–Tropsch synthesis (FTS) of hydrocarbons has received growing attention as a source of low-sulfur diesel fuel because of the uncertainty of crude oil prices. Fischer–Tropsch synthesis has been applied on a large scale in some industrial sectors in Qatar (29,000 barrels per day (bpd)), Malaysia (15,000 bpd), and South Africa (150,000 bpd), and a 140,000 bpd liquid petroleum product capacity is under construction in Qatar (Shell’s Pearl GTL project) [1]. However, the popularity of FTS is hampered by high capital costs as well as high operation and maintenance costs [6]. Higher alcohol (C_2+ alcohols) synthesis from

synthesis gas, as a source of chemical feedstocks, however, might be more commercially attractive. For example, Celanese Corporation reported an expected ethanol price of \$1.4/gallon with their new coal-to-ethanol technology via acetic acid [7,8], and E. I. du Pont de Nemours and Company and BP have a stated goal for a butanol price of \$1/gallon with their bio-based process currently under development [9]. Considering that methanol is produced from syngas over Cu-ZnO catalysts, which possesses huge global demand of approximately 40 million tonnes annually [10], it is reasonable to expect a comparably low price for higher alcohols produced by a similar catalytic process, assuming production and selectivity achievements are realized.

Figure 1.1 Pathways for syngas utilization, depicted on the base of Spath and Dayton [5]

Because of methanol's low solubility in gasoline, it needs to be further converted to another molecule such as methyl *tert*-butyl ether (MTBE) before blended into gasoline. However, MTBE is being phased out as a fuel additive because of environmental concerns. Higher alcohols, on the other hand, have mutual solubility with gasoline and

ethanol has been widely used in the US as a gasoline additive. Since almost all the ethanol used for fuel is produced from fermentation, there is still a need for a more efficient catalytic process for the production of ethanol (and other higher alcohols).

In higher alcohol synthesis from syngas, the major reaction is higher alcohol formation, while methanol synthesis, Fischer–Tropsch synthesis, water-gas shift reaction and the Boudouard reaction comprise the side reactions:

1.2 Catalyst candidates for higher alcohol synthesis: The choice of molybdenum carbide

An effective catalyst for the production of higher alcohols from syngas needs to incorporate multiple functionalities, such as CO activation, hydrogenation, carbon chain growth, alcohol coupling, etc., with C–O bonds being partially preserved. Lee *et al.* [11] depicted the simplified scheme (Figure 1.2) of CO conversion based on the ideas discussed by Ponc and co-workers [12,13]. According to this scheme, all the products can be derived from an adsorbed intermediate $^*\text{C}_m\text{H}_n$, (where * denotes a surface site). This intermediate can undergo four different transformations to products namely: (1) hydrogenation to alkanes, (2) carbonylation to alcohol precursors, (3) desorption as olefins, and (4) further chain growth by inserting $^*\text{CH}_x$. In this competitive process, hydrogenation activity of a catalyst needs to be partially suppressed to enhance

production of alcohols (as well as alkenes). Thus, no single-component transition metal catalyst has been discovered to effectively catalyze higher alcohol synthesis.

Figure 1.2 Reaction pathway for CO hydrogenation adapted from Lee *et al.* [11]

Exploratory research on higher alcohol synthesis from syngas has discovered some promising candidates [13–17]. Rhodium-based catalysts are effective for the formation of ethanol and other C2-oxygenates from syngas [3,18–20]. Although Rh-based catalysts possess the best ethanol selectivity among the various catalysts for syngas conversion investigated [21–24], the high selectivity towards hydrocarbons, especially CH_4 , likely prohibits its large-scale utilization. Furthermore, the very high cost of Rh motivates substantial research interests in the non-precious metal alternatives to Rh.

Several non-precious metal catalysts for higher alcohol synthesis from syngas have thus been evaluated and include, for example, Cu catalysts (Cu/ZnO and Cu/Cr₂O₃, primarily for isobutanol [14]), Cu–Co catalysts [25], Zn–Cr–K [15], and promoted Fischer–Tropsch catalysts [3,19], but improvements in the overall catalytic activity, alcohol selectivity, and long-term stability of these catalytic materials for higher alcohol synthesis are still needed.

Methanol synthesis catalysts $\text{ZnO/Cr}_2\text{O}_3$ (relatively high temperature) and Cu/ZnO (relatively low temperature), if promoted with alkali metal oxides, produce C1-C6 linear and branched alcohols, especially isobutanol [14,26], primarily via aldol condensation or methanol homologation [27]. However, their ethanol selectivity is rather poor because of the fast chain growth of the C2 surface intermediate [28,29]. Alkali-metal-doped Fischer-Tropsch catalysts, although promoting the selectivity of C2+ alcohols over methanol, produce mostly hydrocarbons (> 50%) from synthesis gas [19]. The performance of Cu-Co-based catalysts is also poor from the practical point of view, because of their long-term instability and their low alcohol selectivity [30–34].

Metallic Mo adsorbs CO too strongly for CO dissociation, and hence inhibits the reaction of CO. In the presence of the structurally incorporated C, P, or S, however, the interaction between Mo and CO is weakened, which facilitates CO dissociation, either directly on Mo_2C , or assisted by hydrogen on MoS_2 , Mo_2C , and MoP [17]. When promoted by alkali metals, Mo-based catalysts also show encouraging properties for higher alcohol synthesis from CO hydrogenation [17]. It has also been reported that Mo sulfide, phosphide, nitride, and carbide resist sulfur poisoning to some extent [35]. Additional advantages of Mo-based catalysts for practical applications include: less severe catalyst deactivation due to coke deposition (even with a syngas containing a low H_2/CO ratio of less than 2), higher selectivity to linear alcohols (especially ethanol), and low sensitivity to CO_2 in the syngas [18]. Both supported and unsupported MoS_2 -based catalysts have been heavily investigated for higher alcohol synthesis [36–42] since The Dow Chemical Company first developed it in the 1980's [43–47]. Molybdenum sulfide catalysts effectively produce alcohol from syngas, with alcohol selectivity higher than 75%

(on a CO₂-free basis) and total alcohol yield as high as 400 mg g_{cat}⁻¹ h⁻¹. However, trace amounts of H₂S in the feed were required to sustain the performance of the MoS₂-based catalysts [44]. Moreover, small amounts of sulfur may enter the carbon skeleton of the products, which is problematic as the world moves toward the use of very-low-sulfur fuels [39]. Thus, there is a need for a non-sulfided alternative for MoS₂-based catalyst in this process, among which molybdenum carbide has demonstrated some promise when properly promoted.

After the landmark discovery by Levy and Boudart forty years ago [48], early transition metal carbides are recognized as potential substitutes to Pt-group metal catalysts because of their similar surface electronic properties [49,50]. Using a temperature-programmed carburization with reductive carburizing gas (such as a mixture of CH₄ and H₂), these materials can be synthesized from the corresponding oxide precursors [51]. The carburization temperature is programmed to increase at a constant rate until certain maximum temperature is reached. This method directly converts the oxide precursor into carbide without forming the metallic state that is more prone to sinter and hence to result in low specific surface area or low dispersion [52].

Early transition metal carbides (e.g., molybdenum carbide, Mo₂C) have been demonstrated to be catalytically active for a variety of reactions, such as hydrogenolysis [51], isomerization [54,55], dehydrogenation [56,57], condensation [57,58], water-gas shift [59], CO hydrogenation [11,60–63], etc. When properly promoted, molybdenum carbide has demonstrated modest selectivity to higher alcohols from syngas at appropriate conditions [62,63].

The product distribution observed with Mo-based catalysts in CO hydrogenation followed the classic Anderson–Schulz–Flory distribution for hydrocarbons and C₂+ alcohols [63–65]. A CO insertion mechanism was speculated for the carbon chain growth in the formation of both hydrocarbons and alcohols [36], which has yet been experimentally proved.

Besides the unclear carbon chain growth mechanism, the fundamentals of the catalysts have yet been well interpreted in many other aspects, including the *in situ* metal speciation, interaction between the promoters and the catalyst, reaction kinetics, etc. Moreover, improvement on the catalyst performance is still needed.

1.3 Summary of research topics of interest

1.3.1 Influence of oxygen

It is known that the highly reactive carbide surface is very oxophilic and therefore needs to be passivated before exposure to air. Prior works have described the various behaviors of oxygen-modified carbide surfaces in different reactions. For example, Boudart and co-workers claimed that surface oxygen inhibits the very high reactivity of fresh tungsten carbide for hydrogenolysis of hydrocarbons but forms acid sites that catalyze hydrocarbon isomerization reactions through coupled dehydrogenation and carbenium ion reactions [66–70]. A similar phenomenon was also observed on Mo₂C catalysts [54]. The presence of acid sites on the catalyst formed by passivation would likely be detrimental to the desired product distribution in higher alcohol synthesis from syngas. In other work, Liu *et al.* reported that a carbide-modified W(111) surface was highly selective for the dehydrogenation of cyclohexane to benzene after exposure to O₂ at 900 K, but was inactive to cyclohexane after exposure to O₂ at <600 K [71]. Similarly,

Hwu *et al.* found that a carbide-modified Mo(110) surface exposed to O₂ at 900 K exhibited decomposition activity for cyclohexene, ethylene and methanol, whereas the carbide surface was relatively unreactive toward those substrates after O₂ exposure at 600 K [72]. Nagai *et al.* also show that passivation of molybdenum carbide with dilute O₂ at room temperature reduced its activity in CO₂ hydrogenation to form CO and CH₄ [73]. Using FT-IR spectroscopy, Li and co-workers revealed that a surface passivation procedure with dilute O₂ at room temperature irreversibly modified a fresh molybdenum carbide surface, hence significantly reducing the number of sites for CO adsorption [74,75]. Evidently, carbidic carbon atoms and/or metal atoms react with the O₂ used in passivation, which can significantly modify the observed reactivity of carbide catalysts. Evidently, carbidic carbon atoms and/or metal atoms react with the O₂ used in passivation, which can significantly modify the observed reactivity of carbide catalysts. Therefore, the influence of O₂ passivation on reactivity must be examined as part of any comprehensive study of carbidic materials for catalysis.

1.3.2 CO adsorption on molybdenum carbide

Aegerter *et al.* attributed a feature of 2178 cm⁻¹ to CO adsorption on coordinatively-unsaturated Mo(IV) on a passivated Mo₂C/γ-Al₂O₃ catalyst after activation in H₂ [76]. The features in the range of 2071-2054 cm⁻¹ have been assigned to linearly adsorbed CO on a clean hexagonal Mo₂C foil [77], on carbidic Mo sites present on Mo₂C/γ-Al₂O₃ catalysts [74–76], and on modeled surfaces of hexagonal Mo₂C described by DFT [78,79]. A shoulder CO band at 2125 cm⁻¹ has also been reported when Mo₂C foil was pre-exposed to O₂ [77]. Bands for linearly adsorbed CO (2015 cm⁻¹) and bridge-bonded CO (1850 cm⁻¹) were also seen by high-resolution electron energy

loss spectroscopy (HREELS) on a Mo (110) single crystal with a surface carbide layer [80]. Moreover, ketenylidene species have been proven to be the most stable configuration of adsorbed CO on a C-terminated Mo₂C surface by DFT [81]. Ketenylidene also formed when CO was adsorbed on a W₂C surface that possessed a similar structure to Mo₂C, giving C–O stretching frequencies ranging from 1954 cm⁻¹ to 2041 cm⁻¹ with increasing CO coverage [82].

However, previous works had not demonstrated whether the adsorption modes of CO on Mo₂C mentioned above were catalytically relevant in CO hydrogenation. The CO adsorption experiments on the working catalysts are necessary for a better understanding of the catalyst surface.

1.3.3 The interaction between the alkali metal species and the molybdenum carbide catalyst

The addition of alkali metal species to Mo-based catalysts shifts the product selectivity in syngas conversion from hydrocarbons to alcohols. By using Auger electron spectroscopy, Lee *et al.* observed better dispersion of K promoter on MoS₂ [38] and Mo₂C [11] catalysts for alcohol synthesis after being exposed to syngas reaction conditions, and hence speculated that the promotional effect of alkali metal species was mostly the result of the surface sites being blocked from adsorbing reactants. By using diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), Koizumi *et al.* claimed that syngas adsorption on a MoS₂/γ-Al₂O₃ catalyst for CO hydrogenation was significantly suppressed by K species and the K-promoted Mo species were likely more oxidized than those on K-free MoS₂ [63]. Muramatsu *et al.* also studied the role of a K promoter on a Mo oxide catalyst for alcohol production from syngas and concluded that

K inhibits both dehydration of alcohols (to alkenes) and the hydrogenation of alkenes (to alkanes) [84]. For supported MoS₂-based catalysts, interactions between K promoters and Mo begins with the oxidized catalyst precursors [37,85–87] and that some K–Mo–S and/or K–Mo–S–O species are formed after sulfidation. However, it is still unclear whether the promoters enhance the activity of the catalysts for higher alcohol synthesis. Although CO adsorption has been used to probe the surfaces of MoS₂-based [88–93] and Mo₂C-based [74–77,94] catalysts, few of these studies addressed the promotional influence of the alkali metals on higher alcohol synthesis.

Han *et al.* [95] reported an optimized hexagonal Mo₂C structure for the adsorption of K and Rb atoms and found that they tended to be adsorbed on the C-terminated reconstructed hexagonal Mo₂C(001) surface, where the adsorbed K or Rb atom was coordinated with three C atoms and three Mo atoms. However, it was unclear whether this configuration was catalytically relevant to the actual catalyst surface during reaction.

Therefore, a better interpretation is needed on the interaction between the alkali metal promoter and the Mo₂C catalyst that affects the product distribution in CO hydrogenation, i.e., the structure-function relationship.

1.3.4 Cobalt as a secondary promoter

Since addition of cobalt to alkali-metal-promoted MoS₂ catalysts enhanced their activity in higher alcohol synthesis from syngas [96], and the Mo₂C- and MoS₂-based catalysts behave very similarly in syngas conversion, it is logical to explore the influence of Co on alkali-metal-promoted Mo₂C catalysts in the reaction. In fact, Sun and co-workers studied the influence of CO-hydrogenation-active components (Fe, Co and Ni) on unsupported Mo₂C for conversion of syngas and reported that the alcohol production

rate over Mo₂C catalysts was promoted by added Co and Fe, but not Ni, and Co was best promoter among the three [13,97]. Lucero *et al.* reported that Ni enhanced the productivity and ratio of ethanol to methanol over Na-promoted bulk Mo₂C catalysts [98]. However, the synergetic effects between Mo₂C and the transition metal promoter, especially the atomic interaction, have yet to be well explained. Moreover, optimization of the alcohol selectivity on this type of catalyst is still needed.

1.3.5 Nature of active sites on molybdenum carbide

The apparent reactivity of the Mo₂C-based catalysts was low compared to other elements that are active in CO hydrogenation. For example, the apparent turnover frequencies (TOFs) of CO (normalized by the amount of surface metal atoms) on Mo₂C/ α -Al₂O₃ catalysts [99] were approximately two orders of magnitude lower than that on a Fe–Rh/TiO₂ catalyst under similar conditions [20]. The very low apparent activity can be attributed to either the intrinsic slow turnover of the catalytic cycle or the small concentration of the active sites. Due to the high oxophilicity of Mo₂C, it needs an appropriate *in situ* pretreatment is needed to count the active sites on the surface of Mo₂C, which may not be achieved by a conventional methodology (like CO chemisorption). Therefore, a powerful *in situ* technique is needed to unveil the kinetic information on Mo₂C catalysts in CO hydrogenation.

1.4 Objectives in this study

This study explored the roles of structure, reaction conditions and catalyst passivation on catalyst performance in selective syngas conversion. The research efforts aim to understand:

1. The *in situ* metal speciation, including molybdenum carbide catalysts and the rubidium and cobalt promoters;
2. The nature of the promotional effect on molybdenum carbide, especially from the alkali metals;
3. The intrinsic kinetic parameters of CO hydrogenation on molybdenum carbide.

A variety of *in situ* techniques were used to study the catalysts at syngas working conditions, including X-ray absorption spectroscopy (XAS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and steady-state isotopic transient kinetic analysis (SSITKA). Catalysts were also characterized by transmission electron microscopy, elemental analysis, X-ray powder diffraction and surface area analysis.

Hydrogenation of CO was conducted in a fixed-bed stainless steel reactor at typical conditions of 573 K, 30 bar syngas and $H_2/CO = 1$. Rubidium was chosen to be the alkali metal promoter rather than the conventional potassium for a spectroscopic reason, since it has the appropriate edge energy for *in situ* transmission-mode XAS with high-pressure syngas. All the XAS experiments were conducted at beamlines X18B and X23A2 at National Synchrotron Light Source, Brookhaven National Laboratory. An air-free sample preparation method was also developed for *ex situ* XAS to simplify the operation on the beamline, which involved the use of glovebox. Infrared spectroscopy was performed in diffuse-reflectance-mode with loose-powder samples to simplify the sample preparation (transmission-mode IR needs the sample to be pelletized), and the DRIFTS reactor/cell also allowed sample pretreatment at syngas reaction conditions. The SSITKA method was used to study the intrinsic kinetics of CO hydrogenation on Mo_2C catalysts. The conventional SSITKA system in the lab was substantially upgraded for

multi-product analyses, which avoided problematic fragmentation and overlapping peaks in the mass spectrometer.

References of Chapter 1

- [1] D. Leckel, "Diesel Production from Fischer–Tropsch: The Past, the Present, and New Concepts," *Energy & Fuels* 23 (2009) 2342–2358.
- [2] J. Rostrup-Nielsen, "Fuels and Energy for the Future: The Role of Catalysis," *Catalysis Reviews: Science and Engineering* 46 (2004) 247–270.
- [3] J.J. Spivey, A. Egbebi, "Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas," *Chemical Society Reviews* 36 (2007) 1514–1528.
- [4] J.N. Chheda, G.W. Huber, J.A. Dumesic, "Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals," *Angewandte Chemie International Edition* 46 (2007) 7164–7183.
- [5] P.L. Spath, D.C. Dayton, "Preliminary Screening — Technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas," U.S. Department of Energy Report, Oak Ridge, TN, 2003.
- [6] G.W. Huber, S. Iborra, A. Corma, "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," *Chemical Reviews* 106 (2006) 4044–4098.
- [7] V.J. Johnston, L. Chen, B.F. Kimmich, J.T. Chapman, J.H. Zink, "Direct and selective production of ethanol from acetic acid utilizing a platinum/tin catalyst," U.S. Patent 7863489, 2011, to Celanese Corporation.
- [8] V.J. Johnston, L. Chen, B.F. Kimmich, J.T. Chapman, J.H. Zink, "Direct and selective production of ethanol from acetic acid utilizing a platinum/tin catalyst," U.S. Patent 8071821, 2011, to Celanese Corporation.
- [9] G. Hess, "BP and DuPont plan 'biobutanol'," *Chemical Engineering News* 84 (2006) 9.
- [10] G.A. Olah, A. Goeppert, G.K.S. Prakash, "Beyond Oil and Gas: The Methanol Economy," John Wiley & Sons, 2006.
- [11] J.S. Lee, S. Kim, Y.G. Kim, "Electronic and geometric effects of alkali promoters in CO hydrogenation over K/Mo₂C catalysts," *Topics in Catalysis* 2 (1995) 127–140.
- [12] V. Ponec, "Active centres for synthesis gas reactions," *Catalysis Today* 12 (1992) 227–254.

- [13] K. Fang, D. Li, M. Lin, M. Xiang, W. Wei, Y. Sun, "A short review of heterogeneous catalytic process for mixed alcohols synthesis via syngas," *Catalysis Today* 147 (2009) 133–138.
- [14] P. Forzatti, E. Tronconi, I. Pasquon, "Higher alcohol synthesis," *Catalysis Reviews: Science and Engineering* 33 (1991) 109–168.
- [15] I. Wender, "Reactions of synthesis gas," *Fuel Processing Technology* 48 (1996) 189–297.
- [16] R.G. Herman, "Advances in catalytic synthesis and utilization of higher alcohols," *Catalysis Today* 55 (2000) 233–245.
- [17] S. Zaman, K.J. Smith, "A review of molybdenum catalysts for synthesis gas conversion to alcohols: catalysts, mechanisms and kinetics," *Catalysis Reviews: Science and Engineering* 54 (2012) 41–132.
- [18] M.M. Bhasin, G.L. O'Connor, "Procede de preparation selective de derives hydrocarbones oxygenes a deux atomes de carbone," Belgian Patent 824822, 1975.
- [19] V. Subramani, S.K. Gangwal, "A review of recent literature to search for an efficient catalytic process for the conversion of syngas to ethanol," *Energy & Fuels* 22 (2008) 814–839.
- [20] M.A. Haider, M.R. Gogate, R.J. Davis, "Fe-promotion of supported Rh catalysts for direct conversion of syngas to ethanol," *Journal of Catalysis* 261 (2009) 9–16.
- [21] S.S.C. Chuang, R.W. Stevens, R. Khatri, "Mechanism of C₂+ oxygenate synthesis on Rh catalysts," *Topics in Catalysis* 32 (2005) 225–232.
- [22] J. Hu, Y. Wang, C. Cao, D.C. Elliott, D.J. Stevens, J.F. White, "Conversion of biomass-derived syngas to alcohols and C₂ oxygenates using supported Rh catalysts in a microchannel reactor," *Catalysis Today* 120 (2007) 90–95.
- [23] Z. Fan, W. Chen, X. Pan, X. Bao, "Catalytic conversion of syngas into C₂ oxygenates over Rh-based catalysts – Effect of carbon supports," *Catalysis Today* 147 (2009) 86–93.
- [24] D. Mei, R. Rousseau, S.M. Kathmann, V.-A. Glezakou, M.H. Engelhard, W. Jiang, C. Wang, M.A. Gerber, J.F. White, D.J. Stevens, "Ethanol synthesis from syngas over Rh-based/SiO₂ catalysts: A combined experimental and theoretical modeling study," *Journal of Catalysis* 271 (2010) 325–342.
- [25] P. Chaumette, P. Courty, A. Kiennemann, R. Kieffer, S. Boujana, G.A. Martin, J.A. Dalmon, P. Meriaudeau, C. Mirodatos, "Evolution of alcohol synthesis catalysts under syngas," *Industrial & Engineering Chemistry Research* 33 (1994) 1460–1467.

- [26] A. Beretta, Q. Sun, R.G. Herman, K. Klier, "Production of methanol and isobutyl alcohol mixtures over double-bed cesium-promoted Cu/ZnO/Cr₂O₃ and ZnO/Cr₂O₃ catalysts," *Industrial & Engineering Chemistry Research* 35 (1996) 1534–1542.
- [27] J.G. Nunan, C.E. Bogdan, K. Klier, K.J. Smith, C.-W. Young, R.G. Herman, "Methanol and C₂ oxygenate synthesis over cesium doped CuZnO and Cu/ZnO/Al₂O₃ catalysts: A study of selectivity and ¹³C incorporation patterns," *Journal of Catalysis* 113 (1988) 410–433.
- [28] K.J. Smith, R.B. Anderson, "A chain growth scheme for the higher alcohols synthesis," *Journal of Catalysis* 85 (1984) 428–436.
- [29] K.J. Smith, C.W. Young, R.G. Herman, K. Klier, "Development of a kinetic model for alcohol synthesis over a cesium-promoted copper/zinc oxide catalyst," *Industrial & Engineering Chemistry Research* 30 (1991) 61–71.
- [30] V. Mahdavi, M.H. Peyrovi, M. Islami, J.Y. Mehr, "Synthesis of higher alcohols from syngas over Cu-Co₂O₃/ZnO, Al₂O₃ catalyst," *Applied Catalysis A: General* 281 (2005) 259–265.
- [31] V. Mahdavi, M.H. Peyrovi, "Synthesis of C₁-C₆ alcohols over copper/cobalt catalysts: Investigation of the influence of preparative procedures on the activity and selectivity of Cu-Co₂O₃/ZnO, Al₂O₃ catalyst," *Catalysis Communications* 7 (2006) 542–549.
- [32] N. Tien-Thao, H. Alamdari, M.H. Zahedi-Niaki, S. Kaliaguine, "LaCo_{1-x}Cu_xO_{3-δ} perovskite catalysts for higher alcohol synthesis," *Applied Catalysis A: General* 311 (2006) 204–212.
- [33] N. Tien-Thao, M.H. Zahedi-Niaki, H. Alamdari, S. Kaliaguine, "Conversion of syngas to higher alcohols over nanosized LaCo_{0.7}Cu_{0.3}O₃ perovskite precursors," *Applied Catalysis A: General* 326 (2007) 152–163.
- [34] N. Tien-Thao, M. Hassan Zahedi-Niaki, H. Alamdari, S. Kaliaguine, "Effect of alkali additives over nanocrystalline Co–Cu-based perovskites as catalysts for higher-alcohol synthesis," *Journal of Catalysis* 245 (2007) 348–357.
- [35] S.T. Oyama, "Novel catalysts for advanced hydroprocessing: transition metal phosphides," *Journal of Catalysis* 216 (2003) 343–352.
- [36] J.M. Christensen, P.A. Jensen, N.C. Schiødt, A.D. Jensen, "Coupling of Alcohols over Alkali-Promoted Cobalt–Molybdenum Sulfide," *ChemCatChem* 2 (2010) 523–526.
- [37] Y. Avila, C. Kappenstein, S. Pronier, J. Barrault, "Alcohol synthesis from syngas over supported molybdenum catalysts," *Applied Catalysis A: General* 132 (1995) 97–109.

- [38] J.S. Lee, S. Kim, K.H. Lee, I.-S. Nam, J.S. Chung, Y.G. Kim, H.C. Woo, "Role of alkali promoters in K/MoS₂ catalysts for CO-H₂ reactions," *Applied Catalysis A: General* 110 (1994) 11–25.
- [39] J.M. Christensen, P.M. Mortensen, R. Trane, P.A. Jensen, A.D. Jensen, "Effects of H₂S and process conditions in the synthesis of mixed alcohols from syngas over alkali promoted cobalt-molybdenum sulfide," *Applied Catalysis A: General* 366 (2009) 29–43.
- [40] V.R. Surisetty, A. Tavasoli, A.K. Dalai, "Synthesis of higher alcohols from syngas over alkali promoted MoS₂ catalysts supported on multi-walled carbon nanotubes," *Applied Catalysis A: General* 365 (2009) 243–251.
- [41] G. Budroni, R. Bruening, D. Ferrari, D. Nieskens, N. Rane, "Conversion of syngas to mixed alcohols on supported CoMoS_x catalysts," *Patent Application* (2012) WO 2012078276 A1 20120614, to The Dow Chemical Company.
- [42] G. Budroni, R. Bruening, D. Ferrari, D. Nieskens, N. Rane, "Conversion of syngas to mixed alcohols on chromium-promoted, supported CoMoS_x catalysts," *Patent application* (2012) WO 2011-US59512 A1 20120614, to The Dow Chemical Company.
- [43] G.J. Quarderer, G.A. Cochran, "Catalytic process for producing mixed alcohols from hydrogen and carbon monoxide," European Patent EP0119609, 1984, to The Dow Chemical Company.
- [44] M.M. Conway, C.B. Murchison, R.R. Stevens, "Method for adjusting methanol to higher alcohol ratios," U.S. Patent 4675344, 1987, to The Dow Chemical Company.
- [45] G.J. Quarderer, G.A. Cochran, "Process for producing alcohols from synthesis gas," U.S. Patent 4749724, 1988, to The Dow Chemical Company.
- [46] R.R. Stevens, "Process for producing alcohols from synthesis gas," U.S. Patent 4752622, 1988, to The Dow Chemical Company.
- [47] R.R. Stevens, "Process for producing alcohols from synthesis gas," U.S. Patent 4882360, 1989, to The Dow Chemical Company.
- [48] R.B. Levy, M. Boudart, "Platinum-like behavior of tungsten carbide in surface catalysis," *Science* 181 (1973) 547–549.
- [49] H.H. Hwu, J.G. Chen, "Surface chemistry of transition metal carbides," *Chemical Reviews* 105 (2005) 185–212.
- [50] J.G. Chen, "Carbide and nitride overlayers on early transition metal surfaces: preparation, characterization, and reactivities," *Chemical Reviews* 96 (1996) 1477–1498.

- [51] J.S. Lee, S.T. Oyama, M. Boudart, "Molybdenum carbide catalysts: I. Synthesis of unsupported powders," *Journal of Catalysis* 106 (1987) 125–133.
- [52] S. T. Oyama, "Preparation and Catalytic Properties of Transition Metal Carbides and Nitrides," *Catalysis Today* 15 (1992) 179-200.
- [53] J.S. Lee, S. Locatelli, S.T. Oyama, M. Boudart, "Molybdenum carbide catalysts 3. Turnover rates for the hydrogenolysis of n-butane," *Journal of Catalysis* 125 (1990) 157–170.
- [54] E.A. Blekkan, C. Pham-Huu, M.J. Ledoux, J. Guille, "Isomerization of *n*-heptane on an oxygen-modified molybdenum carbide catalyst," *Industrial & Engineering Chemistry Research* 33 (1994) 1657–1664.
- [55] M.J. Ledoux, C. Pham-Huu, R.R. Chianelli, "Catalysis with carbides," *Current Opinion in Solid State and Materials Science* 1 (1996) 96–100.
- [56] T. Hyeon, M. Fang, K.S. Suslick, "Nanostructured molybdenum carbide: sonochemical synthesis and catalytic properties," *Journal of the American Chemical Society* 118 (1996) 5492–5493.
- [57] S.K. Bej, C.A. Bennett, L.T. Thompson, "Acid and base characteristics of molybdenum carbide catalysts," *Applied Catalysis A.: General* 250 (2003) 197–208.
- [58] S.K. Bej, L.T. Thompson, "Acetone condensation over molybdenum nitride and carbide catalysts," *Applied Catalysis A: General* 264 (2004) 141–150.
- [59] J. Patt, D.J. Moon, C. Phillips, L. Thompson, "Molybdenum carbide catalysts for water–gas shift," *Catalysis Letter* 65 (2000) 193–195.
- [60] I. Kojima, E. Miyazaki, I. Yasumori, "Synthesis of hydrocarbons from CO and H₂ over metal carbide catalysts," *Journal of the Chemical Society, Chemical Communications* (1980) 573–574.
- [61] I. Kojima, E. Miyazaki, "Catalysis by transition metal carbides: V. Kinetic measurements of hydrogenation of CO over TaC, TiC, and Mo₂C catalysts," *Journal of Catalysis* 89 (1984) 168–171.
- [62] H.C. Woo, K.Y. Park, Y.G. Kim, I.S. Nam, J.S. Chung, J.S. Lee, "Mixed alcohol synthesis from carbon monoxide and dihydrogen over potassium-promoted molybdenum carbide catalysts," *Applied Catalysis* 75 (1991) 267–280.
- [63] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "Performances of mixed alcohols synthesis over potassium promoted molybdenum carbides," *Fuel* 85 (2006) 2662–2665.

- [64] A.K. Gunturu, E.L. Kugler, J.B. Cropley, D.B. Dadyburjor, "A kinetic model for the synthesis of high-molecular-weight alcohols over a sulfided Co-K-Mo/C Catalyst," *Industrial & Engineering Chemistry Research* 37 (1998) 2107–2115.
- [65] K.J. Smith, R.G. Herman, K. Klier, "Kinetic modelling of higher alcohol synthesis over alkali-promoted Cu/ZnO and MoS₂ catalysts". *Chemical Engineering Science* 45 (1990) 2639–2646.
- [66] F.H. Ribeiro, R.A. Dalla Betta, M. Boudart, J. Baumgartner, E. Iglesia, "Reactions of neopentane, methylcyclohexane, and 3,3-dimethylpentane on tungsten carbides: The effect of surface oxygen on reaction pathways," *Journal of Catalysis* 130 (1991) 86–105.
- [67] F.H. Ribeiro, M. Boudart, R.A. Dalla Betta, E. Iglesia, "Catalytic reactions of *n*-alkanes on β -W₂C and WC: The effect of surface oxygen on reaction pathways," *Journal of Catalysis* 130 (1991) 498–513.
- [68] E. Iglesia, J.E. Baumgartner, F.H. Ribeiro, M. Boudart, "Bifunctional reactions of alkanes on tungsten carbides modified by chemisorbed oxygen," *Journal of Catalysis* 131 (1991) 523–544.
- [69] E. Iglesia, F.H. Ribeiro, M. Boudart, J.E. Baumgartner, "Synthesis, characterization, and catalytic properties of clean and oxygen-modified tungsten carbides," *Catalysis Today* 15 (1992) 307–337.
- [70] E. Iglesia, F.H. Ribeiro, M. Boudart, J.E. Baumgartner, "Tungsten carbides modified by chemisorbed oxygen. A new class of bifunctional catalysts," *Catalysis Today* 15 (1992) 455–458.
- [71] N. Liu, S.A. Rykov, J.G. Chen, "A comparative surface science study of carbide and oxycarbide: the effect of oxygen modification on the surface reactivity of C/W(1 1 1)," *Surface Science* 487 (2001) 107–117.
- [72] H.H. Hwu, M.B. Zellner, J.G. Chen, "The chemical and electronic properties of oxygen-modified C/Mo(110): a model system for molybdenum oxycarbides," *Journal of Catalysis* 229 (2005) 30–44.
- [73] M. Nagai, T. Kurakami, S. Omi, "Activity of carbided molybdena-alumina for CO₂ hydrogenation," *Catalysis Today* 45 (1998) 235–239.
- [74] W. Wu, Z. Wu, C. Liang, X. Chen, P. Ying, C. Li, "In situ FT-IR spectroscopic studies of CO adsorption on fresh Mo₂C/Al₂O₃ catalyst," *The Journal of Physical Chemistry B* 107 (2003) 7088–7094.
- [75] W. Wu, Z. Wu, C. Liang, P. Ying, Z. Feng, C. Li, "An IR study on the surface passivation of Mo₂C/Al₂O₃ catalyst with O₂, H₂O and CO₂," *Physical Chemistry Chemical Physics* 6 (2004) 5603–5608.

- [76] P.A. Aegerter, W.W.C. Quigley, G.J. Simpson, D.D. Ziegler, J.W. Logan, K.R. McCrea, S. Glazier, M.E. Bussell, "Thiophene Hydrodesulfurization over Alumina-Supported Molybdenum Carbide and Nitride Catalysts: Adsorption Sites, Catalytic Activities, and Nature of the Active Surface," *Journal of Catalysis* 164 (1996) 109–121.
- [77] J. Wang, M. Castonguay, P.H. McBreen, S. Ramanathan, S.T. Oyama, "Chemisorption of CO and NO molybdenum carbide foils," in: S.T. Oyama (Ed.), *The Chemistry of Transition Metal Carbides and Nitrides*, Springer, 1996: pp. 426–438.
- [78] H. Tominaga, M. Nagai, "Density functional theory of water–gas shift reaction on molybdenum carbide," *The Journal Physical Chemistry B* 109 (2005) 20415–20423.
- [79] X.-R. Shi, J. Wang, K. Hermann, "CO and NO adsorption and dissociation at the β -Mo₂C(0001) surface: A density functional theory study," *The Journal Physical Chemistry C* 114 (2010) 13630–13641.
- [80] B. Frühberger, J.G. Chen, "Modification of the surface reactivity of Mo(110) upon carbide formation," *Surface Science* 342 (1995) 38–46.
- [81] J. Ren, C.-F. Huo, J. Wang, Y.-W. Li, H. Jiao, "Surface structure and energetics of oxygen and CO adsorption on α -Mo₂C(0 0 0 1)," *Surface Science* 596 (2005) 212–221.
- [82] T. Aizawa, S. Otani, "Adsorption of CO and O₂ on W₂C(0001)," *The Journal of Chemical Physics* 135 (2011) 144704.
- [83] N. Koizumi, G. Bian, K. Murai, T. Ozaki, M. Yamada, "In situ DRIFT studies of sulfided K–Mo/ γ -Al₂O₃ catalysts," *Journal of Molecular Catalysis A: Chemical* 207 (2004) 173–182.
- [84] A. Muramatsu, T. Tatsumi, H. Tominaga, "Mixed alcohol synthesis from CO–H₂ by use of KCl-promoted Mo/SiO₂ catalysts," *Bulletin of the Chemical Society of Japan* 60 (1987) 3157–3161.
- [85] M. Jiang, G.-Z. Bian, Y.-L. Fu, "Effect of the K–Mo interaction in K–MoO₃/ γ -Al₂O₃ catalysts on the properties for alcohol synthesis from syngas," *Journal of Catalysis* 146 (1994) 144–154.
- [86] N.F.D. Verbruggen, G. Mestl, L.M.J. von Hippel, B. Lengeler, H. Knoezinger, "Structure of K-doped molybdena-on-alumina catalysts as studied by X-ray absorption and Raman spectroscopy," *Langmuir* 10 (1994) 3063–3072.
- [87] N.F.D. Verbruggen, L.M.J. von Hippel, G. Mestl, B. Lengeler, H. Knoezinger, "Structure of K-doped molybdena-on-silica catalysts as studied by X-ray absorption and Raman spectroscopy," *Langmuir* 10 (1994) 3073–3080.

- [88] Y. Fu, F. Zhao, "The adsorption characteristics of two Mo sites on a sulfided $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ surface," *Catalysis Letters* 12 (1992) 117–125.
- [89] F. Maugé, J.C. Lavalley, "FT-IR study of co adsorption on sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ unpromoted or promoted by metal carbonyls: Titration of sites," *Journal of Catalysis* 137 (1992) 69–76.
- [90] B. Müller, A.D. van Langeveld, J.A. Moulijn, H. Knözinger, "Characterization of sulfided molybdenum/alumina catalysts by temperature-programmed reduction and low-temperature Fourier transform infrared spectroscopy of adsorbed carbon monoxide," *The Journal of Physical Chemistry* 97 (1993) 9028–9033.
- [91] A. Travert, C. Dujardin, F. Maugé, S. Cristol, J.F. Paul, E. Payen, et al., "Parallel between infrared characterisation and ab initio calculations of CO adsorption on sulphided Mo catalysts," *Catalysis Today* 70 (2001) 255–269.
- [92] A.A. Tsyganenko, F. Can, A. Travert, F. Maugé, "FTIR study of unsupported molybdenum sulfide—in situ synthesis and surface properties characterization," *Applied Catalysis A: General* 268 (2004) 189–197.
- [93] A. Travert, C. Dujardin, F. Maugé, E. Veilly, S. Cristol, J.-F. Paul, E. Payen, "CO Adsorption on CoMo and NiMo Sulfide Catalysts: A Combined IR and DFT Study," *The Journal of Physical Chemistry B* 110 (2006) 1261–1270.
- [94] J. Raskó, J. Kiss, "Infrared study of the adsorption of CO and CH_3 on silica-supported MoO_3 and Mo_2C catalysts," *Applied Catalysis A: General* 253 (2003) 427–436.
- [95] J.W. Han, L. Li, D.S. Sholl, "Density functional theory study of H and CO adsorption on alkali-promoted Mo_2C surfaces," *The Journal Physical Chemistry C* 115 (2011) 6870–6876.
- [96] Z. Li, Y. Fu, J. Bao, M. Jiang, T. Hu, T. Liu, Y. Xie, "Effect of cobalt promoter on Co–Mo–K/C catalysts used for mixed alcohol synthesis," *Applied Catalysis A: General* 220 (2001) 21–30.
- [97] M. Xiang, D. Li, H. Xiao, J. Zhang, H. Qi, W. Li, B. Zhong, Y. Sun, "Synthesis of higher alcohols from syngas over Fischer–Tropsch elements modified $\text{K}/\beta\text{-Mo}_2\text{C}$ catalysts," *Fuel* 87 (2008) 599–603.
- [98] A.J. Lucero, V.K. Sethi, W.H. Tuminello, "Process and catalyst for production of mixed alcohols from synthesis gas," U.S. Patent 8048933, 2011, to University of Wyoming Research Corporation.
- [99] H. Shou, D. Ferrari, D.G. Barton, C.W. Jones, R.J. Davis, "Influence of passivation on the reactivity of unpromoted and Rb-promoted Mo_2C nanoparticles for CO hydrogenation," *ACS Catalysis* 2 (2012) 1408–1416.

Chapter 2.

Reactivity and *in situ* X-ray absorption spectroscopy of Rb-promoted Mo₂C/MgO catalysts for higher alcohol synthesis

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Abstract

The influences of MgO support and Rb₂CO₃ promoter on the activity and selectivity of Mo₂C-based catalysts for higher alcohols synthesis from syngas were explored. The reaction was performed in a fixed-bed reactor system operating at 573 K, 30 bar, gas flow rate of 24,000 cm³ g_{M0}⁻¹ h⁻¹ and H₂/CO = 1. When promoted by Rb₂CO₃, the selectivity of alcohols over 5 wt.% Mo₂C/MgO was able to reach 62 C% on a CO₂-free basis, with C1-C4 hydrocarbons being the main side-products. Production of higher alcohols was enhanced at high promoter loading and low conversion. Characterization by X-ray absorption spectroscopy (XAS) indicated that passivated Mo₂C/MgO was more oxidized than bulk Mo₂C, but exposure to reaction conditions for 4 h partially reduced the passivated sample. Electron microscopy and XAS confirmed that Mo₂C was highly dispersed on MgO. The Rb *K* edge structure suggested that the Rb₂CO₃ promoter was structurally modified in the reaction.

2.1 Introduction

Synthesis gas, composed mainly of CO and H₂, can be derived from carbon sources such as coal, oil, natural gas, or biomass. Although world-scale catalytic processes have been developed to convert synthesis gas to diesel fuel or methanol, there is a growing need for its direct conversion to higher alcohols [1–3]. These higher alcohols can be used as liquid carriers of hydrogen, which can be obtained by reforming, or as fuel additives based on their mutual solubility with gasoline and diesel fuels. Higher alcohols can also be dehydrated to olefin feedstocks used to produce polymers.

Molybdenum-based solids are among the most promising catalysts for higher alcohol synthesis (HAS) because of their relatively low cost compared to Pt-group metals. Additional advantages of Mo-based catalysts for practical applications include: less severe catalyst deactivation due to coke deposition (even with a syngas containing a low H₂/CO ratio of less than 2), higher selectivity to linear alcohols (especially ethanol), and low sensitivity to CO₂ in the syngas [4]. In the 1980's, The Dow Chemical Company developed potassium and cobalt promoted molybdenum sulfide (MoS₂) catalysts for HAS [5]. The alcohol formation rate over promoted MoS₂ was reported to be 0.1-0.4 g gcat⁻¹ h⁻¹ at 513–598 K and 48–207 bars, with a selectivity to mixed alcohols (on a CO₂-free basis) as high as ~85% [6–9]. However, trace amounts of hydrogen sulfide (H₂S) in the feed were needed to sustain the performance of the MoS₂ catalysts [6]. Thus, there is an incentive to explore the reactivity of non-sulfided catalysts for HAS, among which molybdenum carbide has demonstrated some promise when properly promoted.

Consistent with the landmark discovery by Levy and Boudart [10], the reactivity of transition metal carbides (TMCs) can be similar to that of expensive Pt-group metals

[11–13], especially in reactions involving the transformation of C–H bonds in hydrocarbons. For example, the hydrogenation performance of TMCs is at the same level of Pt-group metals [14,15]. Park *et al.* also examined the effect of potassium promotion on Fischer–Tropsch synthesis over bulk molybdenum carbide (Mo_2C) catalysts. They found that unsupported molybdenum carbide produced mostly C1–C5 alkanes in CO hydrogenation at atmospheric pressure, and promotion of the catalyst with K_2CO_3 yielded mostly C2–C5 alkenes [16]. They also found that promotion of Mo_2C by K_2CO_3 greatly enhanced the alcohol selectivity during CO hydrogenation and they reported 50.5% alcohol selectivity at 10.3% CO conversion at high pressure [17]. The formation of alcohols from CO hydrogenation over carbide catalysts is thought to be related to the uniformity of the alkali promoter on the carbide surface [18] and to the extent of carburization [19]. Although the promotion of alcohol synthesis by addition of alkali to Mo_2C reduces the overall activity of the catalyst, the addition of Fe, Co and Ni can improve the activity of the promoted system [20–27].

The objective of the current study is to explore the roles of structure and reaction conditions on catalyst performance in higher alcohol synthesis. In particular, the effects of reaction temperature, pressure and gas flow rate on the product distribution over a Rb-promoted, magnesia-supported Mo_2C catalysts were investigated. Magnesia was selected as a support since basic compounds are well-recognized promoters of the reaction. X-ray absorption spectroscopy at the Mo and Rb *K* edges was used to monitor the catalyst structure *in situ*. Catalysts were also characterized by transmission electron microscopy (TEM), elemental analysis, X-ray powder diffraction and BET surface analysis.

2.2 Experimental methods

2.2.1 Catalyst synthesis

A 5 wt.% Mo₂C/MgO sample was prepared by temperature-programmed carburization of MoO₃/MgO with a 20 vol.% CH₄/H₂ mixture. Magnesia (UBE ultrafine single crystal, >99.98%, $S_{\text{BET}} = 35.7 \text{ m}^2 \text{ g}^{-1}$) was first impregnated with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (99.98%, Aldrich) and then dried overnight in air at 400 K and calcined at 773 K in flowing air for 4 h to produce a supported oxide denoted here as MoO₃/MgO. Carburization of MoO₃/MgO was accomplished by temperature-programmed reaction (TPR) at temperatures between 673 K and 973 K with a 20 vol.% CH₄ (GTS-Welco, 99.997%) and 80 vol.% H₂ mixture (GTS-Welco, 99.999%) at a heating rate of 0.5 K min⁻¹ according to the method of Woo *et al.* [17]. After TPR, the temperature was maintained at 973 K for 5 h, followed by another 10 h at 773 K. The catalyst was subsequently quenched to room temperature in flowing H₂. Finally, the 5 wt.% Mo₂C/MgO sample was passivated in a stream of 1 vol.% O₂/N₂ mixture (GTS-Welco, 1.02 vol.% O₂) at room temperature (RT) for 12 h before exposure to air. The supported Mo₂C was further promoted by physically mixing it with Rb₂CO₃ (99.975%, Alfa Aesar). The Rb₂CO₃ loading was varied in the range of 0-15 wt.%.

For comparison, an aqueous solution of Rb₂MoO₄ was impregnated onto MgO. The sample was dried and carburized by the same method to produce carburized Rb₂MoO₄/MgO. As a control, distilled, deionized water was added to pure MgO and the resulting sample was subjected to the same carburization conditions as samples containing Mo.

2.2.2 Catalyst characterization

Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). The Mo loading of the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), while the C loading was evaluated by combustion.

Adsorption of N₂ was performed on a Micromeritics ASAP 2020 automated adsorption system to obtain the BET surface area. A sample was heated under vacuum to 573 K for 10 h prior to adsorption of N₂ at liquid nitrogen temperature.

Electron microscopy was performed on an FEI Titan 300 transmission electron microscope equipped with an EDS system operated at 200 kV. Two catalyst samples, 5 wt.% Mo₂C/MgO and 5 wt.% Rb–5 wt.% Mo₂C/MgO, were reacted for 48 h and passivated with 1% O₂/N₂ (GTS-Welco, 1.02% O₂) at RT before TEM analysis. Catalyst powders were dispersed in *n*-hexane and supported onto a holey carbon film and a continuous carbon film (double film) coated grid (Pacific Grid-Tech). Images were recorded with a Gatan 794 Multi Scan CCD camera and Fischione Instruments Model 3000 annular dark field detector.

The X-ray diffraction patterns were obtained on a Scintag XDS 2000 diffractometer using Cu K α radiation. Scans were collected from 2θ of 5° to 90° at a rate of 2° min⁻¹ for bulk materials and 0.8° min⁻¹ for supported catalysts.

2.2.3 Hydrogenation of carbon monoxide

Hydrogenation of CO was conducted in a fixed-bed stainless steel reactor (BTRS Jr., Autoclave Engineers) with 1.00 g catalyst (0.05 g nominal Mo₂C) of size 40-80 mesh diluted by 2.5 g SiC. The catalysts were tested at nominally identical conditions of 573 K, 30 bar total pressure, syngas (H₂ + CO) flow of 20 cm³ min⁻¹ (STP) and H₂/CO ratio of 1.

The reactor was pressurized to 30 bar at room temperature and heated to 573 K before sampling. The temperature of the catalyst bed was monitored by a thermocouple in contact with the catalyst bed. The purity of CO (GTS-Welco) was 99.9% and H₂ (GTS-Welco) was 99.999%. Additionally, CO was purified by passing it through a silica trap immersed in a Dewar containing a dry ice-acetone mixture (195 K) to remove any trace iron carbonyl before introduction into the reactor [28]. The products were analyzed by two Hewlett-Packard 5890 series II gas chromatographs. The first one was equipped with a flame ionization detector and a 50 m-long HP-1 cross-linked methyl silicone gum capillary column to monitor the formation of hydrocarbons and oxygenates. The second one was equipped with a thermal conductivity detector and a 6-ft long Alltech-8700 packed column and was used to monitor the formation of CO₂.

According to Burch and Petch [29], the conversion of CO was derived from the fraction of CO that formed carbon-containing products. The conversion of CO, if low, can be described as:

$$\text{Conversion (\%)} = \sum n_i M_i \times 100 / M_{\text{CO}},$$

where n_i is the number of carbon atoms in product i , M_i is the percentage of product i detected, and M_{CO} is the percentage of CO in the syngas feed.

The selectivity to product i is based on the total number of carbon atoms in the product and is therefore defined as:

$$\text{Selectivity (\%)} = n_i M_i \times 100 / \sum n_i M_i.$$

The quantitative products comprised more than 93% of the total peak area given by GC-FID.

2.2.4 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) was carried out on a beamline X-18B at the National Synchrotron Light Source, Brookhaven National Laboratory. The NSLS storage ring was operated at 2.8 GeV with a ring current of about 300 mA. The XAS data were obtained in the transmission mode at the Mo *K* edge (20 keV) and at the Rb *K* edge (15.2 keV) with a spot size of 0.5 mm × 3 mm.

Following the designs of Fingland *et al.* [30], an XAS cell depicted in Figure 2.1 was constructed in house specifically for this study. The XAS cell consists of a 6” borosilicate glass tube housed by stainless steel nuts and Teflon ferrules in a temperature-controlled aluminum heating block, with a 1/4” hole in the block to allow for the transmission of X-rays through the tube walls and the catalyst bed. The temperature of the catalyst bed was controlled by an internal K-type stainless steel thermocouple (Omega). The heat to the aluminum block was provided by four 1/4” cartridge heaters connected to an Omega CN 2011 temperature controller. The cell allowed for interrogation of the catalyst under standard reaction conditions of 573 K and 30 bar flowing syngas.

The Mo *K* edge and Rb *K* edge spectra were measured in air at RT with Mo foil (0.015 mm, 99.9%, Goodfellow) and Rb₂CO₃ (99.975%, Alfa Aesar) as references, respectively. For *in situ* experiments, 0.2 g of 5 wt.% Mo₂C/MgO or 5 wt.% Rb–5 wt.% Mo₂C/MgO were loaded into a reactor tube and assembled into the custom-designed XAS cell. After pressurizing the cell with syngas (H₂/CO = 1), it was then heated from RT to 573 K, and held at 573 K for 4 h, with a total syngas flow of 4 cm³ min⁻¹ (STP).

The Mo *K* edge and Rb *K* edge spectra were recorded after the 4 h treatment under reaction conditions, and after quenching the catalysts to RT in H₂.

To further probe the Rb *K* edge, 0.2 g of 5 wt.% Rb–5 wt.% Mo₂C/MgO or 5 wt.% Rb/MgO were loaded into a reactor tube and assembled into the cell. The cell was then heated from RT to 573 K, and held at 573 K for 4 h, in flowing Ar at 4 cm³ min⁻¹. The Rb *K* edge spectra were recorded after the 4 h treatment, and after cooling the catalyst to RT in Ar. In addition, Rb *K* edge spectra of Rb₂CO₃ mixed with liquid water were treated at RT.

The XAS data were processed using the Athena [31] software for background removal, post-edge normalization, and X-ray absorption near edge structure (XANES) analysis. Because the Mo near edge structure has various features that complicate the determination of E_0 , the edge energy, the value of E_0 was assigned here as the energy at the half step height. Metallic Mo foil (0.015 mm, 99.9%, Goodfellow), MoO₂ (99%, Aldrich), and Rb₂MoO₄ (99.5%, Alfa Aesar) were used as standards for Mo residing in 0, +4 and +6 formal oxidation states.

The Extended X-ray Absorption Fine Structure (EXAFS) data analysis was performed using the Artemis software package, which implemented FEFF6 [32]. The normalized EXAFS data were k^3 -weighted and then Fourier transformed from *k*-space in the range 2–14 Å⁻¹. Standard bulk Mo₂C (Aldrich, 99.5%) was used to determine the amplitude reduction factors S_0^2 for Mo–C and Mo–Mo, and Rb₂MoO₄ was used to determine S_0^2 for Mo–O. The values of S_0^2 utilized in the fitting of EXAFS data from the catalyst samples were 0.82, 0.78 and 0.79 for Mo–C, Mo–Mo and Mo–O, respectively. A two-shell fitting procedure was used to analyze carbides (Mo–C, Mo–Mo) and a one-

shell fitting procedure was used to analyze the oxides (Mo–O). The interatomic distances (r), coordination numbers (CN), Debye-Waller factors ($\Delta\sigma^2$) and energy shifts (ΔE_0) were derived from the results.

Figure 2.1 High pressure, borosilicate tubular reactor/X-ray cell.

2.3 Results and discussion

2.3.1 Characterization by X-ray diffraction, elemental analysis, N₂ adsorption, and electron microscopy

The X-ray diffraction patterns of representative samples are provided in Figure 2.2. The pattern for bulk Mo₂C prepared at 973 K (Figure 2.2c) revealed peaks at 34.8, 38.2, 39.8, 62.1, and 75.2°, which are assigned to the {100}, {002}, {101}, {110}, and an unresolved doublet of the {112} and {201} reflections of bulk hexagonal Mo₂C, respectively [33]. The passivated 5 wt.% Mo₂C/MgO catalyst (Figure 2.2b) prepared at 973 K showed XRD peaks corresponding to the structure of MgO (Figure 2.2a) without any clear evidence for crystalline Mo₂C. This result suggests that the Mo₂C particles were

very well-dispersed on the support. It should be noted that MgO reconstructed to $\text{Mg}(\text{OH})_2$ (Figure 2.2d) after impregnation with a water solution followed by drying. However, after calcination at 773 K, the original pattern for MgO was restored. The significant reconstructing of the MgO support during catalyst preparation may have influenced the dispersion of the Mo on the surface.

Figure 2.2 X-ray diffraction patterns of (a) MgO, (b) $\text{Mo}_2\text{C}/\text{MgO}$, (c) Mo_2C , and (d) hydrated MgO. Patterns are offset for clarity.

Table 2.1 Results from elemental analysis

Catalyst composition (nominal)	Loading (wt %)		C/Mo (atomic ratio)	
	Mo	C	Measured	Corrected
5 wt.% $\text{Mo}_2\text{C}/\text{MgO}$	4.77	0.356	0.596	0.424*
“Carburized” MgO	–	0.108	–	–

*Value has been subtracted by the level in “carburized” MgO.

The elemental analysis results for $\text{Mo}_2\text{C}/\text{MgO}$ are listed in Table 2.1. Since MgO can adsorb CO_2 from air, a control experiment was carried by using a “carburized” MgO sample that was exposed to the same treatment as the catalyst synthesis except that no

molybdenum precursor was added. The measured carbon level in the Mo₂C/MgO catalyst was then corrected by the carbon level in the control sample without Mo to give a more reliable analysis. The corrected C/Mo atomic ratio was 0.424, which is close to the expected stoichiometry of Mo₂C (0.5). The small deviation may be caused by the passivation step which may oxidize some of the surface carbon on the sample.

Table 2.2 lists the results of BET surface area analysis of MgO and MgO-supported Mo₂C catalysts prior to use in reaction. The BET surface area of MgO changed from 35.8 m² g⁻¹ to 64.8 m² g⁻¹ after loading with Mo₂C. Considering the small proportion of Mo₂C on the sample, the change in the BET surface area of MgO most likely was the result of the structure change of MgO to Mg(OH)₂ and back to MgO during catalyst synthesis. Addition of a high loading of Rb₂CO₃ to the sample by physically-mixing the two components decreased the overall area of the mixture.

Table 2.2 Results from N₂ Adsorption

Sample	MgO	5%Mo ₂ C/MgO					
		0% Rb	1% Rb	5% Rb	5% Rb	10% Rb	15% Rb
S _{BET} (m ² g ⁻¹)	35.7	64.8	65.7	55.4	55.4	54.2	48.4

Figure 2.3 HAADF images of (a) 5% Mo₂C/MgO, (b) 5%Rb–5%Mo₂C/MgO. Catalysts had been used for 48 h in CO hydrogenation before TEM analysis.

The high angle annular dark field (HAADF) image of 5 wt.% Mo₂C/MgO (Figure 2.3) revealed that the average particle size of Mo₂C was 2.8 ± 0.3 nm. The very small particle size observed by TEM is consistent with the lack of observable crystalline carbide phases by X-ray diffraction.

2.3.2 Role of Rb loading on Mo₂C/MgO

The performance of unpromoted Mo₂C catalysts in the reaction of syngas (H₂/CO: =1) at 573 K and 30 bar pressure is summarized in Table 2.3.

The first two columns in Table 2.3 compare the results from a bulk Mo₂C catalyst and an MgO-supported Mo₂C catalyst. Bulk Mo₂C functions primarily as a Fischer–Tropsch catalyst at 573 K and 30 bar syngas, producing mainly light hydrocarbons and very little alcohols (3.1% on a CO₂-free basis). Supporting the carbide on MgO increased the alcohol selectivity to 24%, at nearly identical levels of CO conversion. Evidently the basic support MgO promoted alcohol production at the expense of hydrocarbon production, most likely at active sites near the carbide/support interface. It should be noted that the selectivity to CO₂ produced via the water gas shift reaction was usually about 40%, and should always be below 50% because of reaction stoichiometry.

Columns 3 through 7 in Table 2.3 illustrate the effect of Rb loading on higher alcohol synthesis over Mo₂C/MgO. Addition of Rb₂CO₃ to supported Mo₂C increased the selectivity to alcohols (on a CO₂-free basis) while lowering the selectivity to hydrocarbons. However, addition of Rb₂CO₃ beyond 10 wt.% did not substantially improve selectivity above about 60% oxygenates but instead decreased CO conversion. Examination of the distribution of alcohols produced over the catalysts shows that the ratio of higher alcohols (ethanol, propanol, etc.) to methanol was nearly 1:1 over

unpromoted Mo₂C/MgO but was 2.4 over Rb-promoted Mo₂C/MgO. Moreover, the addition of Rb promoted the formation of alkenes, because the C₄+ alkene/C₄+ alkane ratio increased from 0.47 on unpromoted 5 wt.% Mo₂C/MgO to 2.1 on 10 wt.% Rb–5 wt.% Mo₂C/MgO. These results are consistent with prior work on potassium-promoted bulk Mo₂C catalysts [17,34,35].

The fourth and fifth entries in Table 2.3 demonstrate the reproducibility of the reactivity results by reporting two separate runs of 5 wt.% Rb–5 wt.% Mo₂C/MgO catalysts. The results suggest good experimental reproducibility since the conversion of CO (3.5% and 3.0%) and product distribution are very similar.

Table 2.3 Conversion of synthesis gas over Rb-promoted 5 wt.% Mo₂C/MgO catalysts

Catalyst	Bulk	5 wt.% Mo ₂ C/MgO					
Rb loading (wt.%)	0	0	1	5	5	10	15
CO conversion (%)	6.6	5.7	3.8	3.5	3.0	2.8	2.3
CO ₂ selectivity (%)	45	45	46	38	37	35	39
Selectivity (C%, on a CO ₂ -free basis) ^a							
Methane	41	29	19	17	15	16	16
C ₂ hydrocarbons	27	23	16	13	10	10	10
C ₃ hydrocarbons	20	16	12	7.8	6.2	6.1	5.9
C ₄ + linear paraffins	5.4	6.0	7.9	3.3	3.5	1.9	1.6
C ₄ + olefins	2.8	2.8	4.5	4.4	5.2	3.9	4.0
Methanol	2.0	12	15	19	19	19	18
Ethanol	1.1	8.1	16	22	22	23	23
1-Propanol	0	3.5	7.0	11	12	14	16
1-Butanol	0	0	1.8	3.0	4.3	4.3	4.5
1-Pentanol	0	0	0	0	1.9	1.8	0
Rate of CO conversion (mol _{CO} mol _{Mo} ⁻¹ h ⁻¹)	3.3	2.9	1.9	1.7	1.5	1.4	1.1
Rate of alcohol production (g g _{Mo} ⁻¹ h ⁻¹)	0.02	0.11	0.11	0.16	0.14	0.14	0.11

Nominal conditions are $T = 573$ K, $P = 30$ bar, 0.05 g nominal Mo₂C (made into 40–80 mesh pellets if supported on MgO), 2.5 g SiC to dilute the bed, H₂/CO = 1, syngas flow = 20 cm³ (STP) min⁻¹. Data were recorded after 48 h reaction.

^a All the alcohols are linear.

Figure 2.4 Change of catalytic performance of 5 wt.% Rb-5 wt.% Mo₂C during CO hydrogenation at 573 K and 30 bar: (a) CO conversion; (b) CO₂ selectivity to CO₂; (c) selectivity to hydrocarbons; (d) selectivity to alcohols.

Figure 2.4 illustrates how the CO conversion and product selectivities over 5 wt.% Rb–5 wt.% Mo₂C/MgO changed with time over a 48 h time interval. The catalyst deactivated about a third of its initial activity after about 24 hours, but remained fairly stable thereafter. The selectivity to hydrocarbons, alcohols and CO₂ all changed sharply during the first 3 h, and were relatively stable after about a day. Most importantly, the alcohol selectivity was very low initially and gradually increased with time on stream, suggesting a restructuring of the active phase during this start-up period. Generally, molybdenum-based catalysts for mixed alcohols synthesis exhibit an induction period during CO hydrogenation [16–18,35,37]. This induction period may coincide with the distribution of Rb promoter over the catalyst surface since it was initially physically mixed with Mo₂C/MgO.

Figure 2.5 Reaction pathway for CO hydrogenation adapted from [18]

Lee *et al.* [18] depicted the simplified scheme (Figure 2.5) of CO conversion based on the ideas discussed by Ponc [38,39]. According to this scheme, all the products

can be derived from an adsorbed intermediate $*C_mH_n$, (where $*$ denotes a surface site). This intermediate can undergo four different transformations to products namely: (1) hydrogenation to alkanes, (2) carbonylation to alcohol precursors, (3) desorption as olefins, and (4) further chain growth by inserting $*CH_x$. In this competitive process, hydrogenation activity of a catalyst needs to be partially suppressed to enhance production of alcohols and alkenes; thus, trends in alcohol and alkene selectivities should be similar, as reaction conditions or catalyst properties are varied. Lee *et al.* [18] suggested that alkali promoters on Mo_2C catalysts for CO hydrogenation have two effects: an electronic effect and a geometric effect. The electronic effect is thought to increase the electron density of the catalyst, thus inhibiting the oxidative addition of hydrogen to the surface. The geometric effect involves the blockage of surface sites that are potential sites for the adsorption of reactants. They concluded that the geometric effect of adding K_2CO_3 on Mo_2C was the primary mode of promoting alcohol formation during CO hydrogenation. Because the optimal ratio of K to Mo was different for alkene and alcohol formation, Lee *et al.* also suggested that alkene formation may be attributed to the combination of geometric and electronic effects. Muramatsu *et al.* [35] also studied the roles of potassium promoter on a Mo oxide catalyst for alcohol production from syngas, and concluded that potassium inhibits dehydration of alcohols to alkenes as well as the hydrogenation of alkenes to alkanes.

For CO hydrogenation over Mo_2C/MgO catalysts, the selectivities of both alcohols and alkenes increased with the loading of Rb_2CO_3 promoter, which is consistent with Figure 2.5. The EDS spectra of 5 wt.% Rb–5 wt.% Mo_2C/MgO catalyst after 48 h syngas reaction, corresponding to the sample in Figure 2.3b, revealed the presence of Rb

distributed over the sample after reaction, which is consistent with a site blocking mechanism described above. However, the formation of higher alcohols with increased loading of Rb promoter may result from chain growth reactions on the promoted carbide catalyst or coupling of lower molecular weight alcohols over basic sites provided by Rb promoter. Further investigations are needed to explore this aspect.

2.3.3 Influence of process variables: gas flow rate, temperature, pressure, and H_2/CO ratio

The influence of gas flow rate on the overall CO conversion is shown in Figure 2.6 at the nominal conditions of 30 bar and a H_2/CO ratio of 1, with temperature varying from 553 K to 593 K. As expected, CO conversion decreased with gas low rate and increased with temperature.

Figure 2.6 Influence of gas flow rate on CO conversion (including CO_2) over 5 wt.% Rb–5 wt.% Mo_2C/MgO (30 bar, $H_2/CO = 1$).

Table 2.4 compares the behavior of 5 wt.% Rb–5 wt.% Mo₂C/MgO at the same pressure (30 bar) and same CO conversion level by varying WHSV and temperature. The selectivity of alcohols was independent of temperature over the range of 573 K to 593 K at a constant conversion of CO equal to about 2.7% (excluding CO₂). However, the selectivity to alcohols and hydrocarbons is a strong function of CO conversion, as revealed in Figure 2.7. At 30 bar syngas pressure, alcohol selectivity is preferred at low CO conversion, which is also observed over alkali-promoted MoS₂-based catalysts for higher alcohol synthesis [37].

Table 2.4 Comparison of catalyst activity at similar CO conversion level by varying temperature and gas flow rate.

CO conversion (%)	4.2	4.5	4.4
CO ₂ selectivity (%)	37	38	37
CO conversion (% , excluding CO ₂)	2.6	2.7	2.7
Pressure (bar)	30	30	30
Temperature (K)	573	583	593
H ₂ /CO	1	1	1
Gas flow rate (cm ³ g _{Mo} ⁻¹ h ⁻¹)	12,000	24,000	48,000
Selectivity (C%, on a CO ₂ -free basis)			
Methane	16	18	18
C2 hydrocarbons	11	11	12
C3 hydrocarbons	7.0	6.9	7.0
C4+ paraffins	3.8	3.2	2.3
C4+ olefins	5.1	5.0	5.4
Methanol	18	19	18
Ethanol	20	20	20
1-Propanol	12	11	11
1-Butanol	3.9	3.7	4.1
1-Pentanol	1.7	1.4	1.8

Figure 2.7 Influence of CO conversion on product distribution during HAS over 5 wt.% Rb-5 wt.% Mo₂C/MgO: (a) selectivity of total hydrocarbons and total alcohols; (b) selectivity of CO₂; (c) selectivity of individual alcohols; (d) ratio of alkenes and alkanes. * HC refers to hydrocarbon.

Table 2.5 Impact of partial pressure on production distribution of CO hydrogenation over 5 wt.% Rb-5 wt.% Mo₂C/MgO catalyst

Temperature (K)	573	573	573
P_{CO} (bar)	7.5	15	15
P_{H_2} (bar)	15	15	7.5
Total flow rate (cm ³ (STP) min ⁻¹ , H ₂ + CO)	15	20	15
CO conversion (%)	4.8	3.2	2.1
Rate of CO conversion (mol _{CO} mol _{M₀} ⁻¹ h ⁻¹)	0.024	0.016	0.010
CO ₂ selectivity (%)	30	35	28
Selectivity (C%, on a CO ₂ -free basis)			
Hydrocarbons	46	39	41
Methane	20	15	15
C2 hydrocarbons	12	9.7	12
C3 hydrocarbons	6.8	5.9	6.8
C4+ linear paraffins	3.1	3.2	2.1
C4+ linear olefins	3.7	4.8	5.2
Methanol	22	19	20
Higher alcohols	33	41	39
Ethanol	20	22	21
1-Propanol	8.6	12	12
1-Butanol	2.8	4.1	4.0
1-Pentanol	1.0	1.9	1.7

Table 2.5 summarizes the effect of reactant partial pressures on the CO conversion and product selectivity over 5 wt.% Rb-5 wt.% Mo₂C/MgO at 573 K. The results indicate the overall reaction is positive order in H₂ but is inhibited by CO at the tested conditions. The changes in conversion during the various runs in Table 2.5 account for observed changes in alcohol and hydrocarbon selectivity.

Table 2.6 presents the influence of total syngas pressure on the CO conversion and selectivity of CO hydrogenation over 5 wt.% Rb-5 wt.% Mo₂C/MgO at 573 K with H₂/CO = 1 at a total flow rate of 20 cm³ (STP) min⁻¹. The CO conversion increased with pressure over the range of 10 bar to 30 bar while simultaneously the selectivity to higher alcohols slightly improved from 37% to 41%.

Table 2.6 Effect of pressure on reactivity of CO hydrogenation over a 5 wt.% Rb–5 wt.% Mo₂C/MgO catalyst

Pressure (bar)	10	20	30
Temperature (K)	573	573	573
H ₂ /CO	1	1	1
H ₂ + CO (cm ³ min ⁻¹)	20	20	20
CO conversion (%)	1.8	2.9	3.6
CO ₂ selectivity (%)	32	38	41
Selectivity (C%, on a CO ₂ -free basis)			
Hydrocarbons	44	39	39
CH ₄	18	16	15
C2 hydrocarbons	13	11	9.7
C3 hydrocarbons	6.8	5.9	5.9
C4+ linear paraffins	1.5	1.8	3.2
C4+ linear olefins	5.0	4.2	4.9
Methanol	19	22	20
Higher alcohols	37	39	41
Ethanol	22	22	22
1-Propanol	10	11	12
1-Butanol	3.4	4.2	4.1
1-Pentanol	1.4	1.7	1.9

2.3.4 X-ray absorption spectroscopy

The X-ray absorption near edge structure (XANES) at the Mo *K* edge of reference compounds and catalysts are provided in Figure 2.8 and a correlation of edge position of the samples (determined at half step height) to the oxidation state of standard Mo compounds is illustrated in Figure 2.9. The edge position of a sample prior to carburization indicated that calcined Mo on MgO was in a +6 oxidation state. Carburization resulted in significant reduction of Mo, which is consistent with the formation of a carbide surface compound. Bulk Mo₂C showed a slightly higher absorption edge energy than Mo foil (Figure 2.8a and Figure 2.9), but the Mo in Mo₂C was significantly reduced from that in MoO₃. The absorption edge of passivated 5 wt.% Mo₂C/MgO catalyst before reaction was shifted +1.8 eV from bulk Mo₂C (Figure 2.8b), but was still 1.5 eV lower than the edge position of MoO₃, which indicates the supported

Mo₂C catalysts were partially oxidized, with the surface of the Mo₂C particles likely being an oxycarbide. Most probably, passivation of the freshly prepared carbide catalysts is responsible for the oxidation. The *in situ* treatment of Mo₂C/MgO catalysts in 30 bar syngas at 573 K for 4 h partially reduced the passivated 5 wt.% Mo₂C/MgO (Figure 2.8 and Figure 2.9), but the Mo was still more oxidized than in bulk Mo₂C (Figure 2.9). The small shifts in E_0 illustrated in Figure 2.9 caused by the addition of Rb₂CO₃ to the corresponding unpromoted Mo₂C/MgO were within the experimental error.

The shift of the Mo *K* edge to lower energy during the induction period of the reacting catalyst was likely caused by the removal of surface oxygen atoms that were introduced by passivation. Griboval-Constant *et al.* suggested that part of the surface oxygen introduced by passivation of hexagonal Mo₂C probably reacted with carbidic carbon, which was removed from the uppermost surface layer during this induction period [39]. Ranhotra *et al.* hypothesized that removal of surface oxygen during the induction period must be coincident with the elimination of some surface carbon because oxygen atoms are more strongly bonded to Mo than carbon [41]. Clearly, the passivation layer on Mo₂C can significantly affect the surface structure of the catalyst. Wu *et al.* observed that fresh hexagonal Mo₂C had many more sites for CO adsorption than a passivated sample, and few of the passivated sites could be recovered by H₂ reduction at 673 K and 773 K. From our XANES results, we conclude that the passivated sites on Mo₂C/MgO catalysts could not be fully recovered since Mo remained partially oxidized *in situ*.

Figure 2.8 X-ray absorption near edge structure (XANES) at the Mo K edge of: (a) Mo reference standards, (b) Mo₂C/MgO, (c) Rb-Mo₂C/MgO. MoO₃/MgO is the catalyst precursor before carburization.

Figure 2.9 Correlation of the Mo *K* edge energy (E_0 defined as energy at half step) to the oxidation state of reference compounds (triangles) and supported catalyst (circles).

Fourier transforms of the Mo *K* edge extended X-ray absorption fine structure (EXAFS) are presented in Figure 2.10. The coordination numbers (CN), interatomic distances (r), and Debye–Waller factors ($\Delta\sigma^2$) obtained by curve fitting are summarized in Table 2.7. Example curve fits associated with the results in Table 2.7 are compared to the experimental EXAFS for Mo *K* edge EXAFS of 5 wt.% Rb–5 wt.% Mo₂C/MgO (treated *in situ* for 4 h) in Figure 2.11. All of the *R*-factors of the fits are 0.1 or less.

Figure 2.10 Magnitude of the Fourier transform (not corrected for phase shifts) of the k^3 -weighted Mo K edge EXAFS of Mo standards compared to MgO-supported Mo species: (a) Mo_2C , (b) $\text{Rb-Mo}_2\text{C/MgO}$ RT after rxn, (c) $\text{Mo}_2\text{C/MgO}$ RT after rxn, (d) Mo foil, (e) MoO_3/MgO , (f) Rb_2MoO_4 . Spectra are offset for clarity.

The Mo EXAFS of the MoO_3/MgO sample (Figure 2.10e) before carburization was quite different from bulk MoO_3 (Figure 2.10g). No Mo–Mo interaction was observed in the supported sample and the Mo–O appeared to be contracted from the bulk oxide. The lack of Mo–Mo contributions indicates that Mo was very highly dispersed on the MgO support. Indeed, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ precursor solution reacted with the MgO support during catalyst preparation because the odor of ammonia was detected during wet impregnation. In the EXAFS analysis, the Mo–O distance in MoO_3/MgO was exactly the same as that in Rb_2MoO_4 , which suggests that our precursor of Mo_2C supported on MgO was a surface Mg molybdate.

Table 2.7 Results from the analysis of Mo EXAFS

Sample	Shell	CN	ΔE_0 (eV)	r (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	R - factor
Rb ₂ MoO ₄	Mo–O	4 ^a	7.4 ± 2.6	1.77 ± 0.01	2.5 ± 1.0	0.023
MoO ₃ /MgO	Mo–O	3.0 ± 0.4	1.8 ± 2.1	1.77 ± 0.01	3.8 ± 0.8	0.013
Mo ₂ C (bulk)	Mo–C (O)	3 ^a	4.0 ± 3.5	2.12 ± 0.02	3.1 ± 2.0	0.005
	Mo–Mo	12 ^a	-3.1 ± 0.8	2.97 ± 0.00	5.9 ± 3.8	
Mo ₂ C/MgO, <i>in situ</i> ^b	Mo–C (O)	5.1 ± 1.7	-2.5 ± 4.2	2.15 ± 0.02	6.2 ± 2.8	0.108
	Mo–Mo	7.8 ± 4.0	-25 ± 5	2.92 ± 0.02	13 ± 3	
Mo ₂ C/MgO, RT after rxn ^b	Mo–C (O)	5.3 ± 1.5	0.3 ± 3.5	2.16 ± 0.02	5.0 ± 2.2	0.068
	Mo–Mo	9.0 ± 3.2	-23 ± 3	2.93 ± 0.02	11 ± 2	
Rb–Mo ₂ C/MgO, <i>in situ</i> ^b	Mo–C (O)	5.1 ± 1.6	-2.6 ± 3.9	2.15 ± 0.02	6.0 ± 2.5	0.099
	Mo–Mo	8.2 ± 4.2	-26 ± 4	2.91 ± 0.02	14 ± 3	
Rb–Mo ₂ C/MgO, RT after rxn ^b	Mo–C (O)	5.8 ± 1.8	-2.4 ± 3.9	2.15 ± 0.02	5.7 ± 2.5	0.082
	Mo–Mo	8.5 ± 3.5	-24 ± 4	2.92 ± 0.02	11 ± 3	

In situ condition: $T = 573 \text{ K}$, $P = 30 \text{ bar}$, syngas flow rate = $24000 \text{ cm}^3 \text{ g}_{\text{Mo}}^{-1} \text{ min}^{-1}$.

Fitting parameters: FT range Δk : $2\text{--}14 \text{ Å}^{-1}$; fitting range ΔR : $1\text{--}3 \text{ Å}$; weighting: k^3 ;

$S_0^2(\text{Mo–C}) = 0.82$, $S_0^2(\text{Mo–Mo}) = 0.78$, $S_0^2(\text{Mo–O}) = 0.77$.

^a Value was assigned in curving fitting based on standard structure. ^b R_{bkg} was set to 1.2 in background removal to reduce the noise oscillation below 1 Å in R space.

Contributions from Mo–Mo in the Mo EXAFS of the Mo₂C catalysts were observed after carburization of the MoO₃/MgO sample in CH₄/H₂. It should be noted that the low intensity of the Mo–Mo peaks in the Fourier transform of the carburized catalysts in Figure 2.11 were partly the result of a lower coordination number (CN=8~9, Figure 2.11b and c) than that of the bulk hexagonal Mo₂C standard (CN=12, Figure 2.11a). According to Jentys [41], the low Mo–Mo coordination numbers suggest that about 70% of the Mo atoms were exposed to the surface of the Mo₂C clusters, with a corresponding particle size of about 2 nm, which is slightly smaller than that derived from TEM analysis ($2.8 \pm 0.3 \text{ nm}$). This small difference could be the result of some particle aggregation observed in TEM, and/or the shape of the Mo₂C clusters deviating from a perfect sphere. The ΔE_0 values (about -20 eV) need to fit the Mo –Mo contributions in the supported

catalysts were much greater than that reported for Mo₂C supported on Al₂O₃ [11] and zeolite [43,44]. In Figure 2.10, the Mo–Mo peak position in Mo₂C/MgO catalysts deviates about $-0.12 \text{ \AA}$ from that in bulk Mo₂C, and about $+0.15 \text{ \AA}$ from metallic Mo. This shift might suggest the existence of metallic Mo in the Mo₂C/MgO catalyst. In fact, Lee and Boudart observed a Mo–Mo distance at $2.80 \text{ \AA}$ in Al₂O₃ supported metallic Mo [11], which is between bulk Mo metal ($2.72 \text{ \AA}$) and bulk Mo₂C ($2.97 \text{ \AA}$). However, results from XANES and elemental analysis both suggest the formation of carbidic Mo rather than metallic Mo. Therefore, we conclude that the Mo₂C/MgO catalysts have the local structure of carbidic Mo species, with a Mo–Mo distance ($2.92 \text{ \AA}$) contracted from the bulk Mo₂C ($2.97 \text{ \AA}$) because of the small particle size.

The Mo–C interaction in EXAFS of fresh supported Mo₂C catalysts has been studied elsewhere [11,43,44], and the coordination number of Mo–C varies from 0.6 to 2. In our study, the coordination numbers of the metal–nonmetal interactions in Mo₂C/MgO catalysts are all about 5, which exceed the value of 3 in bulk Mo₂C. Because the backscattering functions of C and O are similar, it was not possible to distinguish the different atom types in the EXAFS fitting. Considering the high percentage of surface Mo in Mo₂C/MgO catalysts, almost all the surface Mo atoms will likely be bonded to oxygen atoms from passivation and could result in a high CN for the nonmetal. This speculation is consistent with the finding of Hwu *et al.* [45], who claim that an oxygen modified Mo₂C surface can exist at 600 K. Although it is believed that some of the passivated Mo sites can be recovered by reduction to give sites for adsorption, the recovery could be fairly limited [33]. Moreover, even if some of the Mo sites are recovered, the reactant CO and absorbed reaction intermediates could also contribute to the coordination

environment around Mo. In summary, the high CN of nonmetal (C and O) in Mo₂C/MgO catalysts is a combination of carbidic carbon, oxygen coming from passivation and the chemically adsorbed reaction intermediates, with a Mo–C (O) distance of 2.15 Å, which is slightly elongated from the Mo–C bonds in bulk Mo₂C (2.12 Å).

Figure 2.11 Comparison of curve fit to experimental Mo K edge EXAFS of the 5 wt.% Rb–5 wt.% Mo₂C/MgO catalyst in 30 bar syngas at 573 K (a) Magnitude (solid line) and the imaginary part (dash line) of the Fourier transform of EXAFS compared to the result from the curve fit (circle); (b) k^3 -weighted Mo K edge EXAFS (solid line) and the result from curve fit (circle).

Figure 2.12 XANES at the Rb *K* edge. Solid lines are spectra recorded at RT without any pretreatment. Dashed lines are spectra recorded at RT after various treatments: (a) $\text{Rb}_2\text{CO}_3\text{-Mo}_2\text{C/MgO}$ (before and after exposure to 30 bar syngas at 573 K for 4 h), (b) $\text{Rb}_2\text{CO}_3\text{-Mo}_2\text{C/MgO}$ (before and after heating in Ar at 573 K for 4 h), (c) $\text{Rb}_2\text{CO}_3\text{/MgO}$ (before and after heating in Ar at 573 K for 4 h), (d.1) $\text{Rb}_2\text{CO}_3\text{/H}_2\text{O}$ paste at RT, (d.2) Rb_2CO_3 as received. Spectra are offset for clarity.

Figure 2.12 presents the near edge features of Rb species in different samples. The Rb_2CO_3 sample directly from the as-received bottle (Figure 2.12d.2) has a double-peak near edge feature, which can be removed by hydration with a small amount of liquid water (Figure 2.12d.1). Physically-mixing Rb_2CO_3 with MgO or $\text{Mo}_2\text{C/MgO}$, yielded a spectrum consistent with the hydrated sample (Figure 2.12c.1 and Figure 2.12d.1). As shown in Figure 2.12c, heating of $\text{Rb}_2\text{CO}_3\text{/MgO}$ in Ar regenerated the double peak feature that is similar to bulk Rb_2CO_3 in Figure 2.12d.2. However, after heating the

carbide sample in either Ar or syngas, the double peak edge structure of Rb_2CO_3 was not formed, which suggests a possible structural change of the Rb_2CO_3 on our active catalyst samples. Sarkar *et al.* observed similar Rb *K* edge spectra for rubidium promoted Fischer–Tropsch catalysts, but concluded the promoter resembled Rb_2CO_3 [45]. Additional studies are required to determine the nature of the supported Rb phase since the EXAFS above the Rb *K* edge was uninformative. We speculate that Mo may catalyze the decomposition of Rb_2CO_3 to more basic oxides or hydroxides. Earlier work in our laboratory showed that BaCO_3 decomposition was facilitated by H_2 in the presence of a transition metal such as Ru [47].

2.4 Conclusion

The synthesis of higher alcohols during CO hydrogenation reactions over $\text{Mo}_2\text{C}/\text{MgO}$ catalysts at 30 bar and 573 K was promoted by both the basic support MgO and the presence of added Rb_2CO_3 promoter. Bulk Mo_2C was an effective Fischer–Tropsch catalyst under the standard conditions used here and produced only trace alcohols. Supporting Mo_2C onto MgO as 2-3 nm sized particles promoted the alcohol synthesis reaction, although hydrocarbons were still favored over alcohols. Addition of Rb_2CO_3 to $\text{Mo}_2\text{C}/\text{MgO}$ substantially improved the selectivity to alcohols at the expense of hydrocarbons. Higher alcohol synthesis was favored at high syngas pressure and low CO conversion.

Results from X-ray diffraction, transmission electron microscopy and X-ray absorption fine structure confirmed the high dispersion of Mo_2C on MgO. Near edge spectroscopy followed the incomplete reduction of passivated $\text{Mo}_2\text{C}/\text{MgO}$ at reaction conditions, and confirmed the presence of partially oxidized Mo during reaction. *In situ*

EXAFS revealed that the Mo₂C clusters had a longer average Mo–C (O) interatomic distance (2.15 Å) and a shorter average Mo–Mo distance (2.92 Å) than bulk Mo₂C, presumably because of the high dispersion on MgO. The relatively large coordination of C (O) to Mo suggested the existence of surface oxycarbide layer on Mo₂C clusters. Electron microscopy and Rb *K* edge XANES indicated Rb was well-distributed over the surface, but was chemically modified from bulk Rb₂CO₃.

References of Chapter 2

- [1] R.G. Herman, “Advances in catalytic synthesis and utilization of higher alcohols,” *Catalysis Today* 55 (2000) 233–245.
- [2] P. Forzatti, E. Tronconi, I. Pasquon, “Higher alcohol synthesis,” *Catalysis Reviews: Science and Engineering* 33 (1991) 109–168.
- [3] K. Fang, D. Li, M. Lin, M. Xiang, W. Wei, Y. Sun, “A short review of heterogeneous catalytic process for mixed alcohols synthesis via syngas,” *Catalysis Today* 147 (2009) 133–138.
- [4] V. Subramani, S.K. Gangwal, “A review of recent literature to search for an efficient catalytic process for the conversion of syngas to ethanol,” *Energy & Fuels* 22 (2008) 814–839.
- [5] G.J. Quarderer, G.A. Cochran, “Catalytic process for producing mixed alcohols from hydrogen and carbon monoxide,” European Patent EP0119609, 1984, to The Dow Chemical Company.
- [6] M.M. Conway, C.B. Murchison, R.R. Stevens, “Method for adjusting methanol to higher alcohol ratios,” U.S. Patent 4675344, 1987, to The Dow Chemical Company.
- [7] G.J. Quarderer, G.A. Cochran, “Process for producing alcohols from synthesis gas,” U.S. Patent 4749724, 1988, to The Dow Chemical Company.
- [8] R.R. Stevens, “Process for producing alcohols from synthesis gas,” U.S. Patent 4752622, 1988, to The Dow Chemical Company.
- [9] R.R. Stevens, “Process for producing alcohols from synthesis gas,” U.S. Patent 4882360, 1989, to The Dow Chemical Company.
- [10] R.B. Levy, M. Boudart, “Platinum-like behavior of tungsten carbide in surface catalysis,” *Science* 181 (1973) 547–549.

- [11] J.S. Lee, M. Boudart, "In situ carburization of metallic molybdenum during catalytic reactions of carbon-containing gases," *Catalysis Letters* 20 (1993) 97–106.
- [12] J.S. Lee, S.T. Oyama, M. Boudart, "Molybdenum carbide catalysts: I. Synthesis of unsupported powders," *Journal of Catalysis* 106 (1987) 125–133.
- [13] J.S. Lee, S. Locatelli, S.T. Oyama, M. Boudart, "Molybdenum carbide catalysts 3. Turnover rates for the hydrogenolysis of *n*-butane," *Journal of Catalysis* 125 (1990) 157–170.
- [14] S.T. Oyama, "Preparation and catalytic properties of transition metal carbides and nitrides," *Catalysis Today* 15 (1992) 179–200.
- [15] J.G. Chen, "Carbide and nitride overlayers on early transition metal surfaces: Preparation, characterization, and reactivities," *Chemical Reviews* 96 (1996) 1477–1498.
- [16] K.Y. Park, W.K. Seo, J.S. Lee, "Selective synthesis of light olefins from syngas over potassium-promoted molybdenum carbide catalysts," *Catalysis Letters* 11 (1991) 349–356.
- [17] H.C. Woo, K.Y. Park, Y.G. Kim, I. Nam, J.S. Chung, J.S. Lee, "Mixed alcohol synthesis from carbon monoxide and dihydrogen over potassium-promoted molybdenum carbide catalysts," *Applied Catalysis* 75 (1991) 267–280.
- [18] J.S. Lee, S. Kim, Y.G. Kim, "Electronic and geometric effects of alkali promoters in CO hydrogenation over K/Mo₂C catalysts," *Topics in Catalysis* 2 (1995) 127–140.
- [19] L. Leclercq, A. Almazouari, M. Dufour, G. Leclercq, "Carbide-oxide interactions in bulk and supported tungsten carbide catalyst for alcohol synthesis," in: S.T. Oyama (Ed.), *The Chemistry of Transition Metal Carbides and Nitrides*, Springer, 1996: pp. 345–361.
- [20] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "K/Fe/ β -Mo₂C: A novel catalyst for mixed alcohols synthesis from carbon monoxide hydrogenation," *Catalysis Communications* 8 (2007) 88–90.
- [21] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "Synthesis of higher alcohols from syngas over K/Co/ β -Mo₂C catalysts," *Catalysis Communications* 8 (2007) 503–507.
- [22] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "Potassium and nickel doped β -Mo₂C catalysts for mixed alcohols synthesis via syngas," *Catalysis Communications* 8 (2007) 513–518.

- [23] M. Xiang, D. Li, H. Xiao, J. Zhang, W. Li, B. Zhong, Y. Sun, "K/Ni/ β -Mo₂C: A highly active and selective catalyst for higher alcohols synthesis from CO hydrogenation," *Catalysis Today* 131 (2008) 489–495.
- [24] M. Xiang, D. Li, H. Xiao, J. Zhang, H. Qi, W. Li, B. Zhong, Y. Sun, "Synthesis of higher alcohols from syngas over Fischer–Tropsch elements modified K/ β -Mo₂C catalysts," *Fuel* 87 (2008) 599–603.
- [25] N. Wang, K. Fang, M. Lin, D. Jiang, D. Li, Y. Sun, "Synthesis of higher alcohols from syngas over Fe/K/ β -Mo₂C catalyst," *Catalysis Letters* 136 (2010) 9–13.
- [26] N. Wang, K. Fang, D. Jiang, D. Li, Y. Sun, "Iron carbide promoted K/ β -Mo₂C for higher alcohols synthesis," *Catalysis Today* 158 (2010) 241–245.
- [27] L. Zhao, K. Fang, D. Jiang, D. Li, Y. Sun, "Sol-gel derived Ni–Mo bimetallic carbide catalysts and their performance for CO hydrogenation," *Catalysis Today* 158 (2010) 490–495.
- [28] J.T. Calla, R.J. Davis, "Oxygen-exchange reactions during CO oxidation over titania- and alumina-supported Au nanoparticles," *Journal of Catalysis* 241 (2006) 407–416.
- [29] R. Burch, M. Petch, "Investigation of the synthesis of oxygenates from carbon monoxide/hydrogen mixtures on supported rhodium catalysts," *Applied Catalysis A: General* 88 (1992) 39–60.
- [30] B. Fingland, F. Ribeiro, J. Miller, "Simultaneous measurement of X-ray absorption spectra and kinetics: A fixed-bed, plug-flow *operando* reactor," *Catalysis Letters* 131 (2009) 1–6.
- [31] B. Ravel, M. Newville, "ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT," *Journal of Synchrotron Radiation* 12 (2005) 537–541.
- [32] S. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, M.J. Eller, "Multiple-scattering calculations of x-ray-absorption spectra," *Physical Review B* 52 (1995) 2995–3009.
- [33] W. Wu, Z. Wu, C. Liang, X. Chen, P. Ying, C. Li, "In situ FT-IR spectroscopic studies of CO adsorption on fresh Mo₂C/Al₂O₃ catalyst," *The Journal of Physical Chemistry B* 107 (2003) 7088–7094.
- [34] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "Performances of mixed alcohols synthesis over potassium promoted molybdenum carbides," *Fuel* 85 (2006) 2662–2665.
- [35] H. Kim, K.H. Lee, J.S. Lee, "Carbon monoxide hydrogenation over molybdenum carbide catalysts," *Research on Chemical Intermediates* 26 (2000) 427–443.

- [36] Muramatsu, T. Tatsumi, H. Tominaga, "Mixed alcohol synthesis from CO-H₂ by use of KCl-promoted Mo/SiO₂ catalysts," *Bulletin of the Chemical Society of Japan* 60 (1987) 3157–3161.
- [37] J. Christensen, P. Mortensen, R. Trane, P. Jensen, A. Jensen, "Effects of H₂S and process conditions in the synthesis of mixed alcohols from syngas over alkali promoted cobalt-molybdenum sulfide," *Applied Catalysis A: General* 366 (2009) 29–43.
- [38] V. Ponec, "Active centres for synthesis gas reactions," *Catalysis Today* 12 (1992) 227–254.
- [39] G. van der Lee, V. Ponec, "On some problems of selectivity in syngas reactions on the group VIII metals," *Catalysis Reviews: Science and Engineering* 29 (1987) 183–218.
- [40] Griboval-Constant, J. Giraudon, G. Leclercq, L. Leclercq, "Catalytic behavior of cobalt or ruthenium supported molybdenum carbide catalysts for FT reaction," *Applied Catalysis A: General* 260 (2004) 35–45.
- [41] G.S. Ranhotra, A.T. Bell, J.A. Reimer, "Catalysis over molybdenum carbides and nitrides: II. Studies of CO hydrogenation and C₂H₆ hydrogenolysis," *Journal of Catalysis* 108 (1987) 40–49.
- [42] Jentys, "Estimation of mean size and shape of small metal particles by EXAFS," *Physical Chemistry Chemical Physics* 1 (1999) 4059–4063.
- [43] S. Liu, L. Wang, R. Ohnishi, M. Ichikawa, "Bifunctional catalysis of Mo/HZSM-5 in the dehydroaromatization of methane to benzene and naphthalene XAFS/TG/DTA/MASS/FTIR characterization and supporting effects," *Journal of Catalysis* 181 (1999) 175–188.
- [44] W. Ding, S. Li, G. D Meitzner, E. Iglesia, "Methane conversion to aromatics on Mo/H-ZSM5: Structure of molybdenum species in working catalysts," *The Journal of Physical Chemistry B* 105 (2001) 506–513.
- [45] H.H. Hwu, M.B. Zellner, J.G. Chen, "The chemical and electronic properties of oxygen-modified C/Mo(110): A model system for molybdenum oxycarbides," *Journal of Catalysis* 229 (2005) 30–44.
- [46] Sarkar, G. Jacobs, Y. Ji, H.H. Hamdeh, B.H. Davis, "Fischer–Tropsch synthesis: Characterization Rb promoted iron catalyst," *Catalysis Letters* 121 (2008) 1–11.
- [47] B.C. McClaine, S.E. Siporin, R.J. Davis, "X-ray and IR spectroscopy of barium-promoted, zeolite-supported ruthenium catalysts for ammonia synthesis," *The Journal of Physical Chemistry B* 105 (2001) 7525–7532.

Chapter 3.

Influence of passivation on the reactivity of unpromoted and Rb-promoted Mo₂C nanoparticles for CO hydrogenation

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Abstract

Unpromoted and Rb-promoted Mo₂C nanoparticles (~1 nm in size) were synthesized on α -alumina and used for CO hydrogenation. The reaction was performed in a fixed-bed reactor system operating at 573 K and 30 bar with a gas flow rate of 24,000 cm³ g_{Mo}⁻¹ h⁻¹ and H₂/CO = 1. Unpromoted Mo₂C functioned as a Fischer–Tropsch catalyst producing mostly hydrocarbons at the standard conditions. Passivation of freshly synthesized Mo₂C nanoparticles in 1% O₂ prior to CO hydrogenation decreased the Fischer–Tropsch activity of the catalyst by about 40% compared to a non-passivated sample. Addition of Rb promoter to Mo₂C shifted the selectivity of the catalyst by inhibiting the formation of hydrocarbons while enhancing the formation of alcohols. The presence of Rb with Mo₂C also reduced substantially the sensitivity of the catalyst to passivation by 1% O₂ compared to unpromoted Mo₂C. The partial oxidation of the Mo₂C nanoparticles by passivation and partial reduction by syngas was confirmed by Mo *K* edge X-ray absorption spectroscopy.

3.1 Introduction

Limited crude oil reserves and competition with the food industry associated with fermentation-based biofuel production inspire new efforts on effective catalytic transformations of alternative carbon sources to produce energy carriers and chemical feedstocks. Production of higher alcohols from the catalytic conversion of synthesis gas ($\text{CO}+\text{H}_2$) derived from coal, natural gas or renewable biomass is one strategy that has shown some promise [1–4].

Although Rh-based catalysts are effective for the formation of ethanol and other C2-oxygenates from syngas [5–7], the very high cost of Rh likely prohibits its large scale utilization. Several non-precious metal catalysts for higher alcohol synthesis have thus been evaluated and include, for example, MoS_2 , Cu–Co, Cu–Zn–Al and Zn–Cr–K, but improvements in the overall catalytic activity, alcohol selectivity, and long-term stability of these materials are still needed [2].

Early transition metal carbides are also recognized as potential substitutes to precious metal catalysts because of their similar surface electronic properties [8–10]. For example, molybdenum carbide catalysts are well-known to produce hydrocarbons from syngas via Fischer–Tropsch synthesis [11–13], but the selectivity of the reaction shifts from hydrocarbons to higher alcohols when appropriate promoters and reaction conditions are used [14,15]. The highly reactive carbide surface is very sensitive to oxygen and therefore needs to be passivated before exposure to air. Prior works have described the various behaviors of oxygen-modified carbide surfaces in different reactions. For example, Ribeiro *et al.* and Iglesia *et al.* claimed that surface oxygen inhibits the very high reactivity of fresh tungsten carbide for hydrogenolysis of

hydrocarbons. However, partial oxidation of the tungsten carbide surface also forms acid sites that catalyze hydrocarbon isomerization reactions through coupled dehydrogenation and carbenium ion reactions [16–20]. For a reaction such as higher alcohol synthesis from syngas, the presence of acid sites on the catalyst formed by passivation would likely be detrimental to the desired product distribution. In other work, Liu *et al.* reported that a carbide-modified W(111) surface was highly selective for the dehydrogenation of cyclohexane to benzene after exposure to O₂ at 900 K, but was inactive to cyclohexane after exposure to O₂ at <600 K [21]. Similarly, Hwu *et al.* found that a carbide-modified Mo(110) surface exposed to O₂ at 900 K exhibited decomposition activity for cyclohexene, ethylene and methanol, whereas the carbide surface was relatively unreactive toward those substrates after O₂ exposure at 600 K [22]. Nagai *et al.* also showed that passivation of molybdenum carbide with dilute O₂ at room temperature reduced its activity in CO₂ hydrogenation to form CO and CH₄ [23]. Using FT-IR spectroscopy, Wu *et al.* revealed that a surface passivation procedure with dilute O₂ at room temperature irreversibly modified a fresh molybdenum carbide surface, hence significantly reducing the number of sites for CO adsorption [24,25].

Evidently, carbidic carbon atoms and/or metal atoms react with the O₂ used in passivation, which can significantly modify the observed reactivity of carbide catalysts. Therefore, the influence of O₂ on reactivity must be examined as part of any comprehensive study of carbidic materials for catalysis. In this work, the influence of passivation on the structure and CO hydrogenation activity of alumina-supported Mo₂C catalysts, with and without alkali metal promoter, was explored.

3.2 Experimental methods

3.2.1 Catalyst synthesis

Incorporation of Mo onto the alumina support (Mager Scientific, >99.98%, predominantly α -phase, $S_{\text{BET}} = 26.8 \text{ m}^2 \text{ g}^{-1}$) was accomplished by incipient wetness impregnation of an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (99.98%, Aldrich) followed by drying in air for 12 h at 400 K and calcining in flowing air for 5 h at 773 K to produce a supported molybdenum oxide, denoted here as $\text{MoO}_3/\text{Al}_2\text{O}_3$. The sample of $\text{MoO}_3/\text{Al}_2\text{O}_3$ was then reduced at 673 K in flowing H_2 (GTS-Welco, 99.999%) for 5 h prior to carburization. The supported oxide sample after reduction is denoted here as $\text{MoO}_2/\text{Al}_2\text{O}_3$ for reference. (The formation of a partially reduced Mo species is verified by X-ray absorption spectroscopy reported later.) The partially reduced $\text{MoO}_2/\text{Al}_2\text{O}_3$ sample was either carburized or promoted with Rb prior to carburization. The Rb-promoted $\text{MoO}_2/\text{Al}_2\text{O}_3$ samples were prepared by grinding Rb_2CO_3 (99.975%, Alfa Aesar) together with $\text{MoO}_2/\text{Al}_2\text{O}_3$ in a mortar and pestle. Carburization of $\text{MoO}_2/\text{Al}_2\text{O}_3$ and Rb-promoted $\text{MoO}_2/\text{Al}_2\text{O}_3$ was performed in a stainless steel tube reactor (26.7 cm length, 1.27 cm OD, 0.85 cm ID, see Figure 3.1a) by heating at a rate of 5 K min^{-1} from room temperature to 673 K and at a rate of 1 K min^{-1} from 673 K to 900 K in 11.1 vol.% C_2H_6 (GTS-Welco, 99.997%) and 88.9 vol.% H_2 (GTS-Welco, 99.999%) at a total gas flow rate of $67.5 \text{ cm}^3 \text{ min}^{-1}$. After ramping to 900 K in $\text{C}_2\text{H}_6/\text{H}_2$, the temperature was maintained at 900 K for 8 h. Ethane was used as a carbon source instead of methane to reduce the temperature for carburization [26,27], since elemental analysis revealed that 74% of the total Rb was vaporized during carburization in CH_4/H_2 at 973 K. The catalyst was subsequently cooled to room temperature in flowing Ar (GTS-Welco, 99.999%,

additionally purified by an OMI-2 purifier (Sigma-Aldrich)). The catalysts were used “as carburized” or passivated in a stream of 1.04 vol.% O₂/N₂ mixture (GTS-Welco) at room temperature for 12 h. After carburization or passivation, the reactor containing the catalyst (Figure 3.1a) was purged with purified flowing Ar, sealed by a cap (Swagelok) on the downstream end and a 3-way valve (Swagelok) on the upstream end, and installed in the high pressure CO hydrogenation reactor system.

Figure 3.1 (a) Reactor for carburization and CO hydrogenation, and (b) XAS sample tube. Both were used for air-free handling.

3.2.2 Hydrogenation of carbon monoxide

Hydrogenation of CO was conducted in a BTRS Jr. system (Autoclave Engineers) equipped with the fixed-bed stainless steel reactor (Figure 3.1a) used to carburize the catalyst. The reactor contained nominally 0.05 g Mo₂C, composed of about 1.0 g of Mo₂C/Al₂O₃ or Rb-promoted Mo₂C/Al₂O₃. The catalysts were tested at identical conditions of 573 K, 30 bar total pressure, syngas (H₂ + CO) flow of 20 cm³ min⁻¹ (STP) and H₂/CO = 1. The reactor was pressurized to 30 bar at room temperature and heated to 573 K before sampling. The catalyst temperature was monitored with a thermocouple in

contact with the catalyst bed. The purity of CO (GT&S) was 99.9% and H₂ (GT&S) was 99.999%. Additionally, CO was purified by passing it through a silica trap immersed in a dry ice-acetone mixture (195 K) to remove any trace iron carbonyl before introduction to the reactor. The products were analyzed by two Hewlett-Packard 5890 series II gas chromatographs. The first one was equipped with a flame ionization detector and a 50 m-long HP-1 cross-linked methyl silicone gum capillary column to monitor the formation of hydrocarbons (C1-C10) and alcohols (C1-C7). The second one was equipped with a thermal conductivity detector and a 6-ft long Alltech-8700 packed column and was used to monitor the formation of CO₂.

The conversion of CO was derived from the fraction of CO that formed carbon-containing products. The conversion of CO, if low, can be described as:

$$\text{Conversion (\%)} = \sum n_i M_i \times 100 / M_{\text{CO}} \text{ [28],}$$

where n_i is the number of carbon atoms in product i , M_i is the percentage of product i detected, and M_{CO} is the percentage of CO in the syngas feed.

The selectivity to product i is based on the total number of carbon atoms in the product and is therefore defined as:

$$\text{Selectivity (\%)} = n_i M_i \times 100 / \sum n_i M_i.$$

The conversion and selectivities were based on the identified products, which present 93%-95% of the total peak area in GC chromatograms.

3.2.3 Catalyst characterization

Elemental analyses of representative samples were performed by Galbraith Laboratories (Knoxville, TN). The loading of molybdenum and rubidium was determined

by inductively coupled plasma atomic emission spectroscopy (ICP-AES), while the loading of carbon was evaluated by combustion and coulometric measurement.

Electron microscopy was performed on an FEI Titan transmission electron microscope operated at 200 kV. Two passivated catalysts, 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ and 1.5 wt.% $\text{Rb}-5$ wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, were reacted in syngas for 48 h and subsequently passivated again with 1.02 vol.% O_2/N_2 (GTS-Welco) at room temperature before TEM analysis. Catalyst powders were dispersed in *n*-hexane and supported onto a lacey carbon film coated grid. Images were recorded with a Gatan 794 Multi Scan CCD camera.

X-ray absorption spectroscopy (XAS) was performed at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The non-passivated samples before reaction and all of the samples after reaction were sealed in the reactor and transferred into a glovebox. In the glovebox, all the samples were loaded into borosilicate glass tubes (15 cm length, 0.64 cm OD, 0.40 cm ID, see Figure 3.1b) and sealed with silicone plugs on both ends to avoid exposure to air. The sealed glass tubes were further wrapped in parafilm and stored in air-tight plastic bags before being taken out of the glovebox. The samples in these sealed tubes were used for *ex situ* XAS studies on beam lines X23A2 and X18B at the NSLS. The storage ring was typically operated at 2.8 GeV with a ring current of about 300 mA. The XAS data were obtained in the transmission mode at the Mo *K* edge (20 keV) with a spot size of 0.5 mm×3 mm at X-18B and 0.5 mm×5 mm at X-23A2. The Mo *K* edge spectra were measured at room temperature with Mo foil (0.015 mm, 99.9%, Goodfellow) as a reference.

The XAS data were processed using the Athena [29] software for background removal, post-edge normalization, and X-ray absorption near edge structure (XANES)

analysis. Because the Mo near edge structure has various features that complicate the determination of E_0 , the edge energy, the value of E_0 was assigned here as the energy at the half step height. Metallic Mo foil, MoO₂ (99%, Aldrich), and MoO₃ (99.99%, Aldrich) were used as standards for Mo residing in 0, +4 and +6 formal oxidation states. Standard bulk Mo₂C (Aldrich, 99.5%) was used to determine the amplitude reduction factors S_0^2 for Mo–C and Mo–Mo. The values of S_0^2 utilized in the fitting of extended X-ray absorption fine structure (EXAFS) data from the catalyst samples were 0.86 and 0.76 for Mo–C and Mo–Mo, respectively. The EXAFS results were fitted in *R*-space using two shells (Mo–C & Mo–Mo) generated theoretically using FEFF 6.0A [30]. The interatomic distances (*r*), coordination numbers (CN), Debye-Waller factors ($\Delta\sigma^2$) and energy shifts (ΔE_0) were derived from the fitting results in the Artemis software package [29].

3.3 Results and discussion

Although elemental analysis of a 5 wt.% Mo₂C/Al₂O₃ catalyst showed a C/Mo molar ratio of 0.39, which is slightly lower than the expected value from stoichiometry (0.5), the EXAFS results discussed later confirmed the formation of a supported carbide. Elemental analysis of a 1.5 wt.% Rb–5 wt.% Mo₂C/Al₂O₃ revealed a Rb/Mo molar ratio of 0.31, which was close to the nominal value (0.34). Evidently, the low temperature carburization with C₂H₆/H₂ successfully avoided the volatilization of Rb promoter.

The performance of non-passivated alumina-supported Mo₂C catalysts in the reaction of syngas (H₂/CO = 1) at 573 K and 30 bar pressure is summarized in Table 3.1. Unpromoted Mo₂C/Al₂O₃ functions primarily as an active Fischer–Tropsch catalyst with 20% CO conversion, producing mainly hydrocarbons (98% on a CO₂-free basis). The

addition of 1, 1.5 or 2 wt.% Rb_2CO_3 to 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ increased the selectivity to alcohols (42%, 56% or 64%, respectively) at the expense of overall CO conversion (down to 2.6% at the highest promoter loading), which is consistent with our previous study on a Rb-promoted $\text{Mo}_2\text{C}/\text{MgO}$ catalyst [31], and with prior work on potassium-promoted bulk Mo_2C catalysts [14,15,32]. Clearly, there is a trade-off between rate of CO conversion and selectivity to alcohols.

Table 3.1 Reactivity of non-passivated 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalysts in syngas reaction

Rb loading (wt.%)	0	1.0	1.5	2.0
CO conversion (%)	20	11	5.0	2.6
CO ₂ selectivity (%)	47	45	52 ^a	42
Selectivity (C %, on a CO ₂ -free basis)				
Total hydrocarbons	98	58	44	36
Methane	31	16	15	12
C2 hydrocarbons	25	14	11	9.4
C3 hydrocarbons	21	12	7.5	5.8
C4+ linear paraffins	12	7.0	2.8	2.0
C4+ linear olefins	2.1	6.5	5.7	5.1
Branched hydrocarbons	5.8	2.3	1.5	1.3
Total alcohols	2.4	42	56	64
Methanol	1.5	12	16	18
Ethanol	0.7	15	21	22
1-Propanol	0.3	8.6	12	15
1-Butanol	0.0	2.7	4.2	4.6
2-Butanol	0.0	1.4	1.0	0.8
C5+ alcohols	0.0	1.7	1.9	4.3
(C2+ alcohols)/(methanol)	0.66	2.5	2.5	2.5
Rate of CO consumption ($\text{mol}_{\text{CO}} \text{ mol}_{\text{Mo}}^{-1} \text{ h}^{-1}$)	9.9	5.5	2.5	1.3
Rate of hydrocarbon production ($\text{g g}_{\text{Mo}}^{-1} \text{ h}^{-1}$)	0.80	0.28	0.082	0.044
Rate of alcohol production ($\text{g g}_{\text{Mo}}^{-1} \text{ h}^{-1}$)	0.037	0.32	0.17	0.12

T = 573 K, P = 30 bar, 0.05 g nominal Mo_2C (~1.0 g supported catalyst), $\text{H}_2/\text{CO}=1$, syngas flow = 20 cm³ (STP) min⁻¹. Data were recorded after 48 h reaction.

^a The excess to the theoretical limit (50%) is likely due to a small experimental error.

Figure 3.2 Change in catalytic performance of non-passivated 1.5 wt.% Rb-5 wt.% Mo₂C/Al₂O₃ during CO hydrogenation at 573 K and 30 bar over time: (a) CO conversion; (b) selectivity of CO₂; (c) selectivity of total hydrocarbons and of total alcohols; (d) selectivity of C1-C5 linear alcohols.

The change of catalytic performance with time for non-passivated 1.5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst is presented in Figure 3.2 as an example. Although the catalyst deactivated continuously over the run, most of the deactivation occurred over the first 20 h, during which the conversion of CO declined by half. Likewise, the major changes in selectivity to hydrocarbons and alcohols occurred during the initial 20 h.

Figure 3.3 Change in production rates of hydrocarbons (square) and alcohols (circle) during CO hydrogenation at 573 K and 30 bar over: (a) 1.5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, non-passivated, dry impregnation (DI) of Rb_2CO_3 before carburization; (b) 5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, non-passivated, DI of Rb_2CO_3 after carburization.

To explore the influence of carburization on the effectiveness of the Rb promoter, dry impregnation of Rb_2CO_3 onto non-passivated 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ was performed in a glovebox to achieve a 5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$. The catalytic performance of a 1.5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst prepared with promoter incorporated prior to carburization and the 5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst with promoter impregnated after carburization is compared in Figure 3.3a and Figure 3.3b, respectively. Evidently, when the Rb_2CO_3 promoter was added after carburization (Figure 3.3b), the catalyst exhibited a negligible initial production rate of alcohols and a relatively high initial production rate of hydrocarbons. However, the production rates varied sharply during the first 8 h of reaction. In contrast, when the Rb_2CO_3 promoter was added before carburization, a relatively steady production rate of alcohols was observed from the beginning of the reaction (Figure 3.3a). These results are consistent with the mechanism of promotion of MoS_2 and Mo_2C catalysts for CO hydrogenation proposed by Lee et al. [33,34], which involves the spreading of the alkali metal promoter over the active sulfide or carbide at reaction conditions. For a sample that was promoted prior to carburization (Figure 2a), the carburization treatment at elevated temperature evidently facilitated the effective spreading of the promoter over the catalyst, whereas for a sample promoted after carburization (Figure 3.3b), at least 8 h of syngas reaction were needed to disperse the Rb promoter. A previous study of Rb-promoted Mo_2C supported on MgO concluded that the structure of bulk Rb_2CO_3 added to the catalyst was altered by exposure to syngas reaction conditions, as observed by Rb K-edge spectroscopy [31]. However, the chemical state of the spreading promoter is not yet known. It is important to note that the production rate of hydrocarbons on the sample that was promoted prior to carburization

(Figure 3.3a) declined by a half over the first 20 h of reaction before reaching a fairly steady rate, whereas the production rate of alcohols deactivated much less severely. The results reported here suggest that although carburization facilitated the spreading of Rb promoter to the active Mo₂C nanoclusters, additional exposure of the catalyst to syngas conditions likely improved the interaction of the promoter with the carbide, which enhanced alcohol selectivity with time on stream during CO hydrogenation.

Table 3.2 Influence of passivation on the reactivity of unpromoted and Rb-promoted 5 wt.% Mo₂C/Al₂O₃ catalysts at similar CO conversion levels

Rb loading (wt.%)	0		1.5	
Passivation	No	Yes	No	Yes
Syngas flow rate (cm ³ g _{Mo} ⁻¹ h ⁻¹)	96,000	53,000	24,000	24,000
CO conversion (%)	5.6	5.5	5.0	4.7
CO ₂ selectivity (%)	46	48	52 ^a	44
Selectivity (C %, on a CO ₂ -free basis)				
Total hydrocarbons	89	98	44	47
Methane	33	45	15	18
C2 hydrocarbons	24	27	11	13
C3 hydrocarbons	17	17	7.5	7.9
C4+ linear paraffins	6.5	4.4	2.8	2.4
C4+ linear olefins	2.0	1.3	5.7	4.4
Branched hydrocarbons	7.0	4.3	1.5	1.3
Total alcohols	11	1.6	56	53
Methanol	4.9	0.89	16	16
Ethanol	4.1	0.70	21	19
1-Propanol	1.8	0.0	12	12
1-Butanol	0.0	0.0	4.2	3.8
2-Butanol	0.0	0.0	1.0	0.8
1-Pentanol	0.0	0.0	1.9	1.6
(C2+ alcohols)/(methanol)	1.2	0.79	2.5	2.4
Rate of CO consumption (mol _{CO} mol _{Mo} ⁻¹ h ⁻¹)	11	6.9	2.5	2.3
Rate of hydrocarbon production (g g _{Mo} ⁻¹ h ⁻¹)	0.85	0.57	0.082	0.098
Rate of alcohol production (g g _{Mo} ⁻¹ h ⁻¹)	0.18	0.017	0.17	0.17

T = 573 K, P = 30 bar, H₂/CO = 1. Data were recorded after 48 h reaction.

^a The excess beyond the theoretical limit (50%) is likely due to experimental error in analysis.

The influence of passivation on the reactivity of unpromoted and Rb-promoted $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalysts can be seen in Table 3.2. Since we have observed in prior work a strong correlation between CO conversion and hydrocarbon selectivity over supported Mo_2C [31], a direct comparison of the selectivities requires the same level of CO conversion. Therefore, the loading of unpromoted 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ (non-passivated and passivated) was adjusted in the reactor to give a comparable conversion of CO at standard conditions with those of the Rb-promoted catalysts. As expected, the unpromoted catalysts produced mainly hydrocarbons, with selectivities of 89 and 98% (on a CO_2 -free basis) over the non-passivated and passivated catalysts, respectively. Passivation decreased the activity of unpromoted 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst by 37% (reducing the CO consumption rate from 11 to $6.9 \text{ mol}_{\text{CO}} \text{ mol}_{\text{Mo}}^{-1} \text{ h}^{-1}$), indicating a strong influence of surface oxygen on the activity of Mo_2C . This result is reminiscent of the work of Wu *et al.*, who claimed that passivation of Mo_2C with an O_2/N_2 mixture partially oxidized the surface of Mo_2C and irreversibly deactivated most of the sites for CO adsorption [24,25]. The rate of alcohol production over the non-passivated unpromoted catalyst at low conversion was $0.18 \text{ g g}_{\text{Mo}}^{-1} \text{ h}^{-1}$, which is nearly identical to the alcohol production rate over the promoted catalyst (Table 3.2), whereas promoter addition decreased the rate of hydrocarbon formation by almost an order of magnitude. These results are similar to those of Tsai *et al.* who used isotopic transient analysis to probe the promotion of a Co-based Fischer–Tropsch catalyst by Cu to form a higher alcohol synthesis catalyst [35]. The addition of Cu promoter significantly decreased the hydrocarbon formation rate on the Co catalyst without affecting the parallel oxygenate synthesis rate, effectively shifting the selectivity of the catalyst from hydrocarbons to

oxygenates. Although the total alcohol production rate over non-passivated Mo_2C was essentially unchanged by the addition of 1.5 wt.% Rb (Table 3.2), the ratio of higher alcohols to methanol (from carbon-based selectivity at constant CO conversion) increased from 1.2 to 2.5 by addition of the promoter. However, the alcohol production rate over an unpromoted catalyst was severely reduced from 0.18 to $0.017 \text{ g g}_{\text{Mo}}^{-1} \text{ h}^{-1}$ by passivation, which is additional evidence of an irreversible surface modification of Mo_2C by oxygen. On the other hand, passivation had only a negligible influence on the activity of Rb-promoted 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst (Table 3.2), indicating that interactions of the Mo_2C with the alkali metal promoter dominate the surface reactivity over that of added oxygen. It should be noted that the selectivity to CO_2 , presumably via the water-gas-shift reaction, was high in all cases ($\sim 40\text{-}50\%$), regardless of passivation or promotion. According to reaction stoichiometry, the maximum selectivity to CO_2 cannot exceed 50%.

Figure 3.4 Evaluation of chain growth probability of linear hydrocarbons (paraffins and olefins combined)

Table 3.3 Chain growth probability of hydrocarbons (paraffins and olefins combined)

Sample	Chain growth probability
5 wt.% Mo ₂ C/Al ₂ O ₃ without passivation	0.36
5 wt.% Mo ₂ C/Al ₂ O ₃ with passivation	0.31
1.5 wt.% Rb–5 wt.% Mo ₂ C/Al ₂ O ₃ without passivation	0.41
1.5 wt.% Rb–5 wt.% Mo ₂ C/Al ₂ O ₃ with passivation	0.38

The chain growth probability (α) based on the C1 to C6 linear hydrocarbons (paraffins and olefins combined) was calculated from the Anderson-Schulz-Flory (ASF) distribution, expressed as:

$$W_n / n = (1 - \alpha)^2 \alpha^{n-1},$$

where W_n is the weight fraction of hydrocarbon molecules containing n carbon atoms among all the hydrocarbons considered. After transforming the ASF distribution to:

$$\log(W_n / n) = (n-1)\log \alpha + 2\log(1-\alpha),$$

the value of α can be determined from the linear fit shown in Figure 3.4. The resulting chain growth probabilities are summarized in Table 3.3. Neither passivation nor Rb promoter had a significant influence on the value of hydrocarbon chain growth probability, which varied from 0.31 to 0.41.

The X-ray absorption near edge structure (XANES) at the Mo K edge of reference compounds and catalysts is summarized in Table 3.4 and Figure 3.5. The shift in the edge position, determined at half step height, is defined as the increase of E_0 value from that of the metallic Mo foil. The calcined alumina-supported Mo species had a similar K edge energy shift (8.2 eV) to that of the Mo(VI) standard, MoO₃ (8.5 eV). After reduction in H₂, the energy shift of E_0 for the alumina-supported Mo species was significantly decreased to 6.2 eV, which is close to that of Mo(IV) in MoO₂ (5.6 eV shift). The addition of Rb promoter did not significantly change the energy shift for MoO₂/Al₂O₃.

Carburization of $\text{MoO}_2/\text{Al}_2\text{O}_3$ and Rb-promoted Mo_2C further reduced the Mo oxidation state, resulting in an E_0 shift of 2.4 eV for $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, which approaches that of bulk Mo_2C (1.5 eV). However, non-passivated $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ still was more oxidized than bulk Mo_2C , which may be attributed to incomplete carburization of the highly dispersed Mo_2C clusters and/or the interaction of Mo with the underlying support. According to the shifts in E_0 reported in Table 3.4, both passivation and addition of Rb promoter resulted in partial oxidation of the Mo_2C clusters. For example, a non-passivated sample of $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ before reaction had an E_0 shift of 2.4 eV relative to Mo foil whereas a passivated sample had an E_0 shift of 3.3 eV. The difference between the E_0 of the non-passivated 1.5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ sample (2.8 eV) and the corresponding passivated one (3.1 eV) suggests that the presence of Rb promoter inhibited oxidation of the carbide surface. The shifts in E_0 caused by the CO hydrogenation reaction that are reported in Table 3.4 confirmed that the supported Mo_2C clusters (with and without passivation, with and without promoter) can be reduced by the reactive syngas environment, which is consistent with the observation on an Rb-promoted $\text{Mo}_2\text{C}/\text{MgO}$ catalyst [31]. The very small difference in E_0 (0.1 eV) before and after reaction of non-passivated 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ confirmed the success of our air-free handling of the samples.

Figure 3.5 X-ray absorption near edge structure (XANES) at the Mo *K* edge of: (a) Mo reference standards, (b) alumina-supported Mo species, $\text{MoO}_3/\text{Al}_2\text{O}_3$ (calcined), $\text{MoO}_2/\text{Al}_2\text{O}_3$ (reduced) and $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ (carburized), (c) a comparison between freshly prepared and passivated $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$.

Table 3.4 Shift of the Mo *K* Edge Energy from Mo foil

Mo samples		Shift of E_0 (eV)
Mo foil		0.0
MoO ₂		5.6
MoO ₃		8.5
Bulk Mo ₂ C		1.5
5% Mo/Al ₂ O ₃ , calcined		8.2
5% Mo/Al ₂ O ₃ , reduced		6.2
1.5%Rb-5%Mo/Al ₂ O ₃ , reduction		6.7
5% Mo ₂ C/Al ₂ O ₃ without passivation	before rxn	2.4
	after rxn	2.3
5%Mo ₂ C/Al ₂ O ₃ with passivation	before rxn	3.3
	after rxn	2.8
1.5%Rb-5%Mo ₂ C/Al ₂ O ₃ without passivation	before rxn	2.8
	after rxn	2.2
1.5%Rb-5%Mo ₂ C/Al ₂ O ₃ with passivation	before rxn	3.1
	after rxn	2.9

The structural evolution of the Mo phase during catalyst synthesis can be followed in the Mo *K* edge extended X-ray absorption fine structure (EXAFS). Thus, Fourier transforms of the k^3 -weighted EXAFS of the samples at various stages of the synthesis procedure were compared to those of the reference bulk compounds. According to the EXAFS in Figure 3.6a and the shift in E_0 in Table 3.4, the alumina-supported Mo oxide after calcination is a highly dispersed Mo(VI) oxide with no clear evidence of a Mo–Mo shell. After reduction in H₂, the FT of the EXAFS of alumina-supported Mo oxide (Figure 3.6c and Figure 3.6d) and the shift in E_0 reported in Table 3.4 suggested the formation of a highly dispersed Mo suboxide, likely Mo(IV), as an intermediate during the catalyst synthesis procedure. After carburization, the FT of the EXAFS of both unpromoted (Figure 3.6f) and Rb-promoted (Figure 3.6g) samples revealed a Mo–Mo shell at the same position as the one in bulk Mo₂C (Figure 3.6h), which confirmed the formation of alumina-supported Mo₂C. Kojima and Aika reported that when Cs was

added onto a MoO_3 precursor prior to carburization, the final material tended to form metallic Mo rather than carbidic Mo [36]. However, our procedure involving the addition of Rb promoter prior to carburization was able to produce supported Mo carbide rather than metallic Mo.

Figure 3.6 Fourier transform (not corrected for phase shifts) of k^3 -weighted Mo EXAFS: (a) 5% Mo/ Al_2O_3 , calcined; (b) bulk MoO_3 ; (c) 5 wt.% Mo/ Al_2O_3 , reduced; (d) 1.5 wt.% Rb–5 wt.% Mo/ Al_2O_3 , reduced; (e) bulk MoO_2 ; (f) 5 wt.% Mo, carburized; (g) 1.5 wt.% Rb–5 wt.% Mo, carburized; (h) bulk Mo_2C . Spectra are offset for clarity.

The coordination numbers (CN), interatomic distances (r), and Debye–Waller factors ($\Delta\sigma^2$) obtained by curve fitting of the k^3 -weighted EXAFS of the carbide samples

are summarized in Table 3.5. The number of reliable parameters that can be measured is limited by the Nyquist theorem, given here as $\frac{2\Delta k\Delta R}{\pi} = 15$, and exceeds the number of fitted parameters reported in Table 3.5. Additionally, the R -factors in Table 3.5 are all smaller than 0.07. A sample of the results from curve fitting of 1.5 wt.% Rb–5 wt.% Mo₂C/Al₂O₃ (without passivation, before reaction) is provided in Figure 6 to illustrate the quality of the fits.

Table 3.5 Results from the analysis of Mo EXAFS from carbide catalyst

Catalyst ^a	Shell	CN	r (Å)	$\Delta\sigma^2$ (10 ⁻³ Å ²)	ΔE_0 (eV)	R - factor
Bulk Mo ₂ C	Mo–C	3 ^b	2.11 ± 0.03	3.4 ± 3.4	0.9 ± 5.0	0.009
	Mo–Mo	12 ^b	2.97 ± 0.01	5.6 ± 0.7	-7.8 ± 1.1	
5%Mo ₂ C/Al ₂ O ₃ without passivation	Mo–C	3.3 ± 0.8	2.12 ± 0.02	5.8 ± 2.3	-3.2 ± 3.1	0.047
	Mo–Mo	2.5 ± 0.9	2.98 ± 0.01	7.8 ± 2.1	-5.4 ± 3.0	
5%Mo ₂ C/Al ₂ O ₃ with passivation ^c	Mo–C	1.8 ± 0.8	2.05 ± 0.02	0.0 ± 2.6	-24 ± 8	0.066
	Mo–Mo	2.8 ± 1.1	2.98 ± 0.02	6.6 ± 2.4	-7.5 ± 3.6	
1.5%Rb–5%Mo ₂ C/Al ₂ O ₃ without passivation ^c	Mo–C	2.2 ± 1.2	2.11 ± 0.03	1.9 ± 3.8	-11 ± 8	0.053
	Mo–Mo	5.2 ± 1.7	2.97 ± 0.01	7.2 ± 1.9	-13 ± 3	
1.5%Rb–5%Mo ₂ C/Al ₂ O ₃ with passivation ^c	Mo–C	1.8 ± 1.1	2.08 ± 0.03	3.0 ± 3.4	-22 ± 10	0.061
	Mo–Mo	4.6 ± 1.6	2.97 ± 0.01	7.3 ± 2.0	-13 ± 3	

Fitting parameters: Fourier transform range Δk : 2–11.8 Å⁻¹; fitting range ΔR : 1–3.4 Å; weighting: k^3 ; S_0^2 (Mo–C) = 0.86, S_0^2 (Mo–Mo) = 0.76.

^a Catalysts are all before reaction.

^b Value was assigned in curving fitting based on standard structure.

^c R_{bkg} was set to 1.2 in background removal to remove the noise oscillation below 1 Å in R space.

The low Mo–Mo coordination numbers (2.5–5.2) indicate that the Mo carbide clusters are very highly dispersed on the alumina support, which is consistent with the average particle size of about 1 nm as observed by electron microscopy (Figure 3.8). The formation of very highly dispersed Mo₂C clusters has also been observed on H-ZSM-5

zeolite [37] and $\gamma\text{-Al}_2\text{O}_3$ [38], with Mo–Mo coordination numbers derived from EXAFS as low as 2.6 and 4, respectively.

Figure 3.7 Comparison of the curve fit to experimental Mo K edge EXAFS of the 1.5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst without passivation, before reaction. (a) k^3 -weighted Mo K edge EXAFS (solid line) and the result from curve fit (circles); (b) Magnitude (solid line) and the imaginary part (dashed line) of the Fourier transform of EXAFS compared to the result from the curve fit (circles).

Figure 3.8 Electron micrographs of (a) 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ with passivation after reaction, (b) 1.5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ with passivation and after reaction. Catalysts were used for 48 h in CO hydrogenation before TEM analysis. The scale bars are 5 nm.

3.4 Conclusions

A modified catalyst synthesis method for preparing alkali-promoted supported Mo_2C was developed, with the incorporation of alkali metal promoter accomplished prior to carburization. The new procedure gives 1 nm Mo_2C nanoparticles supported on α -alumina. An unpromoted sample of $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ was active in the Fischer–Tropsch reaction and produced mostly hydrocarbons with a chain growth probability of about 0.36, whereas addition of Rb shifted the selectivity to alcohols primarily by inhibiting the rate of hydrocarbon formation. However, increasing the loading of Rb promoter beyond 1 wt.% decreased the rate of alcohol production, presumably because of blockage of the active sites for alcohol synthesis. The primary role of Rb on the supported carbide clusters appears to be the deactivation of sites used to form hydrocarbons, although we cannot rule out a promotion of higher alcohol synthesis rates on the carbide surfaces or catalysis of alcohol coupling reactions. Passivation of unpromoted 5 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ with a

dilute stream of O₂ decreased the overall activity of the catalyst by 37% and reduced the rate of alcohol production by an order of magnitude, whereas passivation of promoted (1.5 wt.% Rb) 5 wt.% Mo₂C/Al₂O₃ did not significantly affect the activity and product distribution of the catalyst. Spectroscopic characterization at Mo *K* edge was used to follow the evolution of the structure of the catalyst throughout the synthesis procedure as well as to monitor the partial oxidation and reduction of the carbide catalysts during passivation and CO hydrogenation, respectively. The Mo XANES confirmed the reduction of Mo(VI) to Mo(IV) to Mo₂C. However, the supported Mo₂C was always partially oxidized compared to bulk Mo₂C.

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References of Chapter 3

- [1] P. Forzatti, E. Tronconi, I. Pasquon, "Higher alcohol synthesis," *Catalysis Reviews: Science Engineering* 33 (1991) 109–168.
- [2] I. Wender, "Reactions of synthesis gas," *Fuel Processing Technology* 48 (1996) 189–297.
- [3] R.G. Herman, "Advances in catalytic synthesis and utilization of higher alcohols," *Catalysis Today* 55 (2000) 233–245.
- [4] K. Fang, D. Li, M. Lin, M. Xiang, W. Wei, Y. Sun, "A short review of heterogeneous catalytic process for mixed alcohols synthesis via syngas," *Catalysis Today* 147 (2009) 133–138.
- [5] M.M. Bhasin, G.L. O'Connor, "Procede de preparation selective de derives hydrocarbones oxygenes a deux atomes de carbone," Belgian Patent 824822, 1975.
- [6] J.J. Spivey, A. Egbebi, "Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas," *Chemical Society Reviews* 36 (2007) 1514–1528.
- [7] V. Subramani, S.K. Gangwal, "A review of recent literature to search for an efficient catalytic process for the conversion of syngas to ethanol," *Energy & Fuels* 22 (2008) 814–839.
- [8] R.B. Levy, M. Boudart, "Platinum-like behavior of tungsten carbide in surface catalysis," *Science* 181 (1973) 547–549.
- [9] J.G. Chen, "Carbide and nitride overlayers on early transition metal surfaces: Preparation, characterization, and reactivities," *Chemical Reviews* 96 (1996) 1477–1498.
- [10] H.H. Hwu, J.G. Chen, "Surface chemistry of transition metal carbides," *Chemical Reviews* 105 (2005) 185–212.
- [11] K.Y. Park, W.K. Seo, J.S. Lee, "Selective synthesis of light olefins from syngas over potassium-promoted molybdenum carbide catalysts," *Catalysis Letters* 11 (1991) 349–356.
- [12] D.-V.N. Vo, A.A. Adesina, "Fischer–Tropsch synthesis over alumina-supported molybdenum carbide catalyst," *Applied Catalysis A: General* 399 (2011) 221–232.
- [13] D.-V.N. Vo, T.-H. Nguyen, E.M. Kennedy, B.Z. Dlugogorski, A.A. Adesina, "Fischer–Tropsch synthesis: Effect of promoter type on alumina-supported Mo carbide catalysts," *Catalysis Today* 175 (2011) 450–459.

- [14] H.C. Woo, K.Y. Park, Y.G. Kim, I.S. Nam, J.S. Chung, J.S. Lee, "Mixed alcohol synthesis from carbon monoxide and dihydrogen over potassium-promoted molybdenum carbide catalysts," *Applied Catalysis* 75 (1991) 267–280.
- [15] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "Performances of mixed alcohols synthesis over potassium promoted molybdenum carbides," *Fuel* 85 (2006) 2662–2665.
- [16] F.H. Ribeiro, R.A. Dalla Betta, M. Boudart, J. Baumgartner, E. Iglesia, "Reactions of neopentane, methylcyclohexane, and 3,3-dimethylpentane on tungsten carbides: The effect of surface oxygen on reaction pathways," *Journal of Catalysis* 130 (1991) 86–105.
- [17] F.H. Ribeiro, M. Boudart, R.A. Dalla Betta, E. Iglesia, "Catalytic reactions of *n*-alkanes on β -W₂C and WC: The effect of surface oxygen on reaction pathways," *Journal of Catalysis* 130 (1991) 498–513.
- [18] E. Iglesia, J.E. Baumgartner, F.H. Ribeiro, M. Boudart, "Bifunctional reactions of alkanes on tungsten carbides modified by chemisorbed oxygen," *Journal of Catalysis* 131 (1991) 523–544.
- [19] E. Iglesia, F.H. Ribeiro, M. Boudart, J.E. Baumgartner, "Synthesis, characterization, and catalytic properties of clean and oxygen-modified tungsten carbides," *Catalysis Today* 15 (1992) 307–337.
- [20] E. Iglesia, F.H. Ribeiro, M. Boudart, J.E. Baumgartner, "Tungsten carbides modified by chemisorbed oxygen: A new class of bifunctional catalysts," *Catalysis Today* 15 (1992) 455–458.
- [21] N. Liu, S.A. Rykov, J.G. Chen, "A comparative surface science study of carbide and oxycarbide: The effect of oxygen modification on the surface reactivity of C/W(111)," *Surface Science* 487 (2001) 107–117.
- [22] H.H. Hwu, M.B. Zellner, J.G. Chen, "The chemical and electronic properties of oxygen-modified C/Mo(110): A model system for molybdenum oxycarbides," *Journal of Catalysis* 229 (2005) 30–44.
- [23] M. Nagai, T. Kurakami, S. Omi, "Activity of carbided molybdena-alumina for CO₂ hydrogenation," *Catalysis Today* 45 (1998) 235–239.
- [24] W. Wu, Z. Wu, C. Liang, X. Chen, P. Ying, C. Li, "In situ FT-IR spectroscopic studies of CO adsorption on fresh Mo₂C/Al₂O₃ catalyst," *The Journal of Physical Chemistry B* 107 (2003) 7088–7094.
- [25] W. Wu, Z. Wu, C. Liang, P. Ying, Z. Feng, C. Li, "An IR study on the surface passivation of Mo₂C/Al₂O₃ catalyst with O₂, H₂O and CO₂," *Physical Chemistry Chemical Physics* 6 (2004) 5603–5608.

- [26] S. Li, W.B. Kim, J.S. Lee, "Effect of the reactive gas on the solid-state transformation of molybdenum trioxide to carbides and nitrides," *Chemistry of Materials* 10 (1998) 1853–1862.
- [27] J.B. Claridge, A.P.E. York, A.J. Brungs, M.L.H. Green, "Study of the temperature-programmed reaction synthesis of early transition metal carbide and nitride catalyst materials from oxide precursors," *Chemistry of Materials* 12 (2000) 132–142.
- [28] R. Burch, M.I. Petch, "Investigation of the synthesis of oxygenates from carbon monoxide/hydrogen mixtures on supported rhodium catalysts," *Applied Catalysis A: General* 88 (1992) 39–60.
- [29] B. Ravel, M. Newville, "ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT," *Journal of Synchrotron Radiation* 12 (2005) 537–541.
- [30] S.I. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, M.J. Eller, "Multiple-scattering calculations of x-ray-absorption spectra," *Physical Review B* 52 (1995) 2995–3009.
- [31] H. Shou, R.J. Davis, "Reactivity and *in situ* X-ray absorption spectroscopy of Rb-promoted $\text{Mo}_2\text{C}/\text{MgO}$ catalysts for higher alcohol synthesis," *Journal of Catalysis* 282 (2011) 83–93.
- [32] H.G. Kim, K.H. Lee, J.S. Lee, "Carbon monoxide hydrogenation over molybdenum carbide catalysts," *Research on Chemical Intermediates* 26 (2000) 427–443.
- [33] J.S. Lee, S. Kim, K.H. Lee, I.-S. Nam, J.S. Chung, Y.G. Kim, H.C. Woo, "Role of alkali promoters in K/MoS_2 catalysts for $\text{CO}-\text{H}_2$ reactions," *Applied Catalysis A: General* 110 (1994) 11–25.
- [34] J.S. Lee, S. Kim, Y.G. Kim, "Electronic and geometric effects of alkali promoters in CO hydrogenation over $\text{K}/\text{Mo}_2\text{C}$ catalysts," *Topics in Catalysis* 2 (1995) 127–140.
- [35] Y.-T. Tsai, X. Mo, J.G. Goodwin, "The synthesis of hydrocarbons and oxygenates during CO hydrogenation on CoCuZnO catalysts: Analysis at the site level using multiproduct SSITKA," *Journal of Catalysis* 285 (2012) 242–250.
- [36] R. Kojima, K. Aika, "Molybdenum nitride and carbide catalysts for ammonia synthesis," *Applied Catalysis A: General* 219 (2001) 141–147.
- [37] W. Ding, S. Li, G.D. Meitzner, E. Iglesia, "Methane conversion to aromatics on $\text{Mo}/\text{H-ZSM5}$: Structure of molybdenum species in working catalysts," *The Journal of Physical Chemistry B* 105 (2001) 506–513.
- [38] J.S. Lee, M. Boudart, "*In situ* carburization of metallic molybdenum during catalytic reactions of carbon-containing gases," *Catalysis Letters* 20 (1993) 97–106.

Chapter 4.

Use of infrared spectroscopy and density functional theory to study the influence of rubidium on alumina-supported molybdenum carbide catalyst for higher alcohol synthesis from syngas

Adapted from *Journal of Catalysis*, 299, Heng Shou, Liwei Li, Daniela Ferrari, David S. Sholl and Robert J. Davis, “Use of infrared spectroscopy and density functional theory to study the influence of rubidium on alumina-supported molybdenum carbide catalyst for higher alcohol synthesis from syngas,” 150–161, Copyright (2013), with permission from Elsevier

Density-functional-theory calculations were performed by Liwei Li and Dr. David S. Sholl at Georgia Institute of Technology and are included here for completeness.

Abstract

Molybdenum carbide nanoclusters supported on alumina were promoted by Rb_2CO_3 and tested for higher alcohol synthesis from syngas. At 573 K and 30 bar syngas ($\text{H}_2/\text{CO} = 1$), the promoted catalyst demonstrated 63% selectivity to alcohols (on a CO_2 -free basis), with hydrocarbons and ethers as side products. In contrast, the alcohol selectivity of an unpromoted $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst was very low. Diffuse reflectance infrared Fourier transform spectroscopy of adsorbed CO on $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ revealed a significant red shift in the CO band with added Rb promoter, which correlated to a decrease in hydrocarbon production rate and therefore an increase in alcohol selectivity. A quantum chemical description of CO adsorbed on a model Mo_2C surface identified several possible binding modes of the CO. Both reactivity studies and DRIFTS of adsorbed CO demonstrated that mobility of the Rb promoter was enhanced in the presence of water vapor, which facilitates dispersion of Rb across the catalyst surface and effectively neutralizes acid sites that are deleterious to alcohol selectivity.

4.1 Introduction

Limited crude oil reserves and competition with the food industry associated with fermentation-based biofuel production inspire new research efforts on effective catalytic transformations of alternative carbon sources to produce energy carriers and chemical feedstocks. Synthesis gas ($\text{CO} + \text{H}_2$) can be derived from coal, natural gas or renewable biomass, and is a platform for the synthesis of fuels and chemicals.

Fischer–Tropsch synthesis (FTS) of hydrocarbons has received growing attention as a source of low-sulfur diesel fuel because of the uncertainty of crude oil prices. However, higher alcohol (C_2+ alcohols) synthesis from synthesis gas, as a source of chemical feedstocks, might be more commercially attractive. For example, Celanese Corporation reported an expected ethanol price of \$1.4/gallon with their new coal-to-ethanol technology via acetic acid [1,2], and E. I. du Pont de Nemours and Company and BP have a stated goal for a butanol price of \$1/gallon with their bio-based process currently under development [3]. Considering that methanol is currently produced from natural-gas-based syngas at the world scale, it is reasonable to expect a comparably low price for higher alcohols produced by a similar catalytic process, assuming production and selectivity achievements are realized.

Because of methanol's low solubility in gasoline, it needs to be further converted to another molecule such as methyl *tert*-butyl ether (MTBE) before being used as a gasoline blend. However, MTBE is being phased out as a fuel additive due to environmental concerns. Higher alcohols, on the other hand, have mutual solubility with gasoline and ethanol has been widely used in the US as a gasoline additive. Since almost

all the ethanol used for fuel is produced from fermentation, there is still a need for a more efficient catalytic process for the production of ethanol (and other higher alcohols).

An effective catalyst for the production of higher alcohols from syngas is necessarily multifunctional since CO activation, hydrogenation, carbon chain growth, and potentially alcohol coupling processes are all important steps in the reaction. Thus, no single-component transition metal catalyst has been discovered to effectively catalyze higher alcohol synthesis.

Exploratory research on higher alcohol synthesis has discovered some promising candidates [4–8]. Rh-based catalysts are effective for the formation of ethanol and other C₂-oxygenates from syngas [9–11], but the very high cost of Rh likely prohibits its large-scale utilization. Several non-precious metal catalysts for higher alcohol synthesis have thus been evaluated and include, for example, Cu–Co, Cu–Zn–Al and Zn–Cr–K [5], but improvements in the overall catalytic activity, alcohol selectivity, and long-term stability of these catalytic materials for higher alcohol synthesis are still needed.

Molybdenum-based catalysts have been widely used in many hydro-treating processes because of their high activities in desulfurization and denitrogenation with H₂. When promoted by alkali metals, Mo-based catalysts also show encouraging properties for higher alcohol synthesis from CO hydrogenation. Both supported and unsupported MoS₂-based catalysts have been heavily investigated for higher alcohol synthesis [12–15] since it was firstly developed by The Dow Chemical Company in the 1980's [16–20]. However, trace amounts of H₂S in the feed were required to sustain the performance of the MoS₂-based catalysts [17]. Moreover, small amounts of sulfur may enter the carbon skeleton of the products, which is problematic as the world moves toward the use of very-

low-sulfur fuels. Thus, there is a need for a non-sulfided alternative for MoS₂-based catalyst in this process, among which molybdenum carbide has demonstrated some promise when properly promoted [21–25]. Early transition metal carbides are also recognized as potential substitutes to precious metal catalysts because of their similar surface electronic properties [26–28].

The selectivity towards alcohols over alkali-metal-promoted MoS₂-based and Mo₂C-based catalysts in the syngas reaction was reported to be low initially but increased significantly with time on-stream over a period of several hours to several days [23,29–31]. Lee *et al.* suggested that the promotional effect of alkali metal species on MoS₂ [32] and Mo₂C [32] catalysts for alcohol formation during CO hydrogenation was mostly the result of the surface sites being blocked from adsorbing reactants. By using diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), Koizumi *et al.* claimed that syngas adsorption on a MoS₂/γ-Al₂O₃ catalyst for CO hydrogenation was significantly suppressed by K species and the K-promoted Mo species were likely more oxidized than those on K-free MoS₂ [33]. Muramatsu *et al.* also studied the role of a K promoter on a Mo oxide catalyst for alcohol production from syngas and concluded that K inhibits both dehydration of alcohols to alkenes and the hydrogenation of alkenes to alkanes [34]. For supported MoS₂-based catalysts, interactions between K promoters and Mo begins with the oxidized catalyst precursors [12,29,35,36] and that some K–Mo–S and/or K–Mo–S–O species are formed after sulfidation. However, it is still unclear whether the promoters enhance the activity of the catalysts for higher alcohol synthesis. Although CO adsorption has been used to probe the surfaces of MoS₂-based [37–42] and Mo₂C-based [43–47] catalysts, few of these studies addressed the promotional influence

of the alkali metals on higher alcohol synthesis. X-ray absorption spectroscopy of Rb-promoted $\text{Mo}_2\text{C}/\text{MgO}$ catalysts demonstrated that the local environment around the Rb_2CO_3 promoter was structurally-modified during reaction [23], but the actual structural form of the working promoter is not yet known.

The present study uses diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO combined with density functional theory (DFT) to investigate the interactions between Rb and supported- Mo_2C particles. Results from DRIFTS and DFT are used to interpret observed reactivity trends of working catalysts.

4.2 Methods

4.2.1 Catalyst synthesis

Incorporation of Mo onto the alumina support (Mager Scientific, >99.98%, predominantly γ -phase, $S_{\text{BET}} = 76 \text{ m}^2 \text{ g}^{-1}$) was accomplished by incipient wetness impregnation of an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (99.98%, Aldrich) followed by drying in air for 12 h at 400 K and calcining in flowing air for 5 h at 773 K to produce a supported molybdenum oxide, denoted here as $\text{MoO}_3/\text{Al}_2\text{O}_3$. Carburization of $\text{MoO}_3/\text{Al}_2\text{O}_3$ was performed in a quartz tube by heating at a rate of 5 K min^{-1} from room temperature to 573 K and at a rate of 1 K min^{-1} from 573 K to 1033 K in 20 vol.% CH_4 (GTS-Welco, 99.997%) and 80 vol.% H_2 (GTS-Welco, 99.999%) at a total gas flow rate of $75 \text{ cm}^3 \text{ min}^{-1}$ (STP). After ramping to 1033 K in CH_4/H_2 , the temperature was maintained at 1033 K for 1 h. The catalyst was subsequently cooled to 673 K in flowing He (GTS-Welco, 99.999%, additionally purified by a Sigma-Aldrich OMI-2 purifier) and held at 673 K for 5 h in flowing purified H_2 at a flow rate of $60 \text{ cm}^3 \text{ (STP) min}^{-1}$. The catalyst was then cooled to room temperature in flowing purified He before passivation in

a $20 \text{ cm}^3 \text{ min}^{-1}$ (STP) stream of 1.04 vol.% O_2/N_2 mixture (GTS-Welco) at room temperature for 12 h. The alkali-metal-promoted $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ samples were prepared by grinding Rb_2CO_3 (99.975%, Alfa Aesar) together with passivated $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ in a mortar and pestle.

4.2.2 Hydrogenation of carbon monoxide

Hydrogenation of CO was conducted in a fixed-bed stainless steel reactor (BTRS Jr., Autoclave Engineers) with about 1.25 g catalyst (0.025 g nominal Mo_2C). The catalysts were tested at nominally identical conditions of 573 K, 30 bar total pressure, syngas ($\text{H}_2 + \text{CO}$) flow of $10 \text{ cm}^3 \text{ min}^{-1}$ (STP) and $\text{H}_2/\text{CO} = 1$. Additional experimental details can be found in our previous works [23,25].

In another series of studies on representative samples, water was introduced to the catalyst by flowing N_2 (GTS-Welco, 99.999%, additionally purified by a Sigma-Aldrich OMI-2 purifier) to the fixed bed reactor through a saturator with liquid water at 300 K. The samples were sequentially treated at ambient pressure with $50 \text{ cm}^3 \text{ min}^{-1}$ (STP) $\text{H}_2\text{O}/\text{N}_2$ at 300 K for 2 h and with $50 \text{ cm}^3 \text{ min}^{-1}$ (STP) H_2 (GTS-Welco, 99.999%) at 573 K for 12 h prior to syngas reaction.

In control experiments without water, the samples were pretreated with $50 \text{ cm}^3 \text{ min}^{-1}$ (STP) H_2 (GTS-Welco, 99.999%) at 573 K for 12 h prior to syngas reaction.

4.2.3 Catalyst characterization

The X-ray diffraction patterns were obtained on a Scintag XDS 2000 diffractometer using $\text{Cu K}\alpha$ radiation. Scans were collected over a range of 2θ from 5° to 90° at a rate of 2° min^{-1} for bulk materials and $0.8^\circ \text{ min}^{-1}$ for supported catalysts.

Elemental analyses of representative samples were performed by Galbraith Laboratories (Knoxville, TN). The loading of molybdenum and rubidium was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the loading of carbon was evaluated by combustion and coulometric measurement.

X-ray absorption spectroscopy (XAS) was performed on beam lines X23A2 and X18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The storage ring was typically operated at 2.8 GeV with a ring current of about 300 mA. The XAS data were obtained in the transmission mode at the Mo *K* edge (20 keV) with a spot size of 0.5 mm×5 mm. The Mo *K* edge spectra were measured at room temperature with Mo foil (Goodfellow) as a reference. The air-free handling protocols for the non-passivated, unpromoted catalyst before reaction and the Rb-promoted catalyst after syngas reaction have been discussed in our previous work [25]. The XAS data were processed using the Athena [48] software for background removal, post-edge normalization, and X-ray absorption near edge structure (XANES) analysis. The value of E_0 was assigned here as the energy at the half step height. Metallic Mo foil, MoO₂ (99%, Aldrich) and MoO₃ (99.99%, Aldrich) were used as standard references for Mo in various oxidation states. Standard bulk Mo₂C (Alfa Aesar, 99.5%) was used to determine the amplitude reduction factors S_0^2 for Mo–C and Mo–Mo in the fitting of the extended X-ray absorption fine structure (EXAFS). The EXAFS results were fitted in R-space using two shells (Mo–C & Mo–Mo) generated theoretically using FEFF 6.0 [49]. The interatomic distances (r), coordination numbers (CN), Debye-Waller factors ($\Delta\sigma^2$) and energy shifts (ΔE_0) were derived from the fitting results in the Artemis software package [48].

4.2.4 Diffuse reflectance infrared Fourier transform spectroscopy

A Bio-Rad FTIR (FTS-60A) spectrometer outfitted with an MCT detector and an *in situ* reactor cell for DRIFTS (Harrick) was used for the CO adsorption studies. To obtain the spectra, 100 scans were co-added at resolution of 4 cm^{-1} . Samples of 2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalysts with Rb loading varying from 0–10 wt.% were examined by DRIFTS according to the following procedure. A catalyst sample of 30 mg was diluted in 90 mg of KBr powder (Varian Inc.) before being loaded into the DRIFTS cell.

The loaded cell was then purged with He (GTS-Welco, 99.999%, additionally purified by Sigma-Aldrich OMI-2) at a flow rate of $50\text{ cm}^3\text{ min}^{-1}$ (STP) at room temperature for 10 min before being pressurized with equal flow rates of H_2 (GTS-Welco, 99.999%, additionally purified by Alltech All-Pure) and purified CO (GTS-Welco, 99.997%) to 30 bar. The purification system for CO was comprised of a CRS Model 1000 O_2 trap, a homemade carbonyl trap (silica gel in a copper tube immersed in a dry ice/acetone cold bath), a homemade CO_2 trap (Ascarite II CO_2 absorbent in a copper tube) and a homemade moisture trap (Fluka molecular sieves $3\text{\AA}$ loaded in a copper tube). Subsequently, the cell was heated to 573 K at a rate of 10 K min^{-1} and held at 573 K for 12 h in 30 bar flowing syngas ($\text{H}_2/\text{CO} = 1$) with a total flow rate of $4\text{ cm}^3\text{ min}^{-1}$ (STP). The cell was depressurized after 12 h treatment at reaction conditions and purged with $50\text{ cm}^3\text{ min}^{-1}$ (STP) H_2 at 573 K, ambient pressure, for an additional 1 h before cooling to room temperature in flowing He. After recording a background spectrum of the sample, flowing He was replaced with purified CO flowing at a rate of 50 mL min^{-1} for 15 min. The sample was finally purged with flowing purified He at 50 mL min^{-1} for 15 min before recording a spectrum of adsorbed CO at 300 K.

In another series of studies on representative samples, water was introduced to the catalyst by flowing He to the DRIFTS cell through a saturator with liquid water at 300 K. The samples were sequentially treated with the following conditions: 1 bar H₂O/He (50 cm³ min⁻¹, STP) at 300 K for 2 h and 1 bar He (50 cm³ min⁻¹, STP) at 423 K for 1 h; 1 bar H₂ (50 cm³ min⁻¹, STP) at 573 K for 12 h; 30 bar syngas (H₂/CO = 1, total flow rate at STP of 4 cm³ min⁻¹) for 12 h and in 1 bar H₂ (50 cm³ min⁻¹, STP) for 1 h; 1 bar H₂ (50 cm³ min⁻¹, STP) at 573 K for 12 h. After each step of the pretreatment sequence, the sample was cooled to 300 K in flowing purified He (50 cm³ min⁻¹, STP). The background spectra were subsequently recorded at 300 K in flowing He before introducing purified CO (50 cm³ min⁻¹, STP) for 15 min. After purging with flowing purified He at 50 cm³ min⁻¹ for 15 min, the IR spectra of adsorbed CO were recorded at 300 K.

In control experiments without water, the samples were pretreated with 50 cm³ min⁻¹ (STP) purified H₂ at 573 K for 12 h and purged in purified He before introducing purified CO at 300 K.

4.2.5 Computational methods

Plane wave DFT calculations were performed with the Vienna *ab initio* simulation package (VASP). We employed the revised Perdew-Burke-Ernzerhof (rPBE) generalized gradient functional [50,51] along with the projector augmented wave (PAW) [52,53] method to describe ionic cores. A plane wave expansion with a cutoff of 400 eV was used for all calculations. Geometries were relaxed using a conjugate gradient algorithm until the forces on all unconstrained atoms were less than 0.03 eV/Å.

Figure 4.1 Reconstructed bare hexagonal $\text{Mo}_2\text{C}(001)$ surface. Mo atoms are shown as green spheres and C atoms as cyan spheres.

The surface structure of the molybdenum carbide catalyst modeled in this work is based on the reconstructed C-terminated hexagonal $\text{Mo}_2\text{C}(001)$ surface discussed in a previous study [54], which is illustrated in Figure 4.1. In that study, by comparing surface free energy and adsorption energy of alkali metal (K and Rb) atoms for different low-Miller-index surfaces of Mo_2C , the $\text{Mo}_2\text{C}(001)$ surface was found to be one of the major surfaces in predicted Mo_2C particles as well as have the greatest affinity and dipole moment for Rb atoms. This surface is also known to favor a reconstruction in the absence of adsorbates [55–57], which results in both Mo-top and C-top sites for CO adsorption. Moreover, in spite of the potential support effect, the behavior of bulk Mo_2C catalysts and Mo_2C catalysts [21,22] and Mo_2C catalysts on various supports (MgO [23], $\alpha\text{-Al}_2\text{O}_3$ [25] and mixed-phase Al_2O_3 as illustrated in Section 3.3) is similar, which suggests that the actual sites on various Mo_2C catalysts for CO hydrogenation would have a similar configuration. Given all the factors mentioned above, $\text{Mo}_2\text{C}(001)$ was chosen as a representative surface for modeling.

A $6 \times 6 \times 1$ Monkhorst-Pack k-point mesh was used for (1×1) surface unit cell, which was sufficient to give well-converged results. For calculations on a (2×2) surface unit cell, the number of k-points in the Monkhorst-Pack meshes was reduced to $3 \times 3 \times 1$.

Geometries and energies for gas phase species were calculated using supercells equivalent to those for the largest slab calculations. When examining adsorption, molecules were placed on only one side of the slab. Dipole corrections were therefore applied in computing all of the energies reported below [58,59]. The adsorption energy, $E_{\text{adsorption}}$, of an atom or molecule was defined by

$$E_{\text{adsorption}} = E_{\text{surface}} + E_{\text{adsorbate}} - E_{\text{total}},$$

where E_{total} is the total energy of the system containing the adsorbed species, E_{surface} is the total energy for the optimized bare surface, and $E_{\text{adsorbate}}$ is the total energy for the adsorbate in the gas phase. With this definition, positive adsorption energies correspond to energetically favored states. Adsorbate coverages were defined by considering a surface with an adsorbed species on every surface molybdenum atom to have a coverage of 1 monolayer (ML). This means that placing one adsorbate in a 1×1 unit cell gives a coverage of 0.25 ML.

Vibrational frequency calculations were performed with VASP package where the Hessian Matrix was calculated by finite difference approximation with step size of $0.03 \text{ \AA}$ and only the adsorbate plus the surface atom to which it directly bonds were allowed to move. In order to compare with IR experiment, the calculated frequencies for the CO adsorbates are scaled by a factor of 1.009, which reflects the difference between the observed (2143 cm^{-1}) and calculated vibrational frequencies (2124 cm^{-1}) of gaseous CO.

4.3 Results and discussion

4.3.1 Characterization by X-ray diffraction and X-ray absorption spectroscopy

The X-ray diffraction patterns of representative samples are provided in Figure 4.2. Although the alumina support (Figure 4.2b) used for the catalysts has features of γ - Al_2O_3 (Figure 4.2c) and α - Al_2O_3 (Figure 4.2d). The 2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst (Figure 4.2a) prepared at 1033 K showed XRD peaks corresponding to the structure of the alumina support (Figure 4.2b) without any clear evidence for crystalline Mo_2C (Figure 4.2e, the synthesis method can be found in previous work [23]). This result suggests that the Mo_2C particles were well dispersed on the alumina support.

Figure 4.2 X-ray diffraction patterns of (a) 2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, (b) Al_2O_3 (Mager Scientific) used to support Mo_2C , (c) γ - Al_2O_3 reference (Alfa-Aesar), (d) α - Al_2O_3 (Mager Scientific) and (e) bulk Mo_2C . Patterns are offset for clarity.

Figure 4.3 Mo K edge XANES of: (a) Mo standards; (b) alumina-supported Mo samples.

^a Purged in He after carburization, air-free handling for sample preparation

^b Purged in N_2 after syngas reaction, air-free handling for sample preparation

Table 4.1 Shift of the Mo *K* Edge Energy from Mo foil

Mo samples	Shift of E_0 (eV)
Mo foil	0.0
Bulk MoO ₂	5.7
Bulk MoO ₃	8.8
Bulk Mo ₂ C	1.8
2 wt.% Mo ₂ C/Al ₂ O ₃ , non-passivated ^a	2.4
2 wt.% Mo ₂ C/Al ₂ O ₃ , passivated	5.2
10 wt.% Rb–2 wt.% Mo ₂ C/Al ₂ O ₃ , passivated and after 72 h reaction ^b	4.2

^a Purged in He after carburization, air-free handling for sample preparation

^b Purged in N₂ after syngas reaction, air-free handling for sample preparation

Figure 4.4 Fourier transform (not corrected for phase shifts) of k^3 -weighted EXAFS of: (a) 2 wt.% Mo₂C/Al₂O₃, non-passivated (purged in He after carburization, air-free handling for sample preparation); (b) 2 wt.% Mo₂C/Al₂O₃, passivated; (c) 10 wt.% Rb–2 wt.% Mo₂C/Al₂O₃, passivated and after 72 h reaction (purged in N₂ after syngas reaction, air-free handling for sample preparation); (d) Mo₂C standard. Spectra are offset for clarity.

Table 4.2 Results from the analysis of Mo EXAFS from molybdenum carbide samples

Sample	Shell	CN	r (Å)	$\Delta\sigma^2$ (10^{-3} Å ²)	ΔE_0 (eV)	R-factor
Bulk Mo ₂ C standard	Mo–C	3 ^a	2.12 ± 0.02	0.2 ± 3.0	1.7 ± 2.9	0.015
	Mo–Mo	12 ^a	2.97 ± 0.01	4.6 ± 0.7	-8.4 ± 0.3	
2% Mo ₂ C/Al ₂ O ₃ ^{b,d} (non-passivated, air-free)	Mo–C(O)	4.1 ± 0.7	2.21 ± 0.02	6.0 ± 2.6	4.4 ± 1.5	0.042
	Mo–Mo	3.2 ± 1.0	2.89 ± 0.02	10 ± 3	-3.4 ± 1.9	
10% Rb–2% Mo ₂ C/Al ₂ O ₃ , ^{c,d} passivated and after 72 h rxn	Mo–C(O)	2.6 ± 0.5	2.22 ± 0.02	0.0 ± 2.0	6.5 ± 1.7	0.099
	Mo–Mo	2.1 ± 1.2	2.92 ± 0.02	9.9 ± 4.8	-1.7 ± 3.2	

Fitting parameters:

FT range Δk : 2.5–12.5 Å⁻¹; fitting range ΔR : 1–3.4 Å; weighting: k^1 and k^3 ; S_0^2 (Mo–C) = 0.67, S_0^2 (Mo–Mo) = 0.67. Two-shell fits excluded passivated 2 wt.% Mo₂C/Al₂O₃ because of the lack of an obvious Mo–Mo shell (see Figure 4.4b).

^a Value was assigned in curving fitting based on standard structure. ^b Purged in He after carburization, air-free handling for sample preparation ^c Purged in N₂ after syngas reaction, air-free handling for sample preparation ^d R_{bkg} was set to 1.2 in background removal to remove the noise oscillation below 1 Å in R space.

The X-ray absorption near edge structure (XANES) at the Mo K edge of reference compounds and catalysts is summarized in Figure 4.3 and Table 4.1, with the shift in the edge position (determined at half step height) defined as the increase of E_0 value from that of the Mo foil. The Fourier transforms (FT) of k^3 -weighted extended X-ray absorption fine structure (EXAFS) are shown in Figure 4.4 and the structural parameters derived from the corresponding curve fits are presented in Table 4.2. A representative curve fit is presented in Figure 4.5. Non-passivated 2 wt.% Mo₂C/Al₂O₃ (air-free) has a Mo–Mo coordination number of 2.8 (Table 4.2) and an E_0 shift of 2.4 eV (Table 4.1), which is close to that of bulk Mo₂C (1.8 eV). Passivation significantly oxidized the supported carbide as demonstrated by the 5.2 eV shift of E_0 and the reduced magnitude of the Mo–Mo peak in FT of the EXAFS (Figure 4.4b). The value of E_0 of the passivated sample (5.2 eV) was close to that of bulk MoO₃. Elemental analysis of the passivated “Mo₂C”/Al₂O₃ revealed 1.9 wt.% Mo and a carbon-deficient stoichiometry of the

supported molybdenum carbide, which is equivalent to $\text{MoC}_{0.22}$. It should be noted that the carbon level of a “carburized” Al_2O_3 sample that was exposed to the same treatment as the catalyst synthesis, except that no molybdenum precursor was added, was subtracted from the analysis. The results from XANES, EXAFS and elemental analysis indicate that partial oxidation of the freshly prepared molybdenum carbide occurred during the passivation of the catalyst. The oxidation of 2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ after passivation was more severe than the oxidation of 5 wt.% Mo_2C supported on MgO [23] or $\alpha\text{-Al}_2\text{O}_3$ [25], perhaps because of the lower weight loading and very high dispersion of Mo. Evidently there was a strong interaction between the Mo species and the Al_2O_3 support [60,61], which prevented agglomeration of the metal and may have formed a stable surface molybdate species on $\gamma\text{-Al}_2\text{O}_3$ [60]. Treatment of a passivated catalyst by reaction in syngas reduced the E_0 shift to 4.2 eV and restored the Mo–Mo peak in the Fourier transform of Mo the EXAFS (Figure 4.4c), giving a Mo–Mo coordination number of 2.1 (Table 4.2). Thus, molybdenum oxycarbide domains appear to exist under syngas reaction conditions, although we will continue to refer to the catalyst as supported $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$. The highly dispersed molybdenum oxycarbide has a longer Mo–C(O) distance and a shorter Mo–Mo distance than the corresponding values in bulk Mo_2C (Table 4.2). Low Mo–Mo coordination numbers in very highly dispersed Mo_2C clusters have also been reported on H-ZSM-5 zeolite [63], $\alpha\text{-Al}_2\text{O}_3$ [25] and $\gamma\text{-Al}_2\text{O}_3$ [64], with Mo–Mo coordination numbers derived from EXAFS as low as 2.6, 2.5 and 4, respectively.

Figure 4.5 Comparison of curve fit to experimental Mo K edge EXAFS of the non-passivated 2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ (air-free): (a) magnitude (solid line) and the imaginary part (dash line) of the FT of EXAFS compared with the result from the curve fit (circle); (b) k^3 -weighted Mo K edge EXAFS (solid line) and the result from curve fit (circle).

4.3.2 CO adsorption on Mo₂C and Rb-promoted Mo₂C

The formation of products during the syngas pretreatment (573 K, 30 bar syngas, H₂/CO = 1, 12 h reaction in syngas) in the DRIFTS experiments was verified by monitoring the IR spectrum during reaction over a 5 wt.% Rb–2 wt.% Mo₂C/Al₂O₃ catalyst, which is shown in Figure 4.6. The IR spectrum at reaction conditions was obtained after removal of a background that was recorded after the sample was purged at 573 K for 1 h in H₂ at ambient pressure. During the reaction, the bands associated with CH₄, CO₂, H₂O, CH₃CH₂OH and CH₃OH, which appear at 3015, 2360, 1650, 1062 and 1030 cm⁻¹, respectively, were observed during reaction over 5 wt.% Rb–2 wt.% Mo₂C/Al₂O₃ catalysts (Figure 4.6).

Figure 4.6 IR spectroscopy of gaseous species in CO hydrogenation at 573 K, 30 bar syngas over 5 wt.% Rb–2 wt.% Mo₂C/Al₂O₃

The IR spectrum of adsorbed CO on unpromoted 2 wt.% Mo₂C/Al₂O₃ at room temperature after being treated at 573 K, in 30 bar syngas (H₂/CO=1) for 12 h and in 1 bar H₂ for 1 h, is shown in Figure 4.7. The spectrum of adsorbed CO on the unpromoted Mo₂C/Al₂O₃ catalyst, which was very low in intensity, revealed two bands at 2105 and 2014 cm⁻¹, and very small features at 2173 cm⁻¹ and 1946 cm⁻¹. A sample of “carburized” Al₂O₃ pretreated with the same condition showed no feature in the IR spectrum attributed to adsorbed CO.

Figure 4.7 Diffuse reflectance Fourier transform spectra of adsorbed CO on 2 wt.% Mo₂C/Al₂O₃ at room temperature after being pretreated at 573 K, in 30 bar syngas (H₂/CO=1) for 12 h and in 1 bar H₂ for 1 h.

Figure 4.8 Top and side view of CO adsorption on reconstructed hexagonal $\text{Mo}_2\text{C}(001)$ surface: (a) CO-free, (b) CO adsorbed on C-top sites, (c) CO adsorbed on Mo-top sites. Mo, C, and O atoms are shown as green, cyan, and red spheres, respectively.

The corresponding vibrational frequencies derived from DFT calculations of CO adsorbed on a reconstructed hexagonal $\text{Mo}_2\text{C}(001)$ surface (Figure 4.8) are shown in Table 4.3. With a low CO coverage of 0.0625 monolayer (ML), the vibrational frequency of adsorbed CO appears at 2121 cm^{-1} and 1989 cm^{-1} on C-top sites (Figure 4.8b) and on Mo-top sites (Figure 4.8c), respectively, with Mo-top sites providing a stronger binding energy (1.62 eV) than C-top sites (1.55 eV). High CO coverages typically cause a blue shift of the vibrational frequency of adsorbed CO [45,65], in part, a result of the dipole-dipole coupling of adsorbed CO molecules [64]. The DFT calculation results also show that on the unmodified Mo_2C surface with a CO coverage of 0.25 monolayer (ML), the vibrational frequencies of adsorbed CO on both C-top sites and on Mo-top sites were shifted to higher frequency by 20 cm^{-1} . Similar shifts in the CO band were also observed on a $\text{W}_2\text{C}(0001)$ surface by Aizawa and Otani [67], who claimed the features belong to surface ketenylidene (CCO) species formed by adsorbed CO on carbidic carbon. Nevertheless, the assignment of bands associated with CO adsorbed on Mo_2C is not straightforward, as discussed below.

Table 4.3 DFT-simulated CO adsorption on reconstructed Mo₂C (001) surface

CO coverage (ML)	C-top site		Mo-top site	
	Wavenumber (cm ⁻¹)	Adsorption energy (eV)	Wavenumber (cm ⁻¹)	Adsorption energy (eV)
0.0625	2121	1.55	1989	1.62
0.250	2141	1.26	2009	1.56

Aegerter *et al.* attributed a feature of 2178 cm⁻¹ to CO adsorption on coordinatively-unsaturated Mo(IV) on a passivated Mo₂C/ γ -Al₂O₃ catalyst after activation in H₂ [46]. Peri has also reported that CO adsorbed on Mo(IV) appears near 2190 cm⁻¹ [68]. Based on these prior assignments, we attribute the minor peak at 2173 cm⁻¹ in Figure 4.8 to CO adsorbed on oxidized molybdenum species or to the residual gaseous CO in the IR cell.

The features in the range of 2071-2054 cm⁻¹ have been assigned to linearly adsorbed CO on a clean hexagonal Mo₂C foil [45], on carbidic Mo sites present on Mo₂C/ γ -Al₂O₃ catalysts [43,44,46], and on modeled surfaces of hexagonal Mo₂C described by DFT [69,70]. A shoulder CO band at 2125 cm⁻¹ has also been reported when Mo₂C foil was pre-exposed to O₂ [45]. Bands for linearly adsorbed CO (2015 cm⁻¹) and bridge-bonded CO (1850 cm⁻¹) were also seen by high-resolution electron energy loss spectroscopy (HREELS) on a Mo (110) single crystal with a surface carbide layer [71]. Consistent with the XANES of bulk Mo₂C [23,25], the close packed structure of Mo in Mo₂C, and the similar electronegativity values of C (2.55) and Mo (2.16) [72], Mo in Mo₂C should be close to the metallic state so that adsorbed CO on metallic Mo would have similar vibrational frequencies to those on carbidic Mo. In fact, bands for linearly adsorbed CO on metallic Mo have been reported at 2055–2015 cm⁻¹ [68,73], whereas the features of bridged-bonded CO are in the range of 1975–1920 cm⁻¹ [73]. The asymmetric

C–O stretching frequencies of ketenylidene (CCO) species varied from 2130 to 2100 cm^{-1} depending on the groups that attached to the CCO structure [74]. Kettenylidene species has been proven to be the most stable configuration of adsorbed CO on a C-terminated Mo_2C surface by DFT [75]. Kettenylidene also formed when CO was adsorbed on a W_2C surface that processed a similar structure to Mo_2C , giving C–O stretching frequencies varying from 1954 cm^{-1} to 2041 cm^{-1} with increasing CO coverage [67]. Interestingly, DFT calculations suggest that ketenylidene may be involved in the initiation of the carbon chain growth process in Fisher–Tropsch synthesis over iron carbide [76].

Müller *et al.* studied CO adsorption on a $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst, which demonstrates very similar catalytic behavior in CO hydrogenation to Mo_2C , and reported a major IR feature at 2105 cm^{-1} for CO on Mo^{2+} along the edge of the crystallites with a shoulder at 2060 cm^{-1} attributed to CO on less coordinated corner sites [39].

Since the XANES of supported Mo_2C catalysts (Table 4.1, Figure 4.3b, and in Ref. [23,25]) suggest that the supported Mo_2C catalysts are actually oxycarbides even after syngas reaction, the 2105 cm^{-1} peak in Figure 4.7 may result from CO on oxycarbide Mo sites, and the secondary peak at 2014 cm^{-1} could be attributed to CO on the Mo sites with lower valence. However, the difference between them may be also caused by different coordinative environments of Mo, such as corner vs. edge sites as described above for MoS_2 catalysts. Moreover, it is possible that the 2105 cm^{-1} peak is from the ketenylidene-like species with CO linearly adsorbed on C-top sites over the reconstructed hexagonal $\text{Mo}_2\text{C}(001)$ surface (Figure 4.8), as suggested by the DFT calculation (Table 4.4).

Figure 4.9 summarizes the IR spectra of CO adsorbed on $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, as the weight loading of Rb increased from 0% to 10%. Upon addition of promoter, the IR band of CO at 2105 cm^{-1} diminished and the entire band associated with CO red shifted according to the amount of Rb added. On a 10 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst (Figure 4.9e), a very weak CO band appeared at 1900 cm^{-1} . A physical mixture of Rb_2CO_3 and “carburized” Al_2O_3 (ground with mortar and pestle) showed no feature of adsorbed CO after the same pretreatment conditions.

Figure 4.9 Diffuse reflectance Fourier transform spectra of adsorbed CO on samples at room temperature after being pretreated at 573 K, in 30 bar syngas ($\text{H}_2/\text{CO}=1$) for 12 h and in 1 bar H_2 for 1 h (a) 2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, (b) 2 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, (c) 5 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, (d) 7.5 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, (e) 10 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$. Spectra are offset for clarity.

In an effort to interpret the DRIFTS results, Rb and RbO were added to the reconstructed hexagonal Mo₂C(001) surface previously described by DFT (Figure 4.1 and Figure 4.8) and vibrational frequencies of adsorbed CO on this promoted surface were calculated. Figure 4.10 provides illustrations of Rb- and RbO-modified Mo₂C surfaces, with and without added CO. The corresponding vibrational frequencies of adsorbed CO on the Rb-modified surfaces are listed in Table 4.4. At the identical CO coverage of 0.0625 ML, the vibrational frequencies of adsorbed CO were observed to red shift by about 34 cm⁻¹ on the C-top sites (Figure 4.10b and e) and by 47 cm⁻¹ on the Mo-top sites (Figure 4.10c and f) after the surface modification with either Rb or RbO. The calculated red shifts are in good agreement with the IR observations of CO adsorption on the Mo₂C/Al₂O₃ catalysts with increasing Rb loading (Figure 4.9b-e). It is also instructive to compare the binding energy of CO on the promoted and unpromoted surfaces. For instance, the binding energy of CO on C-top sites (1.53 eV, Table 4.4) was almost unchanged from the unpromoted C-top sites (1.55 eV, Table 4.3) at a coverage of 0.0625 ML on the RbO-modified Mo₂C surface. However, the binding energy of CO on the Mo-top sites increased by 0.1 eV as a result of the added RbO, which might explain the decrease and eventual disappearance of the CO peak at about 2100 cm⁻¹ over the Rb-promoted Mo₂C/Al₂O₃ (Figure 4.9b-e). It is possible that the presence of the Rb species shifts the preferred binding from C-top to Mo-Topics in It should be noted that the calculations presented here are specific to one type of Mo₂C surface, and that the size, composition and morphology of the supported “Mo₂C” nanoparticles are very different from the defect-free surface with long range order used for modeling. Since the supported carbide samples investigated in this work were passivated in dilute O₂ prior to reaction or

DRIFTS investigation, the actual catalysts interrogated experimentally were likely to be oxycarbides rather than pure carbides. Indeed, the relatively high binding energy of CO on the simulated Mo_2C surface is consistent with the high affinity of pristine carbides for simple adsorbates. Nevertheless, we used the DFT studies of a model carbide surface to explore the nature of the CO binding mode and the trend in the vibrational frequency of CO with alkali metal addition to that surface.

Figure 4.10 Top and side view of CO adsorption on Rb-modified reconstructed hexagonal $\text{Mo}_2\text{C}(001)$ surface: (a) no adsorbed CO, (b) CO adsorbed on C-top sites, (c) CO adsorbed on Mo-top sites; and CO adsorption on Rb-modified reconstructed hexagonal $\text{Mo}_2\text{C}(001)$ surface: (d) no adsorbed CO, (e) CO adsorbed on C-top sites, (f) CO-adsorbed on Mo-top sites. Mo, C, O and Rb atoms are shown as green, cyan, red and purple spheres, respectively.

Table 4.4 DFT-simulated CO adsorption on modified re-constructed Mo₂C (001) surface

Surface	CO coverage (ML)	C-top site		Mo-top site	
		Wavenumber (cm ⁻¹)	Adsorption energy (eV)	Wavenumber (cm ⁻¹)	Adsorption energy (eV)
Rb-modified	0.0625	2088	1.41	1942	1.70
RbO-modified	0.0625	2086	1.53	1942	1.72

Bugyi and Solymosi studied the interaction of CO with clean and K-covered Mo₂C/Mo(100) surfaces by HREELS [77]. They found that CO adsorbed molecularly on the clean Mo₂C/Mo(100) surface at 140 K, giving an energy loss at 2100 cm⁻¹. Pre-adsorbed K atoms at intermediate coverages (0.5-0.8 monolayer) at 140 K led to an HREELS feature for CO at 1320–1375 cm⁻¹, attributed to a short-range interaction, while the development of features at 1670–1685 and 1860 cm⁻¹ was attributed to long-range interaction in the K–CO co-adsorbed layer [78,79]. They also suggested that K atoms were stabilized mainly by O atoms arising from the decomposition of CO.

Indeed, given the high oxophilicity of both Mo₂C and atomic Rb, neither bare Rb atoms nor oxygen-free Mo₂C surface can likely exist in syngas reaction conditions. Comparing the observed vibrational frequencies of CO adsorbed on Rb-promoted Mo₂C/Al₂O₃ at the surface science results for CO adsorbed on K-modified molybdenum carbide surfaces [77] at relatively low CO coverages, a similar trend is found in the shifts of peaks caused by the addition of alkali metal species. However, the shift in position is about –200 cm⁻¹ from Rb-free Mo₂C/Al₂O₃ to 10 wt.% Rb-promoted Mo₂C/Al₂O₃, which is much less than the approximately –700 cm⁻¹ shift observed on a K-modified Mo₂C/Mo(100) surface from a corresponding K-free surface [77]. This implies that the interaction of CO with cluster of molybdenum carbide was much less influenced by promoter compared to that of the extended surface in ultra high vacuum.

In summary, the shifts in CO band position in Figure 4.9 may indicate a change of preferred binding site for CO molecules from C-top to Mo-top, as suggested by DFT calculations (Table 4.4 and Table 4.5), or a coverage-dependent asymmetric C–O stretching frequency of CCO species formed on the carbide surface [67]. Additionally, the shift could also result from CO moving from a linearly adsorbed configuration to a bridge-bonded one [72]. The low frequency tail of the CO band on unpromoted Mo₂C/Al₂O₃ (Figure 4.7, Figure 4.9a) extends to the region around 1900 cm⁻¹, which is the position of CO on the highly promoted Mo₂C/Al₂O₃. Therefore, addition of the Rb promoter may simply deactivate the sites for CO adsorption at wavenumbers higher than 2000 cm⁻¹, leaving behind only sites with the lower characteristic frequencies. Unfortunately, at this point in time a more definitive explanation of the observed shifts in the spectrum of adsorbed CO cannot be provided.

4.3.3 Reactivity of Mo₂C/Al₂O₃ catalysts

The performance of alumina-supported Mo₂C catalysts in the reaction of syngas (H₂/CO = 1) at 573 K and 30 bar pressure is summarized in Figure 4.5. Unpromoted 2 wt.% Mo₂C/Al₂O₃ functions primarily as an active Fischer–Tropsch catalyst producing mainly hydrocarbons (91% on a CO₂-free basis) at 17% CO conversion. A significant amount of ethers was also observed over the unpromoted catalyst, but the amounts were substantially reduced at high loadings of the Rb promoter. The formation of ethers suggests that alcohols are primary products on unpromoted Mo₂C catalysts, but they are further converted to ethers on the acid sites of the γ -Al₂O₃ portion of the support. This result is consistent with our previous observation concerning the intrinsic alcohol formation activity of unpromoted, non-passivated Mo₂C/ α -Al₂O₃, which is comparable to

the rate of alcohol formation over a 1.5 wt.% Rb–5 wt.% Mo₂C/ α -Al₂O₃ [25]. The addition of 2, 5, 7.5 or 10 wt.% Rb₂CO₃ to 2 wt.% Mo₂C/Al₂O₃ increased the selectivity to alcohols (12%, 50%, 62% or 67%, respectively) at the expense of overall CO conversion (down to 4.9% at the highest promoter loading), which is also consistent with our previous study on Rb-promoted Mo₂C/MgO catalysts [23], and with prior works on potassium-promoted bulk Mo₂C catalysts [21,22,80]. The alcohol production rate peaked at 0.25 g g_{Mo}⁻¹ h⁻¹ when the Rb loading was 7.5 wt.% and slightly decreased to 0.24 g g_{Mo}⁻¹ h⁻¹ on a 10 wt.% Rb–2 wt.% Mo₂C/Al₂O₃ catalyst. With the addition of Rb promoter, the shift of performance of the Mo₂C/Al₂O₃ catalysts in CO hydrogenation from hydrocarbons to alcohols also correlates well to the red shift of the IR band of adsorbed CO (Figure 4.9). It should be noted that in our previous studies of Mo₂C supported on MgO [23] or α -Al₂O₃ [25], we did not report ethers in the product stream since they were present in very small amounts relative to Mo₂C on alumina containing the γ -phase. No conversion of CO was observed over a mixture of Rb₂CO₃ and Al₂O₃ under typical reaction conditions, which proves that molybdenum is associated with the active site.

Given that passivated carbides are also known to possess surface acid sites after exposure to dioxygen [81–86], one interaction between Rb₂CO₃ promoter and Mo₂C/Al₂O₃ catalysts is to neutralize the acid sites on the carbide component and Al₂O₃ support, resulting in an increasing selectivity towards alcohols and decreasing selectivity towards hydrocarbons and ethers.

Table 4.5 Reactivity of 2 wt.% Mo₂C/Al₂O₃ catalysts in syngas reaction

Rb loading (wt.%)	0	2.0	5.0	7.5	10
CO conversion (%)	19	9.1	5.4	5.2	4.9
CO ₂ selectivity (%)	39	37	44	40	41
Selectivity (C %, on a CO ₂ -free basis)					
Total hydrocarbons	75	45	35	30	27
Methane	27	20	16	13	12
C2 hydrocarbons	26	12	7.5	6.9	7.0
C3 hydrocarbons	16	8.2	6.5	5.1	4.3
C4+ linear paraffins	5.5	3.8	1.8	1.6	0.86
C4+ linear olefins	0.19	0.76	1.8	2.1	2.2
Branched hydrocarbons	3.1	0.89	1.0	1.2	0.66
Total ethers ^a	22	43	15	7.7	6.6
Total alcohols	3.2	12	50	62	67
Methanol	3.0	7.4	23	23	18
Ethanol	0.24	3.1	12	15	18
1-Propanol	0.0	1.3	12	18	23
1-Butanol	0.0	0.0	2.5	4.3	5.0
C5+ alcohols	0.0	0.0	1.1	2.8	2.6
(C2+ alcohols)/methanol	0.08	0.59	1.2	1.6	2.7
Rate of CO consumption (mol _{CO} mol _{Mo} ⁻¹ h ⁻¹)	9.3	4.5	2.7	2.6	2.5
Rate of hydrocarbon production (g g _{Mo} ⁻¹ h ⁻¹)	0.67	0.21	0.085	0.074	0.062
Rate of ether production (g g _{Mo} ⁻¹ h ⁻¹)	0.30	0.28	0.046	0.023	0.018
Rate of alcohol production (g g _{Mo} ⁻¹ h ⁻¹)	0.06	0.10	0.21	0.25	0.24

T = 573 K, P = 30 bar, H₂/CO = 1, syngas flow rate = 24,000 cm³ g_{Mo}⁻¹ h⁻¹. Data were recorded after 72 h reaction. ^a Including dimethyl ether, ethyl methyl ether, methyl propyl ether, butyl methyl ether, etc.

4.3.4 Influence of H₂O on Rb-promoted Mo₂C/Al₂O₃

Since the movement of Rb promoter across the catalyst surface is critical to achieve selective alcohol formation, we studied the role of water on activation of the catalyst.

The IR spectra of adsorbed CO on 2 wt.% Mo₂C/Al₂O₃ (Figure 4.11) and 7.5 wt.% Rb–2 wt.% Mo₂C/Al₂O₃ (Figure 4.12) catalysts were recorded after various pretreatment conditions. Water was introduced to the catalyst by flowing He to the DRIFTS cell

through a saturator with liquid water at room temperature. Likewise the rates of production of various molecules (hydrocarbons, ethers, alcohols and total oxygenates) over 7.5 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalysts, with and without water pretreatment, are summarized in Figure 4.13.

Figure 4.11 Influence of pretreatment conditions on the IR bands of adsorbed CO on 2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ with various pretreatment conditions, with (b) – (e) sequentially performed on a separate sample from (a): (a) 1 bar H_2 at 573 K for 12 h; (b) 1 bar $\text{H}_2\text{O}/\text{He}$ at 300 K for 2 h and 1 bar He at 423 K for 1 h; (c) 1 bar H_2 at 573 K for 12 h; (d) 30 bar syngas ($\text{H}_2/\text{CO} = 1$) for 12 h and in 1 bar H_2 for 1 h; (e) 1 bar H_2 at 573 K for 12 h. Spectra are offset for clarity.

Figure 4.12 Influence of pretreatment conditions on the IR bands of adsorbed CO on 7.5 wt.% Rb-2 wt.% Mo₂C/Al₂O₃ with various pretreatment conditions, with (b) – (e) sequentially performed on a separate sample from (a): (a) 1 bar H₂ at 573 K for 12 h; (b) 1 bar H₂O/He at 300 K for 2 h and 1 bar He at 423 K for 1 h; (c) 1 bar H₂ at 573 K for 12 h; (d) 30 bar syngas (H₂/CO = 1) for 12 h and in 1 bar H₂ for 1 h; (e) 1 bar H₂ at 573 K for 12 h. Spectra are offset for clarity.

Figure 4.13 Change in the production rates of hydrocarbons (solid squares), ethers (open circles), alcohols (solid up triangles) and total oxygenates (open down triangles, alcohols and esters combined) over 7.5 wt.% Rb–2 wt.% Mo₂C/Al₂O₃ pretreated with: (a) 1 bar H₂ at 573 K for 12 h; (b) 1 bar H₂O/N₂ at 300 K for 2 h, followed with 1 bar H₂ at 573 K for 12 h.

Despite the different pretreatment conditions (water or no water), the unpromoted Mo₂C/Al₂O₃ catalyst always had a major band for adsorbed CO between 2118 cm⁻¹ and 2102 cm⁻¹ and a secondary peak/shoulder at 2072–2025 cm⁻¹. The results suggest that,

without promoter present, the influence of the water pretreatment was minimal and the catalyst will function primarily as a hydrocarbon formation catalyst, consistent with the known catalytic properties of unpromoted Mo_2C in Table 4.3 and elsewhere [21–25,87]. With pretreatment in H_2 , the IR spectra of CO adsorbed on 7.5 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ (Figure 4.12a) also revealed a major peak at 2105 cm^{-1} and a secondary peak at 2030 cm^{-1} . According to the observed correlation between IR peak position of adsorbed CO in Figure 4.9 and the product distribution reported in Table 4.3, this result would predict that hydrocarbons would be the initial products of CO hydrogenation over the H_2 -pretreated promoted $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst. In fact, the initial rates of production over H_2 -pretreated 7.5 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst (Figure 4.13a) are 0.34 for hydrocarbons and $0.011\text{ g g}_{\text{Mo}}^{-1}\text{ h}^{-1}$ for alcohols, which are comparable to the corresponding productivities over the unpromoted $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst (Table 4.3). Therefore, pretreatment involving only H_2 at reaction temperature does not efficiently disperse the Rb promoter across the catalyst. However, pretreatment with water vapor in flowing He at 300 K for 2 h before H_2 -treatment at 573 K (Figure 4.12c) completely removed the major IR peak of adsorbed CO on 7.5 wt.% Rb–2 wt.% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ at 2105 cm^{-1} and instead resulted in a band centered at 1965 cm^{-1} (Figure 4.12c), which suggests a strong interaction between the Rb promoter and the Mo_2C catalyst. This peak position for adsorbed CO correlates well to the high alcohol productivity of the water-treated catalyst and very short induction period (Figure 4.13b). The IR band of adsorbed CO remained unchanged after syngas reaction and further treatment in H_2 at 573 K. Since the peak for adsorbed CO above 2100 cm^{-1} was not restored by additional treatment in H_2 , the interaction between the Rb promoter and the Mo_2C catalysts that is facilitated by

water is not reversible. These reactivity results coupled to IR spectroscopy clearly show how water plays a critical role in the distribution of the Rb promoter over the Mo_2C clusters, and presumably over the alumina support as well. Since H_2O is a product of CO hydrogenation, the *in situ* formation of water likely facilitates distribution of Rb during the reaction and likely accounts for the induction time observed in Figure 4.13a.

Figure 4.14 Schematic illustration of (a) H_2O molecules adsorbed on Mo_2C surface; (b) OH groups and H atoms adsorbed on Mo_2C surface after the dissociation of adsorbed H_2O ; (c) the energy profile of H_2O dissociation. Mo, C, H and O atoms are shown as green, cyan, white and red spheres, respectively. The energy of the initial state (H_2O^*) is defined as zero.

The shift of peak position observed in the IR bands of adsorbed CO on Mo₂C/Al₂O₃ with the addition of Rb promoter and the deviation of the CO feature on the unpromoted Mo₂C/Al₂O₃ catalyst in IR spectroscopy from that on freshly carburized Mo₂C/ γ -Al₂O₃ [43,44] confirm that Mo₂C surfaces are modified by surface passivation, promoter impregnation and syngas reaction.

According to our DFT calculations, H₂O can easily dissociate to form hydroxyl (OH) groups on the Mo₂C surface with no energy barrier (Figure 4.14), which is consistent with the findings by Tominaga and Nagai [69]. Additionally, Chia *et al.* used DFT to show that hydroxyl groups on oxophilic molybdenum atoms associated with platinum clusters are acidic in nature [88]. Since interstitial carbide is known to modify the d band of molybdenum metal so that carbides exhibit some similar catalytic properties to platinum [27,89], strongly adsorbed hydroxyl groups on molybdenum associated with molybdenum carbide may also be fairly acidic. According to the correlation between the deprotonation energy of surface hydroxyl groups and the corresponding oxygen binding energy reported by Chia *et al.*, a strong metal-oxygen bond weakens the O–H bond, which imparts strong acidity to the surface OH group [86]. In accordance with the DFT correlation by Chia *et al.*, OH groups with deprotonation energies typical of strong acids have oxygen binding energies greater than 5 eV. The calculated oxygen binding energy on the surface of Mo₂C is –7.37 eV, which suggests that a surface hydroxyl group on Mo₂C will be strongly acidic. Thus, alkali metal promoters are needed to neutralize the acidic hydroxyl groups on passivated Mo₂C catalysts. In fact, Lee *et al.* studied the performance of multiple potassium-based promoters on bulk Mo₂C catalysts in CO hydrogenation [32]. Auger electron

spectroscopy revealed that the K promoters that enhanced the selectivity towards alcohols (K_2CO_3 , KOH, CH_3COOK and K_2S) distributed over the Mo_2C surface fairly evenly after syngas reaction, while those did not possess great mobility over the Mo_2C surface (KCl and K_2SO_4) did not substantially increase alcohol selectivity [32]. The difference in the mobility of the various potassium compounds in light of the neutralization reaction between the surface acidic groups on Mo_2C and the alkali metal salts. Clearly, the effective K promoters (K_2CO_3 , KOH, CH_3COOK and K_2S) are the salts of weak acids that can neutralize the surface acidity over Mo_2C , whereas the ineffective promoters are the salts of strong acids. A neutralization mechanism was also hypothesized by Tatsumi *et al.* to interpret how K promoter interacts with MoS_2 catalysts during alcohol synthesis from syngas [90].

4.3.5 Model of catalyst evolution

A working model of the surface of Mo_2C catalysts for CO hydrogenation is sketched in Figure 4.15. In the model, the carbide surface is firstly covered by oxygen atoms after surface passivation. Water in the ambient air and formed *in situ* during syngas reaction can dissociate on the carbide surface to form acidic hydroxyl groups, which are detrimental to alcohol selectivity. Addition of Rb_2CO_3 is needed to both neutralize surface acidity on Mo_2C and Al_2O_3 and inhibit hydrocarbon formation on Mo_2C . However, water that is added to the catalyst or generated *in situ* during CO hydrogenation is needed to distribute the Rb promoter across the catalyst surface. Exposure of the passivated catalysts to the syngas environment partially reduces the passivated carbide to create an active catalyst. The highly promoted catalyst has Rb on the carbide phase,

which perturbed the adsorption mode of CO on the surface and shifted product selectivity from hydrocarbons to alcohols.

Figure 4.15 Working model of the modified Mo_2C surfaces for CO hydrogenation

4.4 Conclusions

An unpromoted sample of $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ was active in the Fischer–Tropsch reaction and produced mostly hydrocarbons from syngas at 573 K and 30 bar. Moreover, the IR spectrum of CO adsorbed on the unpromoted carbide catalyst revealed features at 2105 cm^{-1} and 2014 cm^{-1} . The addition of Rb promoter to $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ gradually shifted the selectivity of the syngas reaction toward alcohols, primarily by inhibiting hydrocarbon and ether formation. The IR features of adsorbed CO on Mo_2C nanoclusters shifted substantially to lower frequencies upon addition of Rb promoter ($\sim 200\text{ cm}^{-1}$ shift from an unpromoted sample to a 10 wt.% Rb-promoted sample). Results from DFT qualitatively reproduced the trends observed by IR spectroscopy and were used to interpret the various features. The interaction of the Rb promoter and the Mo_2C catalyst was facilitated by H_2O added during catalyst pretreatment, and presumably by *in situ* formation of H_2O during syngas reaction. Results from reactivity studies, IR

spectroscopy and DFT were used to derive a model of catalyst evolution during synthesis, pretreatment and reaction.

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References of Chapter 4

- [1] V.J. Johnston, L. Chen, B.F. Kimmich, J.T. Chapman, J.H. Zink, "Direct and selective production of ethanol from acetic acid utilizing a platinum/tin catalyst," U.S. Patent 7863489, 2011, to Celanese Corporation.
- [2] V.J. Johnston, L. Chen, B.F. Kimmich, J.T. Chapman, J.H. Zink, "Direct and selective production of ethanol from acetic acid utilizing a platinum/tin catalyst," U.S. Patent 8071821, 2011, to Celanese Corporation.
- [3] G. Hess, "BP and DuPont plan 'biobutanol'," *Chemical & Engineering News* 84 (2006) 9.

- [4] P. Forzatti, E. Tronconi, I. Pasquon, "Higher alcohol synthesis," *Catalysis Reviews: Science Engineering* 33 (1991) 109–168.
- [5] I. Wender, "Reactions of synthesis gas," *Fuel Processing Technology* 48 (1996) 189–297.
- [6] R.G. Herman, "Advances in catalytic synthesis and utilization of higher alcohols," *Catalysis Today* 55 (2000) 233–245.
- [7] K. Fang, D. Li, M. Lin, M. Xiang, W. Wei, Y. Sun, "A short review of heterogeneous catalytic process for mixed alcohols synthesis via syngas," *Catalysis Today* 147 (2009) 133–138.
- [8] S. Zaman, K.J. Smith, "A review of molybdenum catalysts for synthesis gas conversion to alcohols: Catalysts, mechanisms and kinetics," *Catalysis Reviews: Science and Engineering* 54 (2012) 41–132.
- [9] J.J. Spivey, A. Egbibi, "Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas," *Chemical Society Reviews* 36 (2007) 1514–1528.
- [10] V. Subramani, S.K. Gangwal, "A review of recent literature to search for an efficient catalytic process for the conversion of syngas to ethanol," *Energy and Fuels* 22 (2008) 814–839.
- [11] M.A. Haider, M.R. Gogate, R.J. Davis, "Fe-promotion of supported Rh catalysts for direct conversion of syngas to ethanol," *Journal of Catalysis* 261 (2009) 9–16.
- [12] Y. Avila, C. Kappenstein, S. Pronier, J. Barrault, "Alcohol synthesis from syngas over supported molybdenum catalysts," *Applied Catalysis A: General* 132 (1995) 97–109.
- [13] J.S. Lee, S. Kim, K.H. Lee, I.-S. Nam, J.S. Chung, Y.G. Kim, H.C. Woo, "Role of alkali promoters in K/MoS₂ catalysts for CO-H₂ reactions," *Applied Catalysis A: General* 110 (1994) 11–25.
- [14] J.M. Christensen, P.M. Mortensen, R. Trane, P.A. Jensen, A.D. Jensen, "Effects of H₂S and process conditions in the synthesis of mixed alcohols from syngas over alkali promoted cobalt-molybdenum sulfide," *Applied Catalysis A: General* 366 (2009) 29–43.
- [15] V.R. Surisetty, A. Tavasoli, A.K. Dalai, "Synthesis of higher alcohols from syngas over alkali promoted MoS₂ catalysts supported on multi-walled carbon nanotubes," *Applied Catalysis A: General* 365 (2009) 243–251.
- [16] G.J. Quarderer, G.A. Cochran, "Catalytic process for producing mixed alcohols from hydrogen and carbon monoxide," European Patent EP0119609, 1984, to The Dow Chemical Company.

- [17] M.M. Conway, C.B. Murchison, R.R. Stevens, "Method for adjusting methanol to higher alcohol ratios," U.S. Patent 4675344, 1987, to The Dow Chemical Company.
- [18] G.J. Quarderer, G.A. Cochran, "Process for producing alcohols from synthesis gas," U.S. Patent 4749724, 1988, to The Dow Chemical Company.
- [19] R.R. Stevens, "Process for producing alcohols from synthesis gas," U.S. Patent 4752622, 1988, to The Dow Chemical Company.
- [20] R.R. Stevens, "Process for producing alcohols from synthesis gas," U.S. Patent 4882360, 1989, to The Dow Chemical Company.
- [21] H.C. Woo, K.Y. Park, Y.G. Kim, I.S. Nam, J.S. Chung, J.S. Lee, "Mixed alcohol synthesis from carbon monoxide and dihydrogen over potassium-promoted molybdenum carbide catalysts," *Applied Catalysis* 75 (1991) 267–280.
- [22] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "Performances of mixed alcohols synthesis over potassium promoted molybdenum carbides," *Fuel* 85 (2006) 2662–2665.
- [23] H. Shou, R.J. Davis, "Reactivity and *in situ* X-ray absorption spectroscopy of Rb-promoted Mo₂C/MgO catalysts for higher alcohol synthesis," *Journal of Catalysis* 282 (2011) 83–93.
- [24] J.M. Christensen, L.D.L. Duchstein, J.B. Wagner, P.A. Jensen, B. Temel, A.D. Jensen, "Catalytic conversion of syngas into higher alcohols over carbide catalysts," *Industrial & Engineering Chemistry Research* 51 (2012) 4161–4172.
- [25] H. Shou, D. Ferrari, D.G. Barton, C.W. Jones, R.J. Davis, "Influence of Passivation on the Reactivity of Unpromoted and Rb-Promoted Mo₂C Nanoparticles for CO Hydrogenation," *ACS Catalysis* 2 (2012) 1408–1416.
- [26] R.B. Levy, M. Boudart, "Platinum-like behavior of tungsten carbide in surface catalysis, *Science* 181 (1973) 547–549.
- [27] J.G. Chen, "Carbide and nitride overlayers on early transition metal surfaces: Preparation, characterization, and reactivities," *Chemical Reviews* 96 (1996) 1477–1498.
- [28] H.H. Hwu, J.G. Chen, "Surface chemistry of transition metal carbides," *Chemical Reviews* 105 (2005) 185–212.
- [29] M. Jiang, G.-Z. Bian, Y.-L. Fu, "Effect of the K-Mo interaction in K-MoO₃/γ-Al₂O₃ catalysts on the properties for alcohol synthesis from syngas," *Journal of Catalysis* 146 (1994) 144–154.

- [30] G.-Z. Bian, Y.-L. Fu, M. Yamada, "Reaction stability and structure studies of sulfided $\text{KMoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst for the synthesis of mixed alcohols," *Applied Catalysis A: General* 144 (1996) 79–91.
- [31] H.C. Woo, J.C. Kim, I.S. Nam, J.S. Lee, J.S. Chung, Y.G. Kim, "Surface species on the oxidized $\text{K}_2\text{CO}_3/\text{MoS}_2$ and their effects on catalytic carbon monoxide hydrogenation," *Applied Catalysis A: General* 104 (1993) 199–214.
- [32] J.S. Lee, S. Kim, Y.G. Kim, "Electronic and geometric effects of alkali promoters in CO hydrogenation over $\text{K/Mo}_2\text{C}$ catalysts," *Topics in Catalysis* 2 (1995) 127–140.
- [33] N. Koizumi, G. Bian, K. Murai, T. Ozaki, M. Yamada, "In situ DRIFT studies of sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts," *Journal of Molecular Catalysis A: Chemical* 207 (2004) 173–182.
- [34] A. Muramatsu, T. Tatsumi, H. Tominaga, "Mixed alcohol synthesis from CO-H_2 by use of KCl -promoted Mo/SiO_2 catalysts," *Bulletin of the Chemical Society of Japan* 60 (1987) 3157–3161.
- [35] N.F.D. Verbruggen, G. Mestl, L.M.J. von Hippel, B. Lengeler, H. Knoezinger, "Structure of K-doped molybdena-on-alumina catalysts as studied by X-ray absorption and Raman spectroscopy," *Langmuir* 10 (1994) 3063–3072.
- [36] N.F.D. Verbruggen, L.M.J. von Hippel, G. Mestl, B. Lengeler, H. Knoezinger, "Structure of K-doped molybdena-on-silica catalysts as studied by X-ray absorption and Raman spectroscopy," *Langmuir* 10 (1994) 3073–3080.
- [37] Y. Fu, F. Zhao, "The adsorption characteristics of two Mo sites on a sulfided $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ surface," *Catalysis Letters* 12 (1992) 117–125.
- [38] F. Maugé, J.C. Lavalley, "FT-IR study of CO adsorption on sulfided $\text{Mo/Al}_2\text{O}_3$ unpromoted or promoted by metal carbonyls: Titration of sites," *Journal of Catalysis* 137 (1992) 69–76.
- [39] B. Müller, A.D. van Langeveld, J.A. Moulijn, H. Knözinger, "Characterization of sulfided molybdenum/alumina catalysts by temperature-programmed reduction and low-temperature Fourier transform infrared spectroscopy of adsorbed carbon monoxide," *The Journal of Physical Chemistry* 97 (1993) 9028–9033.
- [40] A. Travert, C. Dujardin, F. Maugé, S. Cristol, J.F. Paul, E. Payen, D. Bougeard, "Parallel between infrared characterisation and ab initio calculations of CO adsorption on sulphided Mo catalysts," *Catalysis Today* 70 (2001) 255–269.
- [41] A.A. Tsyganenko, F. Can, A. Travert, F. Maugé, "FTIR study of unsupported molybdenum sulfide—in situ synthesis and surface properties characterization," *Applied Catalysis A: General* 268 (2004) 189–197.

- [42] A. Travert, C. Dujardin, F. Maugé, E. Veilly, S. Cristol, J.-F. Paul, E. Payen, "CO adsorption on CoMo and NiMo sulfide catalysts: A combined IR and DFT study," *The Journal Physical Chemistry B* 110 (2006) 1261–1270.
- [43] W. Wu, Z. Wu, C. Liang, X. Chen, P. Ying, C. Li, "In Situ FT-IR spectroscopic studies of CO adsorption on fresh Mo₂C/Al₂O₃ catalyst," *The Journal Physical Chemistry B* 107 (2003) 7088–7094.
- [44] W. Wu, Z. Wu, C. Liang, P. Ying, Z. Feng, C. Li, "An IR study on the surface passivation of Mo₂C/Al₂O₃ catalyst with O₂, H₂O and CO₂," *Physical Chemistry Chemical Physics* 6 (2004) 5603–5608.
- [45] J. Wang, M. Castonguay, P.H. McBreen, S. Ramanathan, S.T. Oyama, "Chemisorption of CO and NO molybdenum carbide foils," in: S.T. Oyama (Ed.), *The Chemistry of Transition Metal Carbides and Nitrides*, Springer, 1996: pp. 426–438.
- [46] P.A. Aegerter, W.W.C. Quigley, G.J. Simpson, D.D. Ziegler, J.W. Logan, K.R. McCrea, S. Glazier, M.E. Bussell, "Thiophene hydrodesulfurization over alumina-supported molybdenum carbide and nitride catalysts: Adsorption sites, catalytic activities, and nature of the active surface," *Journal of Catalysis* 164 (1996) 109–121.
- [47] J. Raskó, J. Kiss, "Infrared study of the adsorption of CO and CH₃ on silica-supported MoO₃ and Mo₂C catalysts," *Applied Catalysis A: General* 253 (2003) 427–436.
- [48] B. Ravel, M. Newville, "ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT," *Journal of Synchrotron Radiation* 12 (2005) 537–541.
- [49] S.I. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, M.J. Eller, "Multiple-scattering calculations of x-ray-absorption spectra," *Physical Review B* 52 (1995) 2995–3009.
- [50] J.P. Perdew, K. Burke, M. Ernzerhof, "Generalized gradient approximation made simple," *Physical Review Letters* 77 (1996) 3865–3868.
- [51] J.P. Perdew, K. Burke, M. Ernzerhof, "Generalized gradient approximation made simple," *Physical Review Letters* 78 (1997) 1396.
- [52] P.E. Blöchl, "Projector augmented-wave method," *Physical Review B* 50 (1994) 17953–17979.
- [53] G. Kresse, D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," *Physical Review B* 59 (1999) 1758–1775.

- [54] J.W. Han, L. Li, D.S. Sholl, "Density functional theory study of H and CO adsorption on alkali-promoted Mo₂C surfaces," *The Journal Physical Chemistry C* 115 (2011) 6870–6876.
- [55] R.-L. Lo, K. Fukui, S. Otani, Y. Iwasawa, "High resolution images of Mo₂C(0001)-(3×3)R30° structure by scanning tunneling microscopy," *Surface Science* 440 (1999) L857–L862.
- [56] R.-L. Lo, K. Fukui, S. Otani, S.T. Oyama, Y. Iwasawa, "C-terminated reconstruction and C-chain structure on Mo₂C(0001) surface studied by low energy electron diffraction and scanning tunneling microscopy," *Japanese Journal of Applied Physics* 38 (1999) 3813–3815.
- [57] T. Aizawa, S. Hishita, T. Tanaka, S. Otani, "Surface reconstruction of W₂C(0001)," *Journal of Physics: Condensed Matter* 23 (2011) 305007.
- [58] J. Neugebauer, M. Scheffler, "Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111)," *Physical Review B* 46 (1992) 16067–16080.
- [59] L. Bengtsson, "Dipole correction for surface supercell calculations," *Physical Review B* 59 (1999) 12301–12304.
- [60] B. Scheffer, P. Arnoldy, J.A. Moulijn, "Sulfidability and hydrodesulfurization activity of Mo catalysts supported on alumina, silica, and carbon," *Journal of Catalysis* 112 (1988) 516–527.
- [61] P. Da Costa, C. Potvin, J.-M. Manoli, M. Breysse, G. Djéga-Mariadassou, "Novel phosphorus-doped alumina-supported molybdenum and tungsten carbides: Synthesis, characterization and hydrogenation properties," *Catalysis Letters* 72 (2001) 91–97.
- [62] B.C. Gates, J.R. Katzer, G.C.A. Schuit, *Chemistry of catalytic processes*, McGraw-Hill, 1979.
- [63] W. Ding, S. Li, G.D. Meitzner, E. Iglesia, "Methane conversion to aromatics on Mo/H-ZSM5: Structure of molybdenum species in working catalysts," *The Journal Physical Chemistry B* 105 (2001) 506–513.
- [64] J.S. Lee, M. Boudart, "*In situ* carburization of metallic molybdenum during catalytic reactions of carbon-containing gases," *Catalysis Letters* 20 (1993) 97–106.
- [65] J. Wang, M. Castonguay, J. Deng, P.H. McBreen, "RAIRS and TPD study of CO and NO on β-Mo₂C," *Surface Science* 374 (1997) 197–207.
- [66] A. Crossley, D.A. King, "Infrared spectra for co isotopes chemisorbed on Pt "111": Evidence for strong adsorbate coupling interactions," *Surface Science* 68 (1977) 528–538.

- [67] T. Aizawa, S. Otani, "Adsorption of CO and O₂ on W₂C(0001)," *The Journal of Chemical Physics* 135 (2011) 144704.
- [68] J.B. Peri, "Computerized infrared studies of Mo/Al₂O₃ and Mo/SiO₂ catalysts," *The Journal of Physical Chemistry* 86 (1982) 1615–1622.
- [69] H. Tominaga, M. Nagai, "Density functional theory of water–gas shift reaction on molybdenum carbide," *The Journal Physical Chemistry B* 109 (2005) 20415–20423.
- [70] X.-R. Shi, J. Wang, K. Hermann, "CO and NO adsorption and dissociation at the β -Mo₂C(0001) surface: A density functional theory study," *The Journal Physical Chemistry C* 114 (2010) 13630–13641.
- [71] B. Frühberger, J.G. Chen, "Modification of the surface reactivity of Mo(110) upon carbide formation," *Surface Science* 342 (1995) 38–46.
- [72] W.M. Haynes, ed., *CRC Handbook of Chemistry and Physics*, 92nd ed., Taylor & Francis, 2011.
- [73] M.L. Colaianni, J.G. Chen, W.H. Weinberg, J.T. Yates, "The adsorption and dissociation of carbon monoxide on clean and oxygen-modified molybdenum(110) surfaces," *Journal of the American Chemical Society* 114 (1992) 3735–3743.
- [74] B.D. Wagner, B.R. Arnold, G.S. Brown, J. Lusztyk, "Spectroscopy and absolute reactivity of ketenes in acetonitrile studied by laser flash photolysis with time-resolved infrared detection," *Journal of the American Chemical Society* 120 (1998) 1827–1834.
- [75] J. Ren, C.-F. Huo, J. Wang, Y.-W. Li, H. Jiao, "Surface structure and energetics of oxygen and CO adsorption on α -Mo₂C(0 0 0 1)," *Surface Science* 596 (2005) 212–221.
- [76] L.-J. Deng, C.-F. Huo, X.-W. Liu, X.-H. Zhao, Y.-W. Li, J. Wang, H. Jiao, "Density functional theory study on surface C_xH_y formation from CO activation on Fe₃C(100)," *The Journal Physical Chemistry C* 114 (2010) 21585–21592.
- [77] L. Bugyi, F. Solymosi, "Effects of potassium on the chemisorption of CO on the Mo₂C/Mo(100) surface," *The Journal Physical Chemistry B* 105 (2001) 4337–4342.
- [78] K.J. Uram, L. Ng, J.T. Yates, "Electrostatic effects between adsorbed species—the K–Co interaction on Ni(111) as studied by infrared reflection-absorption spectroscopy," *Surface Science* 177 (1986) 253–277.
- [79] M.D. Alvey, A.-M. Lanzillotto, J.T. Yates, "The effect of potassium on the molecular orientation of CO chemisorbed on Ni(111): An esdiad study," *Surface Science* 177 (1986) 278–290.

- [80] H.G. Kim, K.H. Lee, J.S. Lee, "Carbon monoxide hydrogenation over molybdenum carbide catalysts," *Research on Chemical Intermediates* 26 (2000) 427–443.
- [81] F.H. Ribeiro, R.A. Dalla Betta, M. Boudart, J. Baumgartner, E. Iglesia, "Reactions of neopentane, methylcyclohexane, and 3,3-dimethylpentane on tungsten carbides: The effect of surface oxygen on reaction pathways," *Journal of Catalysis* 130 (1991) 86–105.
- [82] F.H. Ribeiro, M. Boudart, R.A. Dalla Betta, E. Iglesia, "Catalytic reactions of *n*-alkanes on β -W₂C and WC: The effect of surface oxygen on reaction pathways," *Journal of Catalysis* 130 (1991) 498–513.
- [83] E. Iglesia, J.E. Baumgartner, F.H. Ribeiro, M. Boudart, "Bifunctional reactions of alkanes on tungsten carbides modified by chemisorbed oxygen," *Journal of Catalysis* 131 (1991) 523–544.
- [84] E. Iglesia, F.H. Ribeiro, M. Boudart, J.E. Baumgartner, "Synthesis, characterization, and catalytic properties of clean and oxygen-modified tungsten carbides," *Catalysis Today* 15 (1992) 307–337.
- [85] E. Iglesia, F.H. Ribeiro, M. Boudart, J.E. Baumgartner, "Tungsten carbides modified by chemisorbed oxygen: A new class of bifunctional catalysts," *Catalysis Today* 15 (1992) 455–458.
- [86] S.K. Bej, C.A. Bennett, L.T. Thompson, "Acid and base characteristics of molybdenum carbide catalysts," *Applied Catalysis A: General* 250 (2003) 197–208.
- [87] D.-V.N. Vo, A.A. Adesina, "Fischer–Tropsch synthesis over alumina-supported molybdenum carbide catalyst," *Applied Catalysis A: General* 399 (2011) 221–232.
- [88] M. Chia, Y.J. Pagán-Torres, D. Hibbitts, Q. Tan, H.N. Pham, A.K. Datye, M. Neurock, R.J. Davis, J.A. Dumesic, "Selective Hydrogenolysis of Polyols and Cyclic Ethers over Bifunctional Surface Sites on Rhodium–Rhenium Catalysts," *Journal of the American Chemical Society* 133 (2011) 12675–12689.
- [89] S.T. Oyama, "Preparation and catalytic properties of transition metal carbides and nitrides," *Catalysis Today* 15 (1992) 179–200.
- [90] T. Tatsumi, A. Muramatsu, H. Tominaga, "Mechanism of CO hydrogenation to alcohols on potassium-promoted Mo/SiO₂," *Applied Catalysis* 34 (1987) 77–88.

Chapter 5.

Influence of Cobalt on Rubidium-Promoted Alumina-Supported Molybdenum Carbide Catalysts for Higher Alcohol Synthesis from Syngas

Modified with permission from Kehua Yin [+], Heng Shou [+], Daniela Ferrari, Christopher W. Jones and Robert J. Davis, “Influence of cobalt on rubidium-promoted alumina-supported molybdenum carbide catalysts for higher alcohol synthesis from syngas,” *Topics in Catalysis*, 2013. [+] Equal contribution.

Catalyst synthesis and syngas reactivity tests were performed mostly by Kehua Yin and are included here for completeness.

Abstract

The influence of Co addition on the activity and selectivity of Rb-promoted $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ catalysts in CO hydrogenation was explored. The reaction was performed in a fixed-bed reactor system operating at 573 K, 30 bar, and CO/H₂ ratio of 1. Addition of Co enhanced the production rates of hydrocarbons and higher alcohols over Rb-promoted $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ by about 60% without significantly increasing the production rate of methanol, thus shifting the alcohol selectivity toward larger molecules. The addition of Co also lessened the negative impact of CO conversion on oxygenate selectivity over Rb-promoted $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$. Results from X-ray absorption spectroscopy revealed that highly dispersed Co and Mo domains remained more reduced in the bimetallic carbide samples than the corresponding monometallic samples.

5.1 Introduction

The increasing price and limited reserve of crude oil motivate the research of alternatives to petroleum-derived fuels and chemicals. Synthesis gas, commonly referred to as syngas, is a mixture of CO and H₂ that can be derived from natural gas and coal via steam reforming and subsequently converted to liquid fuels and chemicals. Given the abundant reserves of coal and natural gas in North America, there is a motivation to convert coal and natural gas into liquid fuels and chemicals via syngas technology. In addition, renewable biomass is also a potential source of syngas through gasification [1]. Syngas-to-liquid technology has been used to produce methanol as well as diesel fuel (via Fischer–Tropsch synthesis) at an increasing rate. Despite the maturity of these syngas conversion technologies, higher alcohol synthesis from syngas also attracts intensive research interest as a promising approach to produce fuel additives and chemical feedstocks [1]. For example, although bio-ethanol has already been widely used as an additive for gasoline in the United States, an efficient chemical process to produce ethanol and higher alcohols is still desirable.

Several heterogeneous catalysts have been studied for use in higher alcohol synthesis, including Rh-based catalysts, combinations of Fischer–Tropsch catalysts and methanol synthesis catalysts (Co–Cu, for example), and Mo-based catalysts [3]. The Rh-based catalysts produce high ethanol and other C₂-oxygenates [4], but the potential large scale applications of these catalysts in industry are quite limited by the high cost and limited availability of Rh. Molybdenum metal catalysts exhibit low activity for conversion of syngas and low selectivity towards alcohols, unless the Mo is bound to S, C, O and/or P [3]. Molybdenum-based compounds are among most promising catalysts

for higher alcohol synthesis because of their high selectivity to linear alcohols, slow deactivation, and low sensitivity to CO₂ in the syngas stream [4]. Although K- and Co-promoted MoS₂ catalysts effectively produce alcohol from syngas, with alcohol selectivity higher than 75% (on a CO₂-free basis) and total alcohol yield as high as 400 mg g_{cat}⁻¹ h⁻¹ [5], addition of H₂S is required to maintain the activity and higher alcohol selectivity of MoS₂-based catalysts [6], which results in about 2 wt.% sulfur in the condensed alcohol products [7]. The presence of sulfur in the products is undesirable in light of current legislation for automotive fuels in the United States and Europe, and motivates the exploration of new sulfur-free Mo-based catalysts that produce more environmentally friendly products.

Some early transition metal carbides exhibit Pt-group like catalytic activity, which suggests they may serve as alternatives to precious metals [8]. Molybdenum carbide is known to produce light hydrocarbons from syngas, with the selectivity being shifted toward alcohols after promotion by alkali metal species [9–12], and may therefore function as a non-sulfur alternative to molybdenum sulfide catalysts for higher alcohol synthesis. In addition to greater activity, improvement in product selectivity for higher alcohols is needed, especially at high CO conversion [11].

Since addition of cobalt to alkali-metal-promoted MoS₂ catalysts enhanced their activity in higher alcohol synthesis from syngas [13], it is logical to explore the influence of Co on alkali-metal-promoted Mo₂C catalysts in the reaction. In fact, Xiang *et al.* studied the influence of Fischer–Tropsch-active elements (Fe, Co and Ni) on unsupported Mo₂C for conversion of syngas and reported that the alcohol production rate over Mo₂C catalysts was promoted by added Co and Fe, but not Ni, and Co was best promoter

among the three [14]. Lucero *et al.* reported that Ni enhanced the productivity and ratio of ethanol to methanol over Na-promoted bulk Mo₂C catalysts [15].

In this study, Co and Mo precursors were supported on α -Al₂O₃ via co-impregnation and calcination, and subsequently carburized to produce catalysts for syngas conversion. X-ray absorption spectroscopy was used to determine the atomic structure and chemical state of Co and Mo.

5.2 Materials and methods

5.2.1 Catalyst synthesis

The catalysts were prepared by incipient wetness co-impregnation onto the alumina support (Mager Scientific, >99.98 %, predominantly α -phase, $S_{\text{BET}}=27 \text{ m}^2 \text{ g}^{-1}$) with an aqueous solution of (NH₄)₆Mo₇O₂₄·6H₂O (99.98 %, Aldrich) and Co(NO₃)₂·4H₂O (99.999 %, Alfa Aesar). The samples were then dried overnight in air at 400 K, followed by calcination at 773 K in flowing air for 4 h to produce supported molybdenum and cobalt oxide. Carburization of the catalysts was accomplished by temperature-programmed reaction. This step was performed in a quartz tube reactor by heating at a rate of 5 K min⁻¹ from room temperature to 573 K and then at a rate of 1 K min⁻¹ from 573 K to 973 K in a 20 vol.% CH₄ (GTS-Welco, 99.997%) and 80 vol.% H₂ mixture (GTS-Welco, 99.999%). The catalysts were subsequently cooled to room temperature in the same carburization gas, followed by passivation in a stream of 1.03 vol.% O₂/N₂ mixture (GTS-Welco) at room temperature for 6 h before exposure to air. The catalysts were further promoted by physically mixing them with appropriate amounts of Rb₂CO₃

(99.975 %, Alfa Aesar) using a mortar and pestle. The Mo loading was kept at 5 wt.% in all the samples, with the molar ratio of Co/Mo varying from 0 to 1.0.

An alumina-supported, “carburized” Co catalyst was synthesized by the same procedure without including the Mo precursor. The molar loading of Co in this catalyst was equivalent to that of Mo in 5 wt.% Mo.

5.2.2 CO hydrogenation

The hydrogenation of CO was performed in the same fixed-bed stainless steel reactor (BTRS Jr., Autoclave Engineers) used in earlier work at nominally identical conditions of 573 K, 30 bar total pressure, and equimolar H₂ (GTS-Welco, 99.999 %) and CO (GTS-Welco, 99.997 %) [11,12]. The CO was purified by passing it through a silica trap immersed in a dry ice-acetone mixture (195 K) to remove any trace iron carbonyl before introduction to the reactor. The products were analyzed by two Hewlett-Packard 5890 series II gas chromatographs on-line. The first one was equipped with a flame ionization detector and a 50 m-long HP-1 cross-linked methyl silicone gum capillary column to monitor the formation of hydrocarbons and alcohols. The second one was equipped with a thermal conductivity detector and a 6-ft long Alltech-8700 packed column and was used to monitor the formation of CO₂.

The conversion of CO was derived from the fraction of CO that formed carbon-containing products [18]. The conversion of CO, if low, can be described as:

$$\text{Conversion (\%)} = \sum n_i M_i \times 100 / M_{\text{CO}},$$

where n_i is the number of carbon atoms in product i , M_i is the percentage of product i detected, and M_{CO} is the percentage of CO in the syngas feed.

The selectivity to product i is based on the total number of carbon atoms in the product and is therefore defined as:

$$\text{Selectivity (\%)} = n_i M_i \times 100 / \sum n_i M_i.$$

The conversion and selectivities were based on the identified products, which present more than 97% of the total peak area in GC chromatograms.

All the results reported here were obtained at the steady state after at least 60 hours of reaction. Syngas flow rate was adjusted to attain ~3% CO conversion (excluding CO₂).

5.2.3 Characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were obtained on a PANalytical X'Pert Pro MPD Diffractometer with Cu K α radiation. Each sample was scanned at a rate of 0.05° s⁻¹, over a range of 2 θ from 10° to 90°.

Elemental analyses of representative samples were performed at Galbraith Laboratories (Knoxville, TN). The loading of molybdenum and rubidium was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), while the loading of carbon was evaluated by combustion and coulometric measurement.

X-ray absorption spectroscopy (XAS) was performed at beam line X18B of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The storage ring was typically operated at 2.8 GeV with a ring current of about 300 mA. The XAS data were obtained in the transmission mode at the Mo K edge (20 keV) with a spot size of 0.5mm $\times$ 5mm and at the Co K edge (7.7 keV) with a spot size of 0.5mm $\times$ 8mm. The Mo K edge spectra and Co K edge spectra were measured at room temperature with Mo foil (0.015 mm, 99.9%, Goodfellow) and Co foil (0.004 mm, 99.9%, Goodfellow) as

energy references, respectively. The air-free handling protocol for one representative Rb-promoted Co–Mo₂C/ α -Al₂O₃ catalyst after syngas reaction has been discussed in our previous work [12]. The XAS data were processed using the Athena software [16] for background removal, post-edge normalization, and X-ray absorption near-edge structure (XANES) analysis. Standard bulk Mo₂C (Alfa Aesar, 99.5%) was used to determine the amplitude reduction factors, S_0^2 , for Mo–C and Mo–Mo. Cobalt foil (Goodfellow, 99.9%) was used to determine the value of S_0^2 for Co–Co. The interatomic distances (r), coordination numbers (CN), Debye–Waller factors ($\Delta\sigma^2$), and energy shifts (ΔE_0) were derived from the fitting results in the Artemis software package [16]. The EXAFS results were fitted in R-space using two shells (Mo–C & Mo–Mo) or one shell (Co–Co) generated theoretically using FEFF 6.0 [17].

5.3 Results and discussion

The performance of the catalysts in the syngas reaction at 573 K and 30 bar is summarized in Table 5.1. Since the selectivity for alcohols on the Rb-promoted Mo₂C catalysts was observed to decrease with CO conversion [11, 12], the results from all the catalysts in this study were compared at the same CO conversions level (about 3%, excluding CO₂). The CO conversion was adjusted by changing the syngas flow rates until the desired conversion was achieved.

Table 5.1 Reactivity of Co–Mo₂C/ α -Al₂O₃ and Rb-promoted Co–Mo₂C/ α -Al₂O₃ catalysts in CO hydrogenation

Loading of Rb (wt.%)	0					2.5				
Co/Mo (molar ratio)	0	0.2	0.4	1	∞^a	0	0.2	0.4	1	∞^a
CO conversion (%)	6.8	4.1	4.0	2.8	2.8	4.9	6.0	5.7	6.3	3.2
CO ₂ selectivity (%)	45	29	31	19	0.0	49	49	50 ^b	51 ^b	43
CO conversion (%, excluding CO ₂)	3.8	2.9	2.8	2.3	2.8	2.5	3.1	2.9	3.1	1.9
Selectivity (C %, on a CO ₂ -free basis)										
Total hydrocarbons	86	81	79	81	97	51	53	56	57	83
Methane	46	33	31	33	28	23	20	18	18	36
C2 hydrocarbons	25	22	19	14	4.3	14	13	13	13	13
C3 hydrocarbons	16	16	16	15	9.6	7.8	8.9	10	11	11
C4+ hydrocarbons	6.9	9.7	13	19	53	7.0	10	14	14	24
Total ethers	11	7.0	6.0	3.9	0.8	3.2	2.3	2.1	1.8	0.0
Total linear alcohols	3.2	12	15	15	2.4	45	45	42	41	17
Methanol	1.8	7.0	7.4	6.3	1.4	13	11	8.8	6.9	15
Ethanol	0.98	4.1	5.7	6.4	1.0	20	19	18	18	1.8
1-Propanol	0.46	1.3	2.0	2.2	0.0	9.1	9.8	8.9	8.9	0.0
1-Butanol	0.0	0.0	0.0	0.0	0.0	2.7	3.1	3.2	3.7	0.0
C5+ alcohols	0.0	0.0	0.0	0.0	0.0	1.0	1.9	2.4	4.0	0.0
Rate of CO conversion (mg gcat ⁻¹ h ⁻¹)	230	280	330	320	1300	20	57	57	55	22
Rate of production (mg gcat ⁻¹ h ⁻¹)										
CO ₂	100	82	100	59	0	18	28	28	28	9.2
Hydrocarbons	61	87	98	120	640	5.1	8.3	8.6	8.2	5.6
Ethers	11	10	10	7.5	7.0	0.4	0.4	0.4	0.3	0.0
Methanol	2.6	16	19	18	19	2.7	3.8	2.9	2.1	2.1
Higher alcohols	1.5	8.5	14	18	11	4.6	7.5	7.2	7.0	0.2

Mo loading = 5 wt.%, T = 573 K, P = 30 bar, H₂/CO = 1.

Syngas flow rate was adjusted to attain ~3% CO conversion (excluding CO₂).

Data were recorded after >50 h on stream when the catalysts reached steady state (stable activity and product distribution).

^a The molar loading of Co is equivalent to that of Mo in a 5 wt.% Mo sample.

^b The excess beyond the theoretical limit (50%) is likely due to experimental error in analysis.

According to Table 5.1, the unpromoted Co/ α -Al₂O₃ catalyst produced 97% hydrocarbons (3% alcohols) at 2.8% CO conversion, which is consistent with the well-known CO hydrogenation of Co catalysts. The unpromoted Mo₂C catalyst revealed 86% hydrocarbon selectivity (on a CO₂-free basis) and 11% ether selectivity. Since passivation

can introduce surface acid sites on Mo₂C catalysts [19], the alcohol products can undergo secondary dehydration reactions and form ethers [12]. When the loading of Co on Mo₂C/ α -Al₂O₃ increased from 0 to the molar equivalent of Mo, the rate of hydrocarbon formation on the catalysts increased from 61 mg gcat⁻¹ h⁻¹ to 120 mg gcat⁻¹ h⁻¹, while the rate of ether formation reduced from 11 mg gcat⁻¹ h⁻¹ to 7.5 mg gcat⁻¹ h⁻¹. More importantly, the rate of methanol production increased substantially from 2.6 mg gcat⁻¹ h⁻¹ to 18 mg gcat⁻¹ h⁻¹ as the rate of higher alcohol production also increased from 1.5 mg gcat⁻¹ h⁻¹ to 18 mg gcat⁻¹ h⁻¹. The presence of Co with Mo₂C did not significantly influence the total rate of CO conversion, but it decreased the CO₂ selectivity from 45% to 19%, which is consistent with the negligible water-gas-shift activity observed over the Co/ α -Al₂O₃ catalyst. It is important to note that co-existence of Co and Mo decreased the rate of hydrocarbon production by more than 82% from the Co/ α -Al₂O₃ catalyst, which had the same amount of Co. These results indicate a clear interaction between the supported Mo and Co species.

The addition of 2.5 wt.% Rb promoter to 5 wt.% Mo₂C/ α -Al₂O₃ substantially inhibited the production rate of hydrocarbons by an order of magnitude and shifted the oxygenate composition from ethers to predominantly alcohols. Similarly, over the Co-Mo₂C/ α -Al₂O₃ catalysts, the addition of Rb promoter also significantly reduced the production rates of hydrocarbons, ethers and methanol by about an order of magnitude, while decreasing the production rate of higher alcohols by only 30%-60%. The lower overall activity of the Rb-promoted catalysts is consistent with the site-blockage mechanism of alkali metal promoters on Mo-based catalysts for higher alcohol synthesis suggested by Lee *et al.* [20, 21], which has been supported by prior works on Rb-

promoted $\text{Mo}_2\text{C}/\text{MgO}$ [11], Rb-promoted $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ [12] and K-promoted bulk Mo_2C catalysts [9]. The reduced formation of ethers is likely the result of the basic Rb promoter neutralizing the surface acid sites on Mo_2C [19] that may catalyze the dehydration of alcohols. Although the rate of CO_2 production was reduced over the Rb-promoted $\text{Co-Mo}_2\text{C}$, the overall selectivity to CO_2 was about 50%, which is the stoichiometric maximum under our conditions. The $\text{Co}/\alpha\text{-Al}_2\text{O}_3$ catalyst revealed very little activity for higher alcohol synthesis after the addition of Rb, which suggests that the formation of higher alcohols on Rb-promoted $\text{Co-Mo}_2\text{C}$ catalysts is primarily associated with the molybdenum carbide species.

Figure 5.1 Changes in the rate of production of hydrocarbons, methanol and higher alcohols with Co/Mo ratio over 2.5 wt.% Rb-promoted $\text{Co-Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ catalysts in CO hydrogenation at 573 K and 30 bar

The change of production rates with Co/Mo ratio over Rb-promoted catalysts is plotted in Figure 5.1. When the Co/Mo ratio increased from 0 to 0.2, the production rates of hydrocarbons, methanol and higher alcohols both increased by about 50%. Increasing

the Co/Mo ratio from 0.2 to 1 left the production rates of hydrocarbons and higher alcohols almost unchanged, whereas that of methanol decreased to a level slightly less than that before Co promotion. As a consequence, the addition of Co ultimately promoted the formation of higher alcohols over methanol, which is consistent with the promotional effects of Co on K-promoted bulk Mo₂C catalysts [22] and that of Ni on Na-promoted bulk Mo₂C catalysts [15]. Similar trends have been observed on alkali-metal-promoted supported MoS₂ catalysts as well [23, 24]. A density functional theory (DFT) study showed that Co atoms can be incorporated into the S-edge sites of MoS₂, which may generate active Co–Mo–S surface species and increase the activity of the catalyst [25]. Those results are not completely analogous to Mo₂C-based catalysts since Mo₂C is a more metal-like compound and MoS₂ has a covalent layered structure.

The chain growth probability (α) [26] of the linear hydrocarbons produced on these catalysts was calculated from the following expression:

$$X_n / n = (1 - \alpha)^2 \alpha^{n-1},$$

where X_n is the molar fraction of carbon atoms in the hydrocarbon (or alcohol) molecules containing n carbon atoms among all the hydrocarbons considered. The expression above can be transformed to:

$$\log(X_n / n) = (n - 1) \log \alpha + 2 \log(1 - \alpha).$$

Appropriate plots associated with the hydrocarbons and alcohols produced on the different catalysts are presented in Figure 5.2, and the corresponding values of α and R^2 derived from linear fits are listed in Table 5.2.

Figure 5.2 Evaluation of chain growth probability of linear hydrocarbons (paraffins and olefins combined, filled squares) and linear alcohols (open circles) over Co–Mo₂C catalysts with various Co/Mo ratios, without Rb promoter (a-e) and with Rb promoter (f-j).

The chain growth probability of both hydrocarbons and alcohols increased with both the Co/Mo ratio and the addition of Rb promoter (Table 5.2). On Rb-promoted Mo₂C (Figure 5.2f) and Co–Mo₂C (Figure 5.2g-i) catalysts, the R^2 values for alcohols never exceeded 0.97 (Table 5.2), and were always less than the 0.99+ values for hydrocarbons (Table 5.2). The poor linear fit corresponding to the product distribution of the alcohols produced over the Rb-promoted catalysts results primarily from a low rate of methanol production and suggests that the synthesis of alcohols may not be dictated solely by the standard chain growth mechanism described by Anderson–Schulz–Flory (ASF) distribution. Secondary reactions such as coupling, dehydration, and homologation may account for the lower methanol selectivity than that expected from the ASF distribution.

Table 5.2 Chain growth probability (α) and R^2 derived from linear fits

Sample	Hydrocarbons ^a		Alcohols ^b	
	α	R^2	α	R^2
Co/Mo = 0	0.31	0.988	0.29	0.999
Co/Mo = 0.2	0.33	0.991	0.25	0.996
Co/Mo = 0.4	0.40	0.989	0.30	0.986
Co/Mo = 1.0	0.46	0.977	0.34	0.956
Co/Mo = ∞	0.65	0.700	—	—
Co/Mo = 0, Rb-promoted	0.37	0.996	0.32	0.962
Co/Mo = 0.2, Rb-promoted	0.43	0.993	0.36	0.973
Co/Mo = 0.4, Rb-promoted	0.43	0.996	0.40	0.963
Co/Mo = 1.0, Rb-promoted	0.47	0.991	0.45	0.962
Co/Mo = ∞ , Rb-promoted	0.38	0.982	—	—

^a linear paraffins and olefins combined

^b linear alcohols

To explore the effect of Rb loading on catalyst performance, a sample with 5 wt.% Rb was also prepared and evaluated. As summarized in Table 5.3, the alcohol selectivity of the catalyst with 5 wt.% Rb was similar to that with 2.5 wt.% Rb, although the overall activity was lower. These results are consistent with the additional Rb blocking some of the active sites on the catalysts as suggested by Lee *et al.* [20, 21].

Table 5.3 Influence of Rb loading on the reactivity of Co–Mo₂C/ α -Al₂O₃ (molar ratio of Co/Mo = 1) in CO hydrogenation

Rb loading (%)	2.5	5.0
CO conversion (%)	6.3	4.7
CO ₂ selectivity (%)	51 ^a	53 ^a
CO conversion (% , excluding CO ₂)	3.1	2.2
Selectivity (C % , on a CO ₂ -free basis)		
Total hydrocarbons	57	58
Methane	18	20
C2 hydrocarbons	13	14
C3 hydrocarbons	11	9.8
C4+ hydrocarbons	14	14
Total ethers	1.8	1.3
Total alcohols	41	40
Methanol	6.9	7.3
Ethanol	18	17
1-Propanol	8.9	9.0
1-Butanol	3.7	3.4
C5+ linear alcohols	4.0	4.0
Rate of CO conversion (mg gcat ⁻¹ h ⁻¹)	55	40
Rate of production (mg gcat ⁻¹ h ⁻¹)		
CO ₂	28	21
Hydrocarbons	8.2	5.8
Ethers	0.3	0.2
Methanol	2.1	1.5
Higher alcohols	7.0	4.4

Mo loading = 5 wt.%, T = 573 K, P = 30 bar, H₂/CO = 1. Syngas flow rate was adjusted to attain ~3% CO conversion (excluding CO₂). Data were recorded after >60 h on stream when the catalysts reached steady state (stable activity and product distribution).

^a The excess beyond the theoretical limit (50%) is likely due to experimental error in analysis.

Figure 5.3 compares the alcohol selectivity over Rb-promoted $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$, with and without Co, as a function of CO conversion. As the CO conversion increased from 5 to 20% over Rb-promoted $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$, the selectivity to alcohols decreased significantly. In contrast, the alcohol selectivity was less impacted by the CO conversion when Co was added to the catalyst.

Figure 5.3 Change of alcohol selectivity with CO conversion over Rb-promoted $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ (Co/Mo = 0) and Rb-promoted $\text{Co-Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ (Co/Mo = 1) catalysts. The loading of Mo is 5 wt.%. The loading of Rb is 2.5 wt.%. Reaction conditions: 573 K, 30 bar syngas, $\text{H}_2/\text{CO} = 1$.

The X-ray diffraction patterns of the catalysts are provided in Figure 5.4. None of the Co-containing catalysts (Figure 5.4c-f) revealed XRD peaks corresponding to any Co species, suggesting that alumina-supported Co species were highly dispersed. No diffraction peaks associated with Mo_2C were present in the XRD pattern of $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ (Figure 5.4b), which is consistent with our previous work that identified ~ 1 nm Mo_2C particles on $\alpha\text{-Al}_2\text{O}_3$ [12]. When Co was added to the catalyst, the $\{101\}$ reflection

of hexagonal Mo_2C appeared at 39.4° and became more intense with Co loading (Figure 5.4c-e). Liang *et al.* used carbothermal reduction with dihydrogen to synthesize Mo-based bimetallic carbides on activated carbon support [27], and they reported that addition of a second metal component (Co, Ni) to Mo decreased the formation temperature of the carbide, presumably because the second metal facilitated the formation of CH_x species that can accelerate the carburization process. A similar promotional effect of Co on the carburization of Mo may also occur in our synthesis. Thus, the high temperature used in our catalyst carburization may have exceeded the minimum temperature necessary for carburizing the Co–Mo mixed oxide precursor and may have caused growth of Mo_2C domain.

Figure 5.4 X-ray diffraction patterns of (a) $\alpha\text{-Al}_2\text{O}_3$ (Mager Scientific); (b) $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$; (c) $\text{Co-Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$, $\text{Co/Mo} = 0.2$; (d) $\text{Co-Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$, $\text{Co/Mo} = 0.4$; (e) $\text{Co-Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$, $\text{Co/Mo} = 1$; (f) $\text{Co}/\alpha\text{-Al}_2\text{O}_3$. Patterns are offset for clarity.

Figure 5.5 Mo *K* edge XANES of (a) bulk Mo₂C and alumina-supported Co–Mo₂C species with various molar ratios of Co/Mo; (b) a comparison between Co–Mo₂C/ α -Al₂O₃ (Co/Mo = 1.0) and Rb-promoted Co–Mo₂C/ α -Al₂O₃ (Co/Mo = 1.0) after 120 h syngas reaction.

^a Purged in Ar after syngas reaction, air-free handling for sample preparation.

The results from elemental analysis revealed a $\text{MoC}_{0.525}$ stoichiometry for the supported molybdenum carbide sample, which is close to that of bulk Mo_2C . The analysis of a carburized Co–Mo/ α - Al_2O_3 sample (Co/Mo = 1) revealed a stoichiometry of $\text{MoCo}_{0.96}\text{C}_{1.05}$, indicating excess carbon needed for stoichiometric Mo_2C . Although one might propose the excess carbon to be associated with a highly-dispersed Co carbide phase, results from X-ray absorption spectroscopy discussed below were not consistent with that hypothesis.

The X-ray absorption near edge structure (XANES) of the catalyst samples at the Mo *K* edge is summarized in Figure 5.5. The Mo species in $\text{Mo}_2\text{C}/\alpha$ - Al_2O_3 (Co/Mo = 0, Figure 5.5a) was more oxidized than the bulk Mo_2C standard, which is due to the high affinity of surface Mo for oxygen and is consistent with our previous observations on passivated Mo_2C supported on MgO [11] and α - Al_2O_3 [12]. For a carbide sample with relatively high loading of Co, the Mo species in a Co– $\text{Mo}_2\text{C}/\alpha$ - Al_2O_3 sample with Co/Mo = 1.0 (Figure 5.5a) was more reduced than $\text{Mo}_2\text{C}/\alpha$ - Al_2O_3 , but was still more oxidized than bulk Mo_2C . Analysis of a sample with air-free handling after 120 h syngas reaction did not significantly alter the edge position of a 2.5 wt.% Rb-promoted Co– $\text{Mo}_2\text{C}/\alpha$ - Al_2O_3 sample (Co/Mo = 1.0, Figure 5.5b) compared to an unreacted Co– $\text{Mo}_2\text{C}/\alpha$ - Al_2O_3 catalyst analyzed in air.

The Fourier transforms (FT) of k^3 -weighted extended X-ray absorption fine structure (EXAFS) at Mo *K* edge are shown in Figure 5.6 and the structural parameters derived from the corresponding curve fits are presented in Table 5.4. Example curve fits associated with the results in Table 5.4 are compared to the experimental EXAFS for Mo *K* edge EXAFS of Co– $\text{Mo}_2\text{C}/\alpha$ - Al_2O_3 (Co/Mo = 1.0) in Figure 5.7. All of the *R*-factors of

the fits are much less than 0.1, indicating good agreements between the experimental EXAFS and fits. In the $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ sample (Figure 5.6a), the supported Mo_2C had a Mo–Mo coordination number as low as 2.9 (Table 5.4), which is consistent with the highly-dispersed Mo_2C clusters reported on H-ZSM-5 zeolite [28], $\alpha\text{-Al}_2\text{O}_3$ [12], $\gamma\text{-Al}_2\text{O}_3$ [29] and mixed-phase Al_2O_3 , with Mo–Mo coordination numbers derived from EXAFS of 2.6, 2.5, 4 and 3.2, respectively. The Mo–Mo coordination number increased with Co/Mo ratio from 2.9 in $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ to 6.9 (Table 5.4) in the Co– $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ sample with a Co/Mo ratio of 1.0 (Figure 5.6c), which is consistent with the growth of Mo_2C domain suggested by EXAFS (Figure 5.6) and XRD (Figure 5.4). The growth of Mo_2C domains decreased the percentage of surface Mo atoms that can be partially oxidized by O_2 , resulting in a lower average oxidation state of Mo, which is in good agreement with the observation in Mo *K* edge XANES (Figure 5.5a). After 3 days of syngas reaction, the coordination number of Mo–Mo in a Rb-promoted Co– $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ sample (Co/Mo = 1.0) increased slightly from 6.9 to 7.7, which suggests that sintering of Mo_2C domain during reaction was relatively minor. However, no clear evidence of Mo–Co interactions was found in the supported Co– Mo_2C samples (Figure 5.6b-c). Efforts were made to fit the second shell in Figure 5.6 as Mo–Co, but none of the fits were physically realistic ($|\Delta E_0| > 30$ eV, $\Delta\sigma^2 > 0.03$ or $\Delta\sigma^2 < 0$).

Figure 5.6 Fourier transform (not corrected for phase shifts) of k^3 -weighted Mo K edge EXAFS: (a) $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$; (b) $\text{Co-Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$, $\text{Co/Mo} = 0.4$; (c) $\text{Co-Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$, $\text{Co/Mo} = 1.0$; (d) bulk Mo_2C . Spectra are offset for clarity.

Table 5.4 Results from the Analysis of Mo K edge EXAFS

Sample	Shell	CN	r (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	ΔE_0 (eV)	R - factor
Bulk Mo_2C	Mo-C	3 ^a	2.12 ± 0.02	1.2 ± 2.7	0.8 ± 5.7	0.009
	Mo-Mo	12 ^a	2.97 ± 0.01	5.4 ± 0.6	-7.6 ± 1.2	
$\text{Co/Mo} = 0^b$	Mo-C	2.3 ± 1.0	2.09 ± 0.02	0.9 ± 2.2	-12 ± 6	0.065
	Mo-Mo	2.9 ± 1.2	2.98 ± 0.02	7.4 ± 2.3	-8.4 ± 3.8	
$\text{Co/Mo} = 0.4^b$	Mo-C	2.0 ± 1.1	2.10 ± 0.03	0.5 ± 3.1	-12 ± 6	0.037
	Mo-Mo	5.2 ± 1.4	2.98 ± 0.01	6.5 ± 1.4	-9.1 ± 2.6	
$\text{Co/Mo} = 1^b$	Mo-C	2.0 ± 1.0	2.12 ± 0.03	1.2 ± 2.9	-2.5 ± 6.7	0.014
	Mo-Mo	6.9 ± 1.1	2.97 ± 0.01	5.6 ± 0.8	-8.7 ± 1.6	
$\text{Co/Mo} = 1^{b,c}$, w/ Rb, AF after rxn	Mo-C	3.6 ± 1.3	2.12 ± 0.02	1.0 ± 2.2	0.5 ± 4.9	0.031
	Mo-Mo	7.7 ± 1.9	2.97 ± 0.01	7.0 ± 1.3	-8.4 ± 2.4	

Fitting parameters: Fourier transform range, Δk , $2\text{--}13 \text{ Å}^{-1}$; fitting range, ΔR , $1\text{--}3 \text{ Å}$; weighting, k^3 ; $S_0^2(\text{Mo-C}) = 0.73$, $S_0^2(\text{Mo-Mo}) = 0.77$

^a Value was assigned in curving-fitting on the basis of standard structure.

^b The ratio of Co/Mo is mole-based.

^c With Rb promoter, purged in Ar after syngas reaction, air-free handling for sample preparation.

Figure 5.7 Comparison of the curve fit to experimental Mo *K* edge EXAFS of Co–Mo₂C/ α -Al₂O₃ (Co/Mo = 1.0): (a) k^3 -Weighted Mo *K* edge EXAFS (solid line) and the result from curve fit (circles); (b) magnitude (solid line) and the imaginary part (dashed line) of the Fourier transform of EXAFS compared with the result from the curve fit (circles).

The XANES spectra at the Co *K* edge of bulk Co standards and alumina-supported Co samples are summarized in Figure 5.8. The FT of k^3 -weighted Co *K* edge EXAFS are shown in Figure 5.9 and the structural parameters derived from the corresponding curve fits are presented in Table 5.5. Example curve fits associated with the results in Table 5.5 are compared to the experimental EXAFS for Mo *K* edge EXAFS

of Co–Mo₂C/ α -Al₂O₃ (Co/Mo = 1.0) in Figure 5.9. All of the *R*-factors of the fits are much less than 0.1, indicating good agreements between the experimental EXAFS and fits. The XANES spectra suggest that the Co species in “carburized” Co/ α -Al₂O₃ (Co/Mo = ∞ , Figure 5.8b) was severely oxidized after exposure to air, which is even more oxidized than the CoO standard (Figure 5.8a). The FT of Co *K* edge EXAFS showed that alumina-supported “carburized” Co (Figure 5.9a) possessed a similar structure to bulk Co₃O₄ (Figure 5.9b). These results are in good agreement with the high dispersion of Co species suggested by the corresponding XRD pattern (Figure 5.4f), given that the reduction of silica-supported Co₃O₄ is difficult when the diameter of the cluster is below 6 nm [31]. Strong interactions of Co oxide nanoparticles with a silica support were thought to inhibit their reduction [31]. However, the bimetallic samples with a Co/Mo ratio of 0.4 or 1.0 exhibited a lower white line intensity and a lower edge energy in XANES (Figure 5.8b) compared to the supported Co sample. The peak positions in the Fourier transforms of the EXAFS (Figure 5.9d-e) associated with the Co–Mo₂C/ α -Al₂O₃ samples suggest that the Co likely remained in a metallic form when Mo was present. The fits of the EXAFS gave Co–Co coordination numbers in Co–Mo₂C/ α -Al₂O₃ less than 8 (Table 5.5), which corresponds to > 75% dispersion of Co [32], or particles with an average diameter less than 1.4 nm. Clearly, the supported Mo carbide species assisted the Co clusters to form reduced particles. However, no clear evidence of Co–Mo interactions was found in the Co EXAFS of the supported Co–Mo₂C samples (Figure 5.9d-e). Efforts were made to fit the large peak in Figure 5.9d-e as Co–Mo or a mixture of Co–Mo and Co–Co, but none of the fits was realistic ($|\Delta E_0| > 30$ eV or CN < 0). A phase separation involving Co and Mo₂C has been also reported by Xiao *et al.* who used a similar

carburization method from a Co–Mo mixed oxide precursor [33]. Moreover, no evidence for a Co carbide species was revealed by EXAFS of the supported Co–Mo₂C samples, since there was no apparent Co–C interaction present in Figure 5.9d-e and the Co–Co distance in Co₂C (2.62 Å, [34]) is much longer than that in Co metal (observed in this work).

Figure 5.8 Co K edge XANES of (a) Co reference standards; (b) Co–Mo₂C/α-Al₂O₃ catalysts with various molar ratios of Co/Mo. The loading of Mo is 5 wt.%. The molar loading of Co in the sample “Co/Mo = ∞” (Co supported on α-Al₂O₃) is equivalent to that of Mo in a 5 wt.% Mo sample.

Figure 5.9 FT (not phase-shift-corrected) of k^3 -weighted Co K edge EXAFS: (a) 3.1 wt.% Co/ α -Al₂O₃; (b) Co₃O₄; (c) CoO; (d) Co-Mo₂C/ α -Al₂O₃, Co/Mo = 0.4; (e) Co-Mo₂C/ α -Al₂O₃, Co/Mo = 1.0; (f) Co foil. Spectra are offset for clarity. The loading of Mo is 5 wt.%. The Co/Mo ratio is mole-based. The molar loading of Co corresponding to 3.1 wt.% Co is equivalent to that of Mo in a 5 wt.% Mo sample.

Table 5.5 Results from the Analysis of Co K edge EXAFS

Sample	Shell	CN	r (Å)	$\Delta\sigma^2$ (10^{-3} Å ²)	ΔE_0 (eV)	R -factor
Co foil	Co-Co	12 ^a	2.49 ± 0.00	5.9 ± 0.4	5.5 ± 0.4	0.004
Co/Mo = 0.4	Co-Co	5.8 ± 1.4	2.50 ± 0.02	5.3 ± 2.1	-4.7 ± 2.5	0.086
Co/Mo = 1	Co-Co	7.0 ± 1.2	2.50 ± 0.01	5.8 ± 1.4	-5.3 ± 1.7	0.042

Fitting parameters: Fourier transform range, Δk , 2–12 Å⁻¹; fitting range, ΔR , 1–3 Å; weighting, k^1 & k^3 ; S_0^2 (Co-Co) = 0.69.

^a Value was assigned in curving-fitting on the basis of standard structure.

Figure 5.10 Comparison of the curve fit to experimental Co *K* edge EXAFS of Co–Mo₂C/ α -Al₂O₃ (Co/Mo = 1.0): (a) k^3 -Weighted Mo *K* edge EXAFS (solid line) and the result from curve fit (circles); (b) magnitude (solid line) and the imaginary part (dashed line) of the Fourier transform of EXAFS compared with the result from the curve fit (circles).

The evidence for metallic Co co-existing with Mo₂C, as well as lack of a Co–C interaction in Co EXAFS, seems to contradict the excessive carbon found in the MoCo_{0.96}C_{1.05} sample revealed by elemental analysis. However, the extra carbon may result from the residual CH_x species produced during the carburization of Mo assisted by

Co [27], or by the adsorption of atmospheric CO₂ on a partially oxidized Co surface (Figure 5.8b), forming a carbonate surface species.

It has been shown that Ru, Rh, Re and Pt, even in very small amounts (0.05-0.1 wt.%), are able to enhance the reducibility of Co catalysts on various supports (Al₂O₃, SiO₂, TiO₂, ZrO₂, etc.) for Fischer–Tropsch synthesis [35–43]. This improvement in Co reducibility is not likely the result of differences in the Co particle size, as observed by Das *et al.* on Co–Re/Al₂O₃ catalysts [44].

In alumina-supported Pt–Co catalysts, Jacobs *et al.* [45] showed that Pt may locate on the edge of the Co metal clusters without forming Pt–Pt aggregates. The same model may also be applied to the Pt–Co catalysts supported on Al₂O₃ and on NaY zeolite reported by Guzzi *et al.* [46]. Even if there is phase segregation of components in a bimetallic catalyst, a hydrogen spillover mechanism can still account for the influence of Pt, Rh or Ru on the reducibility of Co catalysts [47,48]. In this mechanism, the oxide precursor of Pt, Rh or Ru is reduced to the metallic state at a much lower temperature than Co oxide. Once the non-cobalt metal is reduced, it facilitates the dissociation of H₂ and the spillover of H atoms, thus enhancing the reduction of Co oxide. It has also been shown that for a zeolite-supported Pt–Co catalyst, once the metallic Co was formed, it remained metallic in air with co-existing Pt [46]. However, the Co in analogous alumina-supported bimetallic Pt–Co particles was readily oxidized in air [46]. Since our catalysts are supported on alumina, we do not have a good explanation at this time for the stability of metallic Co in our Co–Mo₂C/ α -Al₂O₃ catalysts in air.

According to the similarity in reactivity between Mo₂C and certain Pt-group metals [49], the enhancement of Co reducibility demonstrated with Co–M catalysts (M =

Ru, Rh or Pt) may be also applicable to the Co–Mo₂C/ α -Al₂O₃ catalysts in this study. Since we have not observed a direct interaction between Co and Mo atoms by X-ray absorption spectroscopy, an interaction may exist at the boundary between a Co domain and a Mo₂C domain. The lack of an obvious Co–Mo interaction in EXAFS likely results from the small fraction of atoms at the interface between the phases. Nevertheless, according to the reactivity results (Table 5.1), a Co–Mo₂C/ α -Al₂O₃ catalyst as prepared in this study cannot be treated as a simple superposition of Co/ α -Al₂O₃ and Mo₂C/ α -Al₂O₃, which also suggests a molecular level interaction between Co and Mo species.

5.4 Conclusions

Bimetallic Co-Mo₂C/ α -Al₂O₃ catalysts were prepared by co-impregnating the Co and Mo precursors, followed by calcination, carburization and passivation. The addition of Co to Rb-promoted Mo₂C/ α -Al₂O₃ enhanced the overall reactivity of Mo₂C catalysts, promoted the formation of higher alcohols over methanol, and effectively reduced the loss of alcohol selectivity at high CO conversion. The results from X-ray absorption spectroscopy revealed that the Co metal and Mo carbide domains on alumina, although very highly dispersed, were capable to keep each other more reduced than their corresponding monometallic samples. Although direct interactions between Co and Mo were not observed spectroscopically, the reactivity patterns reported here clearly suggest a molecular-level interaction between Co and Mo.

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References of Chapter 5

- [1] G.W. Huber, S. Iborra, A. Corma, "Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering," *Chemical Reviews* 106 (2006) 4044–4098.
- [2] K. Fang, D. Li, M. Lin, M. Xiang, W. Wei, Y. Sun, "A short review of heterogeneous catalytic process for mixed alcohols synthesis via syngas," *Catalysis Today* 147 (2009) 133–138.
- [3] S. Zaman, K.J. Smith, "A review of molybdenum catalysts for synthesis gas conversion to alcohols: Catalysts, mechanisms and kinetics," *Catalysis Reviews: Science and Engineering* 54 (2012) 41–132.
- [4] V. Subramani, S.K. Gangwal, A review of recent literature to search for an efficient catalytic process for the conversion of syngas to ethanol, *Energy & Fuels* 22 (2008) 814–839.
- [5] R.R. Stevens, Process for producing alcohols from synthesis gas, U.S. Patent 4752622, 1988, to The Dow Chemical Company.
- [6] M.M. Conway, C.B. Murchison, R.R. Stevens, "Method for adjusting methanol to higher alcohol ratios," U.S. Patent 4675344, 1987 to The Dow Chemical Company.
- [7] J.M. Christensen, P.M. Mortensen, R. Trane, P.A. Jensen, A.D. Jensen, "Effects of H₂S and process conditions in the synthesis of mixed alcohols from syngas over alkali promoted cobalt-molybdenum sulfide," *Applied Catalysis A: General* 366 (2009) 29–43.

- [8] J.G. Chen, Carbide and nitride overlayers on early transition metal surfaces: Preparation, characterization, and reactivities, *Chemical Reviews* 96 (1996) 1477–1498.
- [9] H.C. Woo, K.Y. Park, Y.G. Kim, I.S. Nam, J.S. Chung, J.S. Lee, “Mixed alcohol synthesis from carbon monoxide and dihydrogen over potassium-promoted molybdenum carbide catalysts,” *Applied Catalysis* 75 (1991) 267–280.
- [10] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, “Performances of mixed alcohols synthesis over potassium promoted molybdenum carbides,” *Fuel* 85 (2006) 2662–2665.
- [11] H. Shou, R.J. Davis, “Reactivity and *in situ* X-ray absorption spectroscopy of Rb-promoted Mo₂C/MgO catalysts for higher alcohol synthesis,” *Journal of Catalysis* 282 (2011) 83–93.
- [12] H. Shou, D. Ferrari, D.G. Barton, C.W. Jones, R.J. Davis, “Influence of passivation on the reactivity of unpromoted and Rb-promoted Mo₂C nanoparticles for CO hydrogenation,” *ACS Catalysis* 2 (2012) 1408–1416.
- [13] Z. Li, Y. Fu, J. Bao, M. Jiang, T. Hu, T. Liu, Y. Xie, “Effect of cobalt promoter on Co–Mo–K/C catalysts used for mixed alcohol synthesis,” *Applied Catalysis A: General* 220 (2001) 21–30.
- [14] M. Xiang, D. Li, H. Xiao, J. Zhang, H. Qi, W. Li, B. Zhong, Y. Sun, “Synthesis of higher alcohols from syngas over Fischer–Tropsch elements modified K/β-Mo₂C catalysts,” *Fuel* 87 (2008) 599–603.
- [15] A.J. Lucero, V.K. Sethi, W.H. Tuminello, “Process and catalyst for production of mixed alcohols from synthesis gas,” U.S. Patent 8048933, 2011, to University of Wyoming Research Corporation.
- [16] B. Ravel, M. Newville, “ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT,” *Journal of Synchrotron Radiation* 12 (2005) 537–541.
- [17] S.I. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, M.J. Eller, “Multiple-scattering calculations of x-ray-absorption spectra,” *Physical Review B* 52 (1995) 2995–3009.
- [18] R. Burch, M.I. Petch, “Investigation of the synthesis of oxygenates from carbon monoxide/hydrogen mixtures on supported rhodium catalysts,” *Applied Catalysis A: General* 88 (1992) 39–60.
- [19] S.K. Bej, C.A. Bennett, L.T. Thompson, “Acid and base characteristics of molybdenum carbide catalysts,” *Applied Catalysis A: General* 250 (2003) 197–208.

- [20] J.S. Lee, S. Kim, K.H. Lee, I.-S. Nam, J.S. Chung, Y.G. Kim, H.C. Woo, "Role of alkali promoters in K/MoS₂ catalysts for CO-H₂ reactions," *Applied Catalysis A: General* 110 (1994) 11–25.
- [21] J.S. Lee, S. Kim, Y.G. Kim, "Electronic and geometric effects of alkali promoters in CO hydrogenation over K/Mo₂C catalysts," *Topics in Catalysis* 2 (1995) 127–140.
- [22] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "Synthesis of higher alcohols from syngas over K/Co/ β -Mo₂C catalysts," *Catalysis Communications* 8 (2007) 503–507.
- [23] V.R. Surisetty, I. Eswaramoorthi, A.K. Dalai, "Comparative study of higher alcohols synthesis over alumina and activated carbon-supported alkali-modified MoS₂ catalysts promoted with group VIII metals," *Fuel* 96 (2012) 77–84.
- [24] V.R. Surisetty, A.K. Dalai, J. Kozinski, "Synthesis of higher alcohols from synthesis gas over Co-promoted alkali-modified MoS₂ catalysts supported on MWCNTs," *Applied Catalysis A: General* 385 (2010) 153–162.
- [25] M. Sun, A.E. Nelson, J. Adjaye, "On the incorporation of nickel and cobalt into MoS₂-edge structures," *Journal of Catalysis* 226 (2004) 32–40.
- [26] P.L. Spath, D.C. Dayton, Preliminary Screening — Technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas, U.S. Department of Energy Report, Oak Ridge, TN, 2003.
- [27] C. Liang, W. Ma, Z. Feng, C. Li, "Activated carbon supported bimetallic CoMo carbides synthesized by carbothermal hydrogen reduction," *Carbon* 41 (2003) 1833–1839.
- [28] W. Ding, S. Li, G.D. Meitzner, E. Iglesia, "Methane conversion to aromatics on Mo/H-ZSM5: Structure of molybdenum species in working catalysts," *The Journal Physical Chemistry B* 105 (2001) 506–513.
- [29] J.S. Lee, M. Boudart, "In situ carburization of metallic molybdenum during catalytic reactions of carbon-containing gases," *Catalysis Letter* 20 (1993) 97–106.
- [30] H. Shou, L. Li, D. Ferrari, D.S. Sholl, R.J. Davis, "Use of infrared spectroscopy and density functional theory to study the influence of rubidium on alumina-supported molybdenum carbide catalyst for higher alcohol synthesis from syngas," *Journal of Catalysis* 299 (2013) 150–161.
- [31] A.Y. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson, P. Chaumette, "Reducibility of cobalt species in silica-supported Fischer–Tropsch catalysts," *Journal of Catalysis* 168 (1997) 16–25.

- [32] A. Jentys, "Estimation of mean size and shape of small metal particles by EXAFS," *Physical Chemistry Chemical Physics* 1 (1999) 4059–4063.
- [33] T. Xiao, A.P.E. York, K.S. Coleman, J.B. Claridge, J. Sloan, J. Charnock, M.L.H. Green, "Effect of carburising agent on the structure of molybdenum carbides," *Journal of Materials Chemistry* 11 (2001) 3094–3098.
- [34] Y.-H. Zhao, H.-Y. Su, K. Sun, J. Liu, W.-X. Li, "Structural and electronic properties of cobalt carbide Co_2C and its surface stability: Density functional theory study," *Surface Science* 606 (2012) 598–604.
- [35] K. Takeuchi, T. Matsukaki, H. Arakawa, Y. Sugi, "Synthesis of ethanol from syngas over Co-Re-Sr/ SiO_2 catalysts," *Applied Catalysis* 18 (1985) 325–334.
- [36] K. Takeuchi, T. Matsuzaki, H. Arakawa, T. Hanaoka, Y. Sugi, "Synthesis of C2-oxygenates from syngas over cobalt catalysts promoted by ruthenium and alkaline earths," *Applied Catalysis* 48 (1989) 149–157.
- [37] S. Vada, A. Hoff, E. Ådnanes, D. Schanke, A. Holmen, "Fischer–Tropsch synthesis on supported cobalt catalysts promoted by platinum and rhenium," *Topics in Catalysis* 2 (1995) 155–162.
- [38] A. Feller, M. Claeys, E. van Steen, "Cobalt cluster effects in zirconium promoted Co/ SiO_2 Fischer–Tropsch catalysts," *Journal of Catalysis* 185 (1999) 120–130.
- [39] C.L. Bianchi, "TPR and XPS Investigations of Co/ Al_2O_3 Catalysts Promoted with Ru, Ir and Pt," *Catalysis Letters* 76 (2001) 155–159.
- [40] A. Martínez, C. López, F. Márquez, I. Díaz, "Fischer–Tropsch synthesis of hydrocarbons over mesoporous Co/SBA-15 catalysts: The influence of metal loading, cobalt precursor, and promoters," *Journal of Catalysis* 220 (2003) 486–499.
- [41] C.J. Bertole, C.A. Mims, G. Kiss, "Support and rhenium effects on the intrinsic site activity and methane selectivity of cobalt Fischer–Tropsch catalysts," *Journal of Catalysis* 221 (2004) 191–203.
- [42] W. Chu, P.A. Chernavskii, L. Gengembre, G.A. Pankina, P. Fongarland, A.Y. Khodakov, "Cobalt species in promoted cobalt alumina-supported Fischer–Tropsch catalysts," *Journal of Catalysis* 252 (2007) 215–230.
- [43] J. Hong, P.A. Chernavskii, A.Y. Khodakov, W. Chu, "Effect of promotion with ruthenium on the structure and catalytic performance of mesoporous silica (smaller and larger pore) supported cobalt Fischer–Tropsch catalysts," *Catalysis Today* 140 (2009) 135–141.

- [44] T.K. Das, G. Jacobs, P.M. Patterson, W.A. Conner, J. Li, B.H. Davis, "Fischer–Tropsch synthesis: Characterization and catalytic properties of rhenium promoted cobalt alumina catalysts," *Fuel* 82 (2003) 805–815.
- [45] G. Jacobs, J.A. Chaney, P.M. Patterson, T.K. Das, J.C. Maillot, B.H. Davis, "Fischer–Tropsch synthesis: Study of the promotion of Pt on the reduction property of Co/Al₂O₃ catalysts by *in situ* EXAFS of Co *K* and Pt *L*_{III} edges and XPS," *Journal of Synchrotron Radiation* 11 (2004) 414–422.
- [46] L. Guzzi, D. Bazin, I. Kovács, L. Borkó, Z. Schay, J. Lynch, P. Parent, C. Lafon, G. Stefler, Zs. Koppány, I. Sajó, "Structure of Pt–Co/Al₂O₃ and Pt–Co/NaY bimetallic catalysts: Characterization by *in situ* EXAFS, TPR, XPS and by activity in CO (carbon monoxide) hydrogenation," *Topics in Catalysis* 20 (2002) 129–139.
- [47] A.M. Hilmen, D. Schanke, A. Holmen, "TPR study of the mechanism of rhenium promotion of alumina-supported cobalt Fischer–Tropsch catalysts, *Catalysis Letters* 38 (1996) 143–147.
- [48] F. Diehl, A.Y. Khodakov, "Promotion of Cobalt Fischer–Tropsch catalysts with noble metals: A review," *Oil & Gas Science and Technology - Revue de l'IFP* 64 (2008) 11–24.
- [49] H.H. Hwu, J.G. Chen, "Surface Chemistry of Transition Metal Carbides," *Chemical Reviews* 105 (2005) 185–212.

Chapter 6.

Multi-product steady-state isotopic transient kinetic analysis of CO hydrogenation over supported molybdenum carbide

Modified with permission from Heng Shou and Robert J. Davis, “Multi-product steady state isotopic transient kinetic analysis of CO hydrogenation over supported molybdenum carbide,” to submitted to *Journal of Catalysis*.

Abstract

Isotopic transient analysis of steady state of CO hydrogenation catalyzed by alumina-supported Mo₂C nanoclusters was performed at 573 K, 1.2 bar syngas with H₂/CO = 1. An isotope switch from ¹²CO to ¹³CO during the steady-state reaction produced a rapid transient associated with CO hydrogenation and a very slow transient associated with turnover of ineffective catalytic sites or exchange of carbidic carbon with reaction intermediates. Although the intrinsic turnover frequency for hydrocarbon formation was similar to that observed on late transition metals, the coverage of reaction intermediates on the Mo₂C clusters was very low (<< 1%), which accounts for the overall low activity of Mo₂C. Promotion of Mo₂C with Rb₂CO₃ lowered the coverage of intermediates even further, but increased the selectivity towards alcohols. Very strong interaction of the alcohols with the promoter suggests that Rb may form alkoxides at reaction conditions.

6.1 Introduction

Early transition metal carbides (e.g., molybdenum carbide, Mo_2C) are potentially alternative catalysts to Pt-group metals [1] and are catalytically active in a variety of reactions, such as hydrogenolysis [2], isomerization [3,4], dehydrogenation [5,6], condensation [6,7], water-gas shift [8] and CO hydrogenation [9–20]. Molybdenum carbide catalysts are well-known to produce light hydrocarbons from syngas [15,21,22], but the selectivity of the reaction can be shifted from hydrocarbons to alcohols when appropriate promoters (i.e. alkali metal salts of weak acids [12,18]) and reaction conditions are used [11,14]. Unfortunately, the specific activity of the Mo_2C -based catalysts in CO hydrogenation is very low compared to other catalysts. For example, the apparent turnover frequency, or TOF, of CO on $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ catalysts [17] (normalized by the amount of surface metal atoms) was approximately two orders of magnitude lower than that on an iron-promoted, titania-supported rhodium catalyst under similar conditions [23]. The very low apparent activity of molybdenum carbide can be attributed to either an intrinsically slow rate of catalytic turnover, or to a very small number of the active sites that accomplish the catalytic cycle related to the amount of Mo at the surface. Due to the high oxophilicity of Mo_2C , it is not straightforward to count the active sites that participate in the CO hydrogenation reaction. We therefore used isotopic transient kinetic analysis to probe the kinetics of CO hydrogenation catalyzed by supported molybdenum carbide.

Steady-state isotopic transient kinetic analysis (SSITKA), as developed by Happel [24], Bennett [25], and Biloen [26], is very useful for evaluating fundamental kinetic parameters of operating solid catalysts, including surface coverages of reaction

intermediates, surface residence times, and active site heterogeneities. In addition, the technique can help identify possible mechanisms [27]. For CO hydrogenation, SSITKA has been employed on various metal catalysts including Fe [28–33], Pd [34–37], Co [28,29,38–42], Ru [43], Ni [44,45] and Rh [46,47]. For a complete discussion of SSITKA, please see the review by Shannon and Goodwin [27].

In the current work, we have used SSITKA to probe the kinetics of CO hydrogenation over alumina-supported Mo_2C nanoclusters, with and without Rb promoters. As discussed above, the unpromoted Mo_2C catalyst functioned primarily as a hydrocarbon formation catalyst with a standard Anderson–Schultz–Flory distribution [15,21,22]. Addition of alkali metal promoters to Mo_2C allowed alcohols to be produced in addition to hydrocarbons [11–14,16–18].

6.2 Experimental methods

6.2.1 Catalyst synthesis

The Mo_2C nanoclusters were prepared on $\alpha\text{-Al}_2\text{O}_3$ by incipient wetness impregnation of an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ followed by drying, calcination, reduction and temperature-programmed carburization up to 900 K (with a mixture of C_2H_6 and H_2) as described in detail in previous work [17]. The addition of Rb_2CO_3 promoter was performed between reduction and carburization, by physically mixing Rb_2CO_3 with the supported suboxide precursor in a mortar and pestle [17]. After carburization, the catalysts were cooled to room temperature in flowing He before being passivated in a stream of 1 vol.% O_2/N_2 mixture at room temperature for 12 h. The nominal loading of Mo_2C and Rb on alumina was 5 wt.% and 1.5 wt.%, respectively.

According to the characterization results presented previously [17], the 5 wt.% Mo₂C/Al₂O₃ catalyst showed a 4.7 wt.% Mo loading and a C/Mo molar ratio of 0.39. The results from extended X-ray absorption fine-structure (EXAFS) spectroscopy and electron microscopy confirmed the formation of highly dispersed molybdenum carbide on alumina support, with the particle size of 1 nm. The 1.5 wt.% Rb–5 wt.% Mo₂C/Al₂O₃ catalyst revealed a Rb/Mo molar ratio of 0.31, which was close to the nominal value (0.34). After passivation of the molybdenum carbide catalysts, the surface was partially oxidized [17].

6.2.2 Hydrogenation of carbon monoxide

Hydrogenation of CO was conducted in a fixed-bed stainless steel reactor (3/8 inch OD) with 0.5 g of 5 wt.% Mo₂C/ α -Al₂O₃ or 2.0 g of 1.5 wt.% Rb–5 wt.% Mo₂C/ α -Al₂O₃. The catalysts were tested at nominally identical conditions of 573 K, 1.2 bar total pressure with equivalent partial pressure of H₂ (GTS-Welco, 99.999%) and CO (GTS-Welco, 99.997%).

The products were analyzed by an on-line SRI 8610C gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). A Restek MXT[®]-Q-Bond column (0.53 mm I.D., 30 m length) connected to an FID was used to quantify hydrocarbons and alcohols, while a HayeSep-D column (3.2 mm I.D., 1.8 m length) connected to a TCD was used to analyze CO and CO₂.

The conversion of CO was derived from the fraction of CO that formed carbon-containing products [48]. The conversion of CO, if low, can be described as:

$$\text{Conversion (\%)} = \sum n_i M_i \times 100 / M_{\text{CO}},$$

where n_i is the number of carbon atoms in product i , M_i is the percentage of product i detected, and M_{CO} is the percentage of CO in the syngas feed.

The selectivity towards product i is based on the total number of carbon atoms in the product and is therefore defined as:

$$\text{Selectivity (\%)} = n_i M_i \times 100 / \sum n_i M_i.$$

The conversion and selectivities were based on the identified products, which present more than 97% of the total peak area in GC chromatograms.

6.2.3 Multi-product SSITKA

Our lab has used SSITKA to study a variety of reactions on solid catalysts such as ammonia synthesis on Ru [49,50], CO hydrogenation on Au [51,52], and ethanol coupling on MgO [53]. Our reactor system in previous works analyzed for only one product of the reaction. We therefore needed to make substantial changes to our reactor system to analyze the multiple products formed during CO hydrogenation.

The system used for the multi-product SSITKA experiments is based on the design reported by Goodwin and co-workers [42,46,54] and is shown in Figure 6.1. The isotopic switch from ^{12}CO to ^{13}CO was carried out after the reaction achieved steady state (typically more than 72 hours on stream) at 573 K, 1.2 bar and $\text{H}_2/\text{CO} = 1$. Although higher pressures were utilized in our previous works with supported Mo_2C catalysts (30 bar) [16–18], our SSITKA experiments required us to minimize both gas phase hold-up in the system as well as adsorption on the support. The syngas flow rate was varied from 10.8 to 15.6 $\text{cm}^3 \text{min}^{-1}$ and the Ar flow rate was maintained at 0.2 $\text{cm}^3 \text{min}^{-1}$. During an

isotopic transient experiment, a switch between naturally abundant ^{12}CO (GTS-Welco, 99.997%) with Ar tracer (GTS-Welco, 99.999%) and ^{13}CO (Cambridge Isotopes, 99.5% ^{13}C , 98+% ^{16}O , 99+% ^{13}C) was made using a Valco 2-position valve with an electric actuator. All of the reaction conditions remained undisturbed during the switch, including flow rates, partial pressures and reaction temperature. Backpressure regulators were used to minimize the pressure disturbance during the switch. The gas-phase hold-up of the system was determined by using an Ar tracer fed with the ^{12}CO stream. The multiple products formed during CO hydrogenation created a complex fragmentation pattern in the mass spectrometer. To simplify the product analysis, we first separated the products by gas chromatography, then converted the C2+ products to CH_4 prior to admission to the mass spectrometer. This methodology was used previously by Bennett and co-workers [44,45] and recently by Goodwin and co-workers [42,46,54] to study the kinetics of CO hydrogenation.

In our transient reactor system, a Valco 34-port auto-sampling valve was employed to collect 16 samples during the isotopic transients. The collected effluent samples were separated in a Restek MXT[®]-Q-Bond column (0.53 mm I.D., 30 m length) placed in the same GC oven used for steady-state product analysis. Dihydrogen was used as the carrier gas and as a reactant for the subsequent hydrogenolysis reaction. After separation, the products were fed into a hydrogenolysis reactor containing 5 g of 5 wt.% Pt/ Al_2O_3 (Sigma-Aldrich) held at 673 K to convert CO and all the products to CH_4 . The resulting CH_4 was subsequently fed to the mass spectrometer (Pfeiffer Vacuum) to measure the isotope content of the products. The signal for $m/z = 15$ and 17 were monitored for $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$, respectively. Since the fragmentation of $^{13}\text{CH}_4$ also

contributes to the signal for $^{12}\text{CH}_4$ (14% of the $^{13}\text{CH}_4$ signal according to calibration), the $^{12}\text{CH}_4$ responses ($m/z = 15$) were all corrected by subtracting the fragment from $^{13}\text{CH}_4$.

Figure 6.1 The reaction system for multi-product SSITKA

Because the Restek GC column was unable to separate CO_2 and CH_4 from CO , another series of transient experiments had to be performed. To analyze CH_4 and CO_2 , the hydrogenolysis reactor prior to the MS was bypassed and the responses for CH_4 , CO_2 and the Ar tracer were monitored directly by MS.

Figure 6.2 Example of normalized transient responses for Ar, $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ following a $^{12}\text{CO}/^{13}\text{CO}$ switch during steady state CO hydrogenation. The Ar transient was used to evaluate the gas phase hold-up of the system. The shaded area represents the surface mean residence time of reaction intermediates that lead to CH_4 (τ_{methane}).

Figure 6.2 shows the normalized steady-state transient responses of the $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ produced over 5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ during CO hydrogenation after a switch from ^{12}CO to ^{13}CO . The mean surface residence time of the reaction intermediates leading to a certain product (τ_i) was determined by integrating the area between the normalized transient response of the ^{12}C portion in the corresponding product (F_i) and that of the inert tracer Ar (F_{Ar}):

$$\tau_i = \int (F_i - F_{\text{Ar}}) dt,$$

as depicted in Figure 6.2 by τ_{methane} (shaded area). Because SSITKA is a pseudo first order analysis, the corresponding turnover frequency (TOF) to produce a specific product is simply:

$$\text{TOF}_i = \tau_i^{-1}.$$

The amount of active surface intermediates leading to a specific product (i) can be determined by a straightforward material balance on the reactor:

$$N_i = \tau_i R_i X_i,$$

where R_i is the rate of formation of product i at steady state reaction, and X_i refers to the fractional change in ^{12}C response (after the switch to ^{13}CO) from the initial value. The corresponding surface coverage (θ_i) is thus:

$$\theta_i = N_i / (\text{amount of surface Mo atoms}).$$

Given the nearly 100% dispersion of Mo in the Mo_2C nanoclusters as indicated by transmission electron microscopy (TEM) and extended X-ray absorption fine structure (EXAFS) [17],

$$\theta_i = N_i / (\text{amount of Mo atoms}).$$

We performed this simplified analysis of the transient results (simple carbon material balance) because all of the experiments were performed at identical conditions of pressure and temperature.

In another series of experiments, the desorption of the surface intermediates leading to different products in CO hydrogenation was studied after the CO flow was halted. A switch between CO (GTS-Welco, 99.997%) and Ar (GTS-Welco, 99.999%) was made using the Valco 2-position valve with an electric actuator at the steady state of reaction while the H_2 (GTS-Welco, 99.999%) flow was maintained. The Valco 34-port auto-sampling valve was employed to collect 16 samples of product gas during desorption. The downstream setup (GC column, hydrogenolysis reactor, MS, etc.) was the same as that used for the SSITKA experiments.

Table 6.1 Performance of unpromoted and Rb-promoted 5 wt.% Mo₂C/ α -Al₂O₃ catalysts in CO hydrogenation at near ambient pressure

Rb loading (wt.%)	0 ^a	1.5 ^b
CO conversion (%)	0.72	0.37
Apparent TOF of CO hydrogenation (s ⁻¹) ^c	0.00008	0.00001
CO ₂ selectivity (%)	53 ^d	52 ^d
Selectivity (C%, on a CO ₂ -free basis)		
Paraffins	82	43
Methane	54	33
Ethane	25	5.4
Propane	2.6	2.9
Butane	0.0	2.1
Olefins	18	36
Ethene	11	21
Propene	7.4	9.4
1-Butene	0.0	5.0
Alcohols	0.0	21
Methanol	0.0	11
Ethanol	0.0	5.9
1-Propanol	0.0	3.6

$T = 573$ K, $p = 1.2$ bar, $H_2/CO = 1$, syngas flow rate = $15.6 \text{ cm}^3 \text{ min}^{-1}$, Ar flow rate = $0.2 \text{ cm}^3 \text{ min}^{-1}$. Results were reported after at least 72 h on stream, after steady state was achieved.

^a 0.5 g catalyst

^b 2.0 g catalyst

^c Apparent TOF of CO hydrogenation was calculated with the assumption that every metal atom is a potential active site, given the nearly 100% dispersion of Mo determined by TEM and EXAFS [17].

^d The excess beyond the theoretical limit (50%) is due to experimental error in the TCD.

6.3 Results and discussion

Table 6.1 summarizes the performance of unpromoted and Rb-promoted alumina-supported Mo₂C catalysts in the reaction of syngas ($H_2/CO = 1$) at 573 K and 1.2 bar. The unpromoted 5 wt.% Mo₂C/ α -Al₂O₃ catalyst produced only hydrocarbons (82% paraffins and 18% olefins) and CO₂ at these conditions. The selectivity towards alcohols increased to 21% after addition of 1.5 wt.% Rb, which is in good agreement with the earlier works on the catalytic performance of Mo₂C promoted by alkali metal species in CO

hydrogenation [11,14–19]. It should be noted that the alcohol selectivity during our ambient-pressure CO hydrogenation studies was not as high as that observed at elevated pressure [17]. Nevertheless, the relatively high selectivity towards olefins (36% on a CO₂-free basis) observed at ambient pressure over 1.5 wt.% Rb–5 wt.% Mo₂C/ α -Al₂O₃ is consistent with the findings by Park *et al.* [21] As shown in Table 6.1, the CO conversion was kept below 1%, thus ensuring differential reaction conditions. Figure 6.3 shows that the CO conversion was strictly linear with respect the inverse of the gas flow rate, confirming the differential behavior of the reactor system.

Figure 6.3 Influence of syngas flow rate on the observed conversion of CO, excluding CO₂, over Mo₂C/ α -Al₂O₃ catalysts at steady state. Reaction conditions: 573 K, 1.2 bar, H₂/CO = 1.

6.3.1 Transient analysis of CO hydrogenation over Mo₂C/ α -Al₂O₃

Multi-product SSITKA allows the determination of the surface reaction parameters, including the surface residence times of reaction intermediates (τ) and

amount of intermediates (N) leading to different products. Figure 6.4 presents the transient responses of various products formed over a 5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ catalyst up to 1 h after an isotope switch. All the transient responses were normalized by the steady state signal of ^{12}C before the transient occurred. The ^{12}C transient response over a Mo_2C catalyst typically included a rapid decay, a slow decay, and a persistent background signal of ^{12}C . In other words, the ^{12}C signal did not decay completely to the background level, even after 1 h. The major fraction of the transient response happened quickly and is attributed to a catalytic turnover on sites denoted as Pool A. The origin of the slow decay on sites denoted as Pool B and the background ^{12}C signal are unclear. It has been reported previously that the species adsorbed on the Mo_2C surface can have a fairly high adsorption energy [18,55–57], and that activation of adsorbed CO may involve the formation or participation of the carbidic carbon [18,58–60]. Because $\alpha\text{-Al}_2\text{O}_3$ has been used previously in SSITKA experiments as an inert agent during CO hydrogenation experiments [42], we suspect that re-adsorption of products on the $\alpha\text{-Al}_2\text{O}_3$ support was unlikely to cause the slow transient response. Therefore, we attribute the slow decay in the ^{12}C transient response to either a strong interaction between the adsorbed reaction intermediates and the Mo_2C surface (which may be catalytically relevant), or to the exchange of carbon between the adsorbed reaction intermediates and the underlying carbidic carbon (which is likely to be catalytically irrelevant). The background incorporation of ^{12}C into products after 1 h was presumably due to the very slow exchange of unlabeled carbidic carbon with labeled reactive carbon.

Figure 6.4 Normalized transient responses up to 1 h of (a) $^{12}\text{CO}_2$, (b) $^{12}\text{CH}_4$, and the ^{12}C portion in (c) C_2H_4 and (d) C_2H_6 , over a 5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ catalyst in CO hydrogenation, along with corresponding exponential fits of $F(t) = X_A \exp[-(t-t_0)/T_A] + X_B \exp[-(t-t_0)/T_B] + X_{\text{bkg}}$ (see Table 6.2). Normalization was based on the initial signal. Experimental conditions: $T = 573 \text{ K}$, $P = 1.2 \text{ bar}$, $\text{H}_2/\text{CO} = 1$, syngas flow rate $= 15.6 \text{ cm}^3 \text{ min}^{-1}$, Ar flow rate $= 0.2 \text{ cm}^3 \text{ min}^{-1}$.

Since the isotopic transient responses in Figure 6.4 appear to be composed by two different exponential functions, we fit the curves with the following expression:

$$F(t) = X_A \exp\left(-\frac{t-t_0}{T_A}\right) + X_B \exp\left(-\frac{t-t_0}{T_B}\right) + X_{\text{bkg}},$$

where A, B and bkg stand for the fraction of sites associated with Pool A (rapid turnover), Pool B (slow turnover) and background exchange, respectively. The results of the curve fits are summarized in Table 6.2. The sites associated with Pool A account for about 80% of the C1 products and about 65% of the C2 products formed over 5 wt.% Mo₂C/ α -Al₂O₃. This rapid transient associated with Pool A is nearly complete by 200 s at a flow rate of 15.6 cm³ min⁻¹, so we repeated the transient experiment to collect more samples during the rapid transient. Because our sampling system allowed only 15 samples to be collected after the change in feed, shortening the total collection time allowed us to acquire more points throughout the rapid transient. Table 6.3 compares the fraction of the transients responsible for Pool A derived from both short (measured) and long (fitted) collection times and confirms that our acquisition of rapid transient results (290–430 s) reproduce well the conclusion obtained from the long time transient experiment (3600 s).

The typical transient responses of hydrocarbons and CO₂ associated with Pool A are shown in Figure 6.5, and the calculated values of mean surface residence time (τ) of various hydrocarbons and CO₂ on unpromoted and Rb-promoted Mo₂C at different syngas flow rates are displayed in Figure 6.6. The τ values for the various products in Figure 6.6 were fairly independent of flow rate over the range investigated, indicating that product re-adsorption on the catalyst or support was negligible. Therefore, τ values for each product were averaged and the results are summarized in Table 6.4. The corresponding reaction parameters such as intrinsic TOF and coverage of reaction

intermediate were subsequently calculated from those values. It should be noted that two types of N and θ are shown in Table 6.4, namely “fractional” and “max,” respectively. The “fractional” values were based on the potential existence of catalytically active sites in Pool B, on which reaction intermediates turn over at low rates. On the other hand, the “max” values were calculated assuming the slow transients resulted solely from exchange of carbon between the reaction intermediates and the carbidic carbon of the catalyst, which is not directly involved in the steady state reaction rate. Since neither of the two mechanisms can be excluded, both types of coverages are reported.

Table 6.2 Fractional contribution of different sites on unpromoted Mo₂C catalyst in CO hydrogenation

Product	Pool A (rapid turnover)		Pool B (slow turnover)		Background	Adjusted R^2
	X_A	T_A (s)	X_B	T_B (s)	X_{bkg}	
CO ₂	0.81	37	0.18	520	0.01	0.995
CH ₄	0.82	29	0.08	410	0.10	0.995
C ₂ H ₄	0.66	35	0.18	1400	0.16	0.996
C ₂ H ₆	0.62	35	0.22	1200	0.16	0.996

Experimental conditions: 0.5 g 5 wt.% Mo₂C/ α -Al₂O₃, 573 K, 1.2 bar, H₂/CO = 1, syngas flow rate = 15.6 cm³ min⁻¹, Ar flow rate = 0.2 cm³ min⁻¹. Parameters were derived from

the fits of $F(t) = X_A \exp\left(-\frac{t-t_0}{T_A}\right) + X_B \exp\left(-\frac{t-t_0}{T_B}\right) + X_{\text{bkg}}$, where $X_A + X_B + X_{\text{bkg}} = 1$.

$F(t)$: normalized transient response

X_A (X_B): the fraction of a complete transient contributed by Pool A (B)

X_{bkg} : the fraction of a complete transient contributed by background conversion

t_0 : delay of the signal in the system

T_A (T_B): the system hold-up time corresponding to Pool A (B)

Table 6.3 Comparison of the fraction of transient (X_A) associated with Pool A on 5 wt.% Mo₂C/ α -Al₂O₃: fit of exponential decay vs. absolute changes in transient responses

Product	Fitted X_A		Measured X_A		
CO ₂	0.81	0.89	0.90	0.88	0.90
CH ₄	0.82	0.84	0.84	0.82	0.87
C ₂ H ₄	0.66	0.65	0.67	0.65	0.68
C ₂ H ₆	0.62	0.69	0.68	0.67	0.70
Condition					
Syngas flow rate (cm ³ min ⁻¹)	15.6	15.6	13.2	12.0	10.8
Time of transient (s)	3600	290	350	350	430

Figure 6.5 Typical transient responses associated with Pool A: (a) Ar, $^{12}\text{CH}_4$ and $^{12}\text{CO}_2$ and $^{13}\text{CH}_4$ over 5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$; (b) Ar, ^{12}C (in CO, C_2H_4 , C_2H_6 and C_3H_6) and ^{13}C (in C_2H_6) over 5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$; (c) Ar, $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ over 1.5 wt.% Rb-5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$; (d) Ar, ^{12}C (in CO, C_2H_4 , C_2H_6 and C_3H_6) and ^{13}C (in C_2H_4) over 1.5 wt.% Rb-5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$. $T = 573\text{ K}$, $p = 1.2\text{ bar}$, $\text{H}_2/\text{CO} = 1$, Syngas flow rate $= 13.2\text{ cm}^3\text{ min}^{-1}$, Ar flow rate $= 0.2\text{ cm}^3\text{ min}^{-1}$. Transient responses were normalized by difference between the initial and final signals.

Figure 6.6 Mean surface residence time (τ) of CO (square), and intermediates leading to CO_2 (up triangle), CH_4 (circle), C_2H_4 (down triangle), C_2H_6 (diamond) and C_3H_6 (left triangle) vs. the reciprocal of gas flow rate during steady state of CO hydrogenation over (a) 5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ and (b) 1.5 wt.% Rb-5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$

Table 6.4 Surface reaction parameters for CO hydrogenation on Pool A over 5 wt.% Mo₂C/ α -Al₂O₃ and 1.5 wt.% Rb–5 wt.% Mo₂C/ α -Al₂O₃ catalysts estimated by SSITKA

Molecule	τ_A (s)	TOF _A (s ⁻¹)	R (nmol _C g _{cat} ⁻¹ s ⁻¹)	X_A ^a	N_A ^b (μ mol _C g _{cat} ⁻¹)		θ_A ^c (mmol _C mol _{Mo} ⁻¹)	
					fractional	max	fractional	max
5% Mo ₂ C								
CO	2.1	—	—	—	—	—	—	—
CO ₂	17	—	38	0.90	0.57	0.64	1.2	1.3
Overall CH ^d	15	0.067	34	0.77	0.40	0.53	0.81	1.1
CH ₄	11	0.094	19	0.84	0.18	0.21	0.36	0.42
C ₂ H ₄	18	0.055	3.3	0.67	0.04	0.06	0.08	0.12
C ₂ H ₆	21	0.048	9.1	0.68	0.13	0.19	0.27	0.39
C ₃ H ₆	28	0.036	2.5	0.71	0.05	0.07	0.10	0.14
Total carbon intermediates ^e	—	—	—	—	1.0	1.2	2.0	2.4
1.5% Rb–5% Mo ₂ C								
CO	4.9	—	—	—	—	—	—	—
Overall CH ^d	16	0.062	3.3	0.69	0.035	0.053	0.071	0.11
CH ₄	12	0.087	1.5	0.80	0.014	0.018	0.029	0.036
C ₂ H ₄	18	0.056	1.0	0.71	0.013	0.018	0.026	0.036
C ₂ H ₆	21	0.047	0.3	0.34	0.002	0.006	0.004	0.012
C ₃ H ₆	26	0.038	0.4	0.53	0.006	0.012	0.013	0.024

Experimental conditions: 0.5 g 5 wt.% Mo₂C/ α -Al₂O₃ or 2.0 g 1.5 wt.%–5 wt.% Mo₂C/ α -Al₂O₃; 573 K, 1.2 bar, H₂/CO = 1; syngas flow rate: 10.8, 12.0, 13.2 or 15.6 cm³ min⁻¹; Ar flow rate = 0.2 cm³ min⁻¹.

Results were reported after 72 h on time when the catalysts were at steady state. Values of τ_A , R and X_A were the average of the corresponding results at the 4 syngas flow rates.

^a The fraction of the rate contributed by Pool A (X_A) was determined by the change of corresponding response in MS.

^b N_A represents the amount of reaction intermediate in Pool A: $N_A(\text{fractional}) = \tau_A R_A X_A$, assuming the slow turnovers involve strongly adsorbed intermediates; $N_A(\text{maximum}) = \tau_A R_A$, assuming all the slow turnovers are from the carbon exchange with the carbidic carbon.

^c The carbon in the unit “mmol_C mol_{Mo}⁻¹” refers to those participating in the turnovers on Pool A.

^d Overall CO hydrogenation (CH): $\tau_{A,CH} = N_{A,CH} / R_{CH} X_{A,CH}$, $R_{CH} = \sum R_i$, $N_{A,CH} = \sum N_{A,i}$, $X_{A,CH} = \sum R_i X_{A,i} / \sum R_i$, $\theta_{A,CH} = \sum \theta_{A,i}$. The letter “i” refers to a non-CO₂ product.

^e $N_{A,\text{total}} = \sum N_{A,i}$, $\theta_{A,\text{total}} = \sum \theta_{A,i}$. The letter “i” refers to a product (including CO₂).

The very low apparent TOF of CO hydrogenation over Mo₂C catalysts, as reported in Table 6.1, was very different from the intrinsic TOF (τ^{-1}) determined by SSITKA. The intrinsic TOF for CO hydrogenation associated with Pool A on 5 wt.% Mo₂C/ α -Al₂O₃ (0.067 s^{-1} , Table 6.4) was nearly three orders of magnitude higher than the corresponding apparent one (0.00008 s^{-1} , Table 6.1), and is comparable to the intrinsic TOF of CO hydrogenation derived from SSITKA on a bulk Fe catalyst [54] (0.15 s^{-1} , at 553 K, 1.8 bar and $\text{H}_2/\text{CO} = 20$) and a Rh/SiO₂ catalyst [46] (0.1 s^{-1} , at 553 K, 1.8 bar and $\text{H}_2/\text{CO} = 20$). Likewise, the apparent TOF on a Fe–Rh/TiO₂ catalyst [23] was 0.1 s^{-1} , at 567 K, 20 bar and $\text{H}_2/\text{CO} = 1$. Nørskov and co-workers used a first-principles approach to compare the Brønsted–Evans–Polanyi (BEP) relationship of a variety of adsorbed species on the (211) surfaces of various late transition metals (Ru, Ir, Fe, Co, Rh, Ni and Pd) [61] with a representative Mo₂C(001) surface [57]. The authors concluded the chemistry of carbon on Mo-terminated Mo₂C(001) was indeed similar to that on the late transition metals and suggested Mo₂C should exhibit similar activity to these metals for reactions where hydrocarbons are the main intermediates [57]. Thus, our SSITKA results are in good agreement with the theoretical prediction.

A high intrinsic TOF for CO hydrogenation over Mo₂C (0.067 s^{-1}) relative to a low apparent TOF (0.00008 s^{-1} , Table 6.1) must necessarily correspond to a very low coverage of carbon-containing intermediates. As summarized in Table 6.4, the coverage of carbon-containing reaction intermediates leading to hydrocarbons was $8.4 \text{ mmol}_\text{C} \text{ mol}_\text{Mo}^{-1}$, which is far lower than the coverage of species observed on Fe- [33] and Rh-based [47] catalysts. The low surface coverage of adsorbed species is consistent with a very weak IR band of adsorbed CO on Mo₂C [18,62–64], and might be attributed to

adsorbed oxygen on the molybdenum carbide surface due to the strong oxophilicity of Mo_2C [16,70–72], or to graphitization during reaction [60,73]. The values of τ for hydrocarbons associated with Pool A (Table 6.4) follow the trend, $\tau_{\text{C}_3} > \tau_{\text{C}_2} > \tau_{\text{C}_1}$, which results from the elementary reactions needed to grow the carbon chain. Similarly, unsaturated hydrocarbon (C_2H_4) showed slightly shorter residence time than the corresponding saturated one (C_2H_6), which is related to the time needed for chain termination via hydrogenation. According to Lohitharn and Goodwin [54], the maximum reaction time of carbon chain growth and chain termination via hydrogenation can be estimated by $\tau_{\text{C}_3\text{H}_6} - \tau_{\text{C}_2\text{H}_4} \approx 9$ s and by $\tau_{\text{C}_2\text{H}_6} - \tau_{\text{C}_2\text{H}_4} \approx 3$ s, respectively, and both are slightly longer times than those values on Fe-based catalysts (1.7 s and 0.9 s, respectively) revealed by SSITKA [54].

The mean residence time for CO_2 on 5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ was approximately the same as that for overall CO hydrogenation, indicating water produced in the reaction rapidly consumed CO in the water-gas shift (WGS) reaction. In fact, Mo_2C is known as a good catalyst/catalytic component in WGS [8,65–68].

The corresponding overall surface coverages of reaction intermediates (Pool A and the potentially existing Pool B combined) were derived from the isotopic transient experiment up to 1 h (see Figure 6.4 for example curves) by subtracting the background signal, and the results are summarized in Table 6.5. With Pool B being considered, the residence times for hydrocarbons were increased by an order of magnitude. Nørskov and co-workers used a first-principles approach to predict that if oxygen is a key intermediate on the surface of oxophilic Mo_2C during CO hydrogenation, the activity of CO hydrogenation can be much lower than when hydrocarbons are the main intermediates

[57]. Therefore, Pool B might be composed of those reaction intermediates that have oxygen strongly interacting with the Mo₂C surface. The inclusion of Pool B in the analysis increased the total coverage of reaction intermediates by a factor of 8 ($\theta_{A+B} = 16 \text{ mmol}_C \text{ mol}_{Mo}^{-1}$, $\theta_A = 2 \text{ mmol}_C \text{ mol}_{Mo}^{-1}$).

Table 6.5 Time constants and surface coverages during CO hydrogenation over unpromoted 5 wt.% Mo₂C/ α -Al₂O₃ catalysts estimated by SSITKA (transient response measured up to 1 h, corresponding to Figure 6.4)

Product	τ_{A+B} (s)	R ($\text{nmol}_C \text{ g}_{cat}^{-1} \text{ s}^{-1}$)	X_{A+B} ^a	N_{A+B} ^b ($\mu\text{mol}_C \text{ g}_{cat}^{-1}$)	θ_{A+B} ^c ($\text{mmol}_C \text{ mol}_{Mo}^{-1}$)
CO ₂	97	42	1	3.9	8.0
Overall CH ^d	130	35	0.88	4.1	8.4
CH ₄	57	20	0.91	0.9	2.1
C ₂ H ₄	220	3.9	0.83	0.71	1.5
C ₂ H ₆	250	8.9	0.83	1.9	4.0
C ₃ H ₆	190	2.7	0.85	0.43	0.9
Total carbon intermediates ^e	—	77	0.95	8.1	16
Background carbon (bkg)				0.47 ^f	1.0
Total carbidic carbon				210 ^g	

Experimental conditions: 0.5 g 5 wt.% Mo₂C/ α -Al₂O₃; $T = 573 \text{ K}$, $p = 1.2 \text{ bar}$, $\text{H}_2/\text{CO} = 1$; syngas flow rate = $15.6 \text{ cm}^3 \text{ min}^{-1}$, Ar flow rate = $0.2 \text{ cm}^3 \text{ min}^{-1}$.

^a The fraction of the rate (X) was determined by the change of corresponding response in MS.

^b The concentration of reaction intermediate: $N = \tau_{A+B} R X_{A+B}$.

^c In the unit “ $\text{mmol}_C \text{ mol}_{Mo}^{-1}$,” carbon refers to those participating in the turnovers.

^d $\tau_{CH} = N_{CH} / (R_{CH} X_{CH})$, $N_{CH} = \sum N_i$, $R_{CH} = \sum R_i$, $X_{CH} = \sum R_i X_i / \sum R_i$, $\theta_{CH} = \sum \theta_i$. The letter “ i ” refers to a product (including CO₂).

^e Overall CO hydrogenation (CH): $R_{total} = \sum R_i$, $X_{A+B, total} = \sum R_i X_{A+B, i} / \sum R_i$, $N_{A+B, total} = \sum N_{A+B, i}$, $\theta_{A+B, total} = \sum \theta_{A+B, i}$. The letter “ i ” refers to a product (including CO₂).

^f $N_{bkg} = N_{A+B, total} (1 - X_{A+B, total}) / X_{A+B, total}$.

^g The amount of carbidic carbon is derived from elemental analysis [17].

6.3.2 Transient analysis of CO hydrogenation over Rb-promoted Mo₂C/ α -Al₂O₃

With the addition of Rb promoter, the time constants for the hydrocarbons associated with Pool A were almost the same as those measured on the unpromoted Mo₂C catalyst, but the surface coverages of carbon-containing reaction intermediates were lowered by an order of magnitude (Table 6.4). These results provide direct evidence for the site-blocking mechanism of alkali metal promotion on Mo-based catalysts for the enhancement of alcohol selectivity suggested by Lee and co-workers [12,69] and by our previous studies [16–18].

It should be noted that the CO₂ transient on the Rb-promoted Mo₂C catalyst was not complete after 290–430 s, and labeled alcohols were never observed over that time frame.

Since labeled alcohols were not detected in the effluent of the reactor containing 1.5 wt.% Rb–5 wt.% Mo₂C/ α -Al₂O₃ even after sampling for 2 h beyond the switch to labeled ¹³CO, SSITKA could not be used to quantify the surface coverage of intermediates leading to alcohols. Evidently, the alcohols were strongly retained by the catalyst. To overcome this problem, we decided to perform a long-term transient experiment in which the steady-state CO flow was simply replaced with Ar so that we could follow the desorption of the products formed into a stream of H₂ and Ar. The profiles of normalized desorption rates over 5 wt.% Mo₂C/ α -Al₂O₃ and 1.5 wt.% Rb–5 wt.% Mo₂C/ α -Al₂O₃ are shown in Figure 6.7, and the amount of the reaction intermediates (N) and the corresponding surface coverages (θ) determined from the material balance are summarized in Table 6.6.

Figure 6.7 Transient desorption rates of carbon in various products associated with (a) 5 wt.% Mo₂C/α-Al₂O₃, and (b) 1.5 wt.% Rb-5 wt.% Mo₂C/α-Al₂O₃ in steady-state CO hydrogenation. Results were normalized by the difference between the initial and final desorption rates.

Table 6.6 Coverage of reaction intermediates in CO hydrogenation over 5 wt.% Mo₂C/ α -Al₂O₃ and 1.5 wt.% Rb–5 wt.% Mo₂C/ α -Al₂O₃ catalysts estimated by the interruption of CO flow and subsequent desorption of products (see Figure 6.7)

Product	τ^a (s)	R (nmol _C g _{cat} ⁻¹ s ⁻¹)	X^b	N^c (μ mol _C g _{cat} ⁻¹)	θ^d (mmol _C mol _{Mo} ⁻¹)
5 wt.% Mo ₂ C					
CO ₂	20	41	1	0.8	2
CH ₄	260	20	0.97	4.9	10
C2 hydrocarbons	340	13	0.95	4.2	8
C3 hydrocarbons	920	3.6	1	3.3	7
Total carbon intermediates ^e	—	77	0.98	13	27
Background carbon				0.2 ^f	0.5
1.5 wt.% Rb–5 wt.% Mo ₂ C					
CO ₂	1100	5.1	0.99	5.6	11
Hydrocarbons ^g	10000	3.2	0.87	30	61
CH ₃ OH	9400	0.54	0.81	4.1	8.3
C ₂ H ₅ OH	8200	0.28	0.82	1.8	3.7
<i>n</i> -C ₃ H ₇ OH	10000	0.17	1	1.8	3.7
Total carbon intermediates ^e	—	9.3	0.94	43	88
Background carbon				2.9 ^f	5.9
Total Rb				180 ^h	
Total carbidic carbon				210 ⁱ	

Experimental conditions: 0.5 g 5 wt.% Mo₂C/ α -Al₂O₃ or 2.0 g 1.5 wt.%–5 wt.% Mo₂C/ α -Al₂O₃; $T = 573$ K, $p = 1.2$ bar, H₂/CO = 1 before switch, H₂/Ar = 1 after switch; total flow rate = 15.6 cm³ min⁻¹.

^a Gas phase hold-up of the system was subtracted.

^b The fraction of the rate (X) was determined by the change of corresponding response in MS.

^c The concentration of reaction intermediate: $N = \tau R X$.

^d In the unit “mmol_C mol_{Mo}⁻¹,” carbon refers to those participate in the turnovers.

^e $R_{\text{total}} = \sum R_i$, $X_{\text{total}} = \sum R_i X_i / \sum R_i$, $N_{\text{total}} = \sum N_i$, $\theta_{\text{total}} = \sum \theta_i$. The letter “*i*” refers to a product (including CO₂).

^f $N_{\text{bkg}} = \tau_{\text{total}} R_{\text{total}} (1 - X_{\text{total}})$.

^g The sum of CH₄, C₂H₄, C₂H₆ and C₃H₆, which represents 87% of the total hydrocarbons.

^h The unit of the total Rb concentration is $\mu\text{mol}_{\text{Rb}} \text{g}_{\text{cat}}^{-1}$.

ⁱ The amount of carbidic carbon is derived from elemental analysis [17].

The values of N and θ for the total carbon intermediates on 5 wt.% Mo₂C/ α -Al₂O₃ measured by the desorption experiment ($N = 13 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$, $\theta = 27 \text{ mmol}_C \text{ mol}_{\text{Mo}}^{-1}$, in Table 6.6) are comparable to those derived from SSITKA ($N = 8.1 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$, $\theta = 16 \text{ mmol}_C \text{ mol}_{\text{Mo}}^{-1}$, in Table 6.5), which suggests that desorption experiments with flowing H₂ and Ar provide reasonable estimations of N and θ . Interestingly, increases in the desorption rates of hydrocarbons were observed in the first several minutes of the desorption experiments under flowing H₂ and Ar (the portions exceeding 1 in Figure 6.7), and the effluent CO₂ from 5 wt.% Mo₂C/ α -Al₂O₃ in the desorption experiment ($0.8 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$, in Table 6.6) was much less than the value measured by SSITKA ($3.9 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$, in Table 6.5). These results suggest that the carbon intermediates leading to CO₂ formation during steady-state syngas reaction (presumably associatively adsorbed CO) may undergo hydrogenation to hydrocarbons instead. Additionally, halting the flow of CO may facilitate rapid hydrogenation of adsorbed hydrocarbon fragments thus resulting in a rapid desorption at short times. Nevertheless, these changes in specific products did not significantly affect the overall decay in the overall desorption rate of the carbon intermediates with time on stream, and should not affect the quantification of the total amount of carbon intermediates on the surface at the time of the transient. With added 1.5 wt.% Rb, the mean residence time of CO₂ on 5 wt.% Mo₂C/ α -Al₂O₃ was significantly increased (noted the change in scale of the x-axis in Figure 6.7), indicating a strong affinity between CO₂ and the basic Rb species, which is to be expected. The amount of the total carbon desorbed from the 5 wt.% Mo₂C/ α -Al₂O₃ catalyst increased by a factor of 3 after adding Rb (see Table 6.6), among which $8 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$ was associated

with alcohols. Evidently, the presence of Rb on the catalyst increased the retention of products on the surface during CO hydrogenation. Since the total amount of carbon desorbed from the promoted catalyst ($43 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$) was much less than the amount of Rb ($180 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$) in the catalyst, we concluded that interactions of products and/or reaction intermediates with the Rb promoter is significant. It is possible that Rb alkoxides is one form of the Rb species present during reaction, as suggested by Woo *et al.* [74] Also, given the total amount of the carbidic carbon ($210 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$) exceeded the measured amount of carbon-containing intermediates formed on 5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ ($13 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$) and on 1.5 wt.% Rb–5 wt.% $\text{Mo}_2\text{C}/\alpha\text{-Al}_2\text{O}_3$ ($43 \mu\text{mol}_C \text{ g}_{\text{cat}}^{-1}$), the slow exchange of carbon between the reaction intermediates and the carbidic carbon cannot be completed during the time of measurements.

6.4 Conclusions

The isotopic transient analysis revealed that although the catalytically-relevant pool on Mo_2C catalysts was capable of relatively rapid turnovers in CO hydrogenation (0.067 s^{-1} at 573 K in 1.2 bar syngas), the surface coverage of reaction intermediates was extremely low, resulting in a low apparent activity of the Mo_2C -based catalysts in the CO hydrogenation reaction. The low surface coverage of the reaction intermediates was decreased even further by adding Rb promoter. The added Rb promoter interacted strongly with the alcohols formed during CO hydrogenation, suggesting that Rb alkoxides may be one form of the Rb species present during reaction. Exchange of carbon between the adsorbed reaction intermediates during CO hydrogenation and the carbidic

carbon in the carbide catalysts likely accounted for the long transient response and background level of signal after an isotopic switch.

The results of this work show that appropriately active sites, typical of late transition metals, do indeed exist on supported Mo₂C catalysts for CO hydrogenation, but the number of those sites is very low compare to the total amount of Mo at the surface. Future work with Mo₂C catalysts for CO hydrogenation should involve identification of those sites and optimization of their number density.

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References of Chapter 6

- [1] R.B. Levy, M. Boudart, "Platinum-like behavior of tungsten carbide in surface catalysis," *Science* 181 (1973) 547–549.
- [2] J.S. Lee, S. Locatelli, S.T. Oyama, M. Boudart, "Molybdenum carbide catalysts 3. Turnover rates for the hydrogenolysis of *n*-butane," *Journal of Catalysis* 125 (1990) 157–170.
- [3] E.A. Blekkan, C. Pham-Huu, M.J. Ledoux, J. Guille, "Isomerization of *n*-heptane on an oxygen-modified molybdenum carbide catalyst," *Industrial & Engineering Chemistry Research* 33 (1994) 1657–1664.
- [4] M.J. Ledoux, C. Pham-Huu, R.R. Chianelli, "Catalysis with carbides," *Current Opinion in Solid State and Materials Science* 1 (1996) 96–100.

- [5] T. Hyeon, M. Fang, K.S. Suslick, "Nanostructured molybdenum carbide: sonochemical synthesis and catalytic properties," *Journal of the American Chemical Society* 118 (1996) 5492–5493.
- [6] S.K. Bej, C.A. Bennett, L.T. Thompson, "Acid and base characteristics of molybdenum carbide catalysts," *Applied Catalysis A: General* 250 (2003) 197–208.
- [7] S.K. Bej, L.T. Thompson, "Acetone condensation over molybdenum nitride and carbide catalysts," *Applied Catalysis A: General* 264 (2004) 141–150.
- [8] J. Patt, D.J. Moon, C. Phillips, L. Thompson, "Molybdenum carbide catalysts for water–gas shift," *Catalysis Letters* 65 (2000) 193–195.
- [9] I. Kojima, E. Miyazaki, I. Yasumori, "Synthesis of hydrocarbons from CO and H₂ over metal carbide catalysts," *Journal of the Chemical Society, Chemical Communications* (1980) 573–574.
- [10] I. Kojima, E. Miyazaki, "Catalysis by transition metal carbides: V. Kinetic measurements of hydrogenation of CO over TaC, TiC, and Mo₂C catalysts," *Journal of Catalysis* 89 (1984) 168–171.
- [11] H.C. Woo, K.Y. Park, Y.G. Kim, I.S. Nam, J.S. Chung, J.S. Lee, "Mixed alcohol synthesis from carbon monoxide and dihydrogen over potassium-promoted molybdenum carbide catalysts," *Applied Catalysis* 75 (1991) 267–280.
- [12] J.S. Lee, S. Kim, Y.G. Kim, "Electronic and geometric effects of alkali promoters in CO hydrogenation over K/Mo₂C catalysts," *Topics in Catalysis* 2 (1995) 127–140.
- [13] H.G. Kim, K.H. Lee, J.S. Lee, "Carbon monoxide hydrogenation over molybdenum carbide catalysts," *Research on Chemical Intermediates* 26 (2000) 427–443.
- [14] M. Xiang, D. Li, W. Li, B. Zhong, Y. Sun, "Performances of mixed alcohols synthesis over potassium promoted molybdenum carbides," *Fuel* 85 (2006) 2662–2665.
- [15] D.-V.N. Vo, A.A. Adesina, "Fischer–Tropsch synthesis over alumina-supported molybdenum carbide catalyst," *Applied Catalysis A: General* 399 (2011) 221–232.
- [16] H. Shou, R.J. Davis, "Reactivity and *in situ* X-ray absorption spectroscopy of Rb-promoted Mo₂C/MgO catalysts for higher alcohol synthesis," *Journal of Catalysis* 282 (2011) 83–93.
- [17] H. Shou, D. Ferrari, D.G. Barton, C.W. Jones, R.J. Davis, "Influence of passivation on the reactivity of unpromoted and Rb-promoted Mo₂C nanoparticles for CO hydrogenation," *ACS Catalysis* 2 (2012) 1408–1416.

- [18] H. Shou, L. Li, D. Ferrari, D.S. Sholl, R.J. Davis, "Use of infrared spectroscopy and density functional theory to study the influence of rubidium on alumina-supported molybdenum carbide catalyst for higher alcohol synthesis from syngas," *Journal of Catalysis* 299 (2013) 150–161.
- [19] J.M. Christensen, L.D.L. Duchstein, J.B. Wagner, P.A. Jensen, B. Temel, A.D. Jensen, "Catalytic conversion of syngas into higher alcohols over carbide catalysts," *Industrial & Engineering Chemistry Research* 51 (2012) 4161–4172.
- [20] S.-H. Chai, V. Schwartz, J.Y. Howe, X. Wang, M. Kidder, S.H. Overbury, S. Dai, D. Jiang, "Graphitic mesoporous carbon-supported molybdenum carbides for catalytic hydrogenation of carbon monoxide to mixed alcohols," *Microporous and Mesoporous Materials* 170 (2013) 141–149.
- [21] K.Y. Park, W.K. Seo, J.S. Lee, "Selective synthesis of light olefins from syngas over potassium-promoted molybdenum carbide catalysts," *Catalysis Letters* 11 (1991) 349–356.
- [22] D.-V.N. Vo, T.-H. Nguyen, E.M. Kennedy, B.Z. Dlugogorski, A.A. Adesina, "Fischer–Tropsch synthesis: Effect of promoter type on alumina-supported Mo carbide catalysts," *Catalysis Today* 175 (2011) 450–459.
- [23] M.A. Haider, M.R. Gogate, R.J. Davis, "Fe-promotion of supported Rh catalysts for direct conversion of syngas to ethanol," *Journal of Catalysis* 261 (2009) 9–16.
- [24] J. Happel, "Transient tracing," *Chemical Engineering Science* 33 (1978) 1567.
- [25] C.O. Bennett, "Understanding heterogeneous catalysis through the transient method," *ACS Symposium Series* 1 (1982) 1–32.
- [26] P. Biloen, "Transient kinetic methods," *Journal of Molecular Catalysis* 21 (1993) 17–24.
- [27] S.L. Shannon, J.G. Goodwin, "Characterization of Catalytic Surfaces by Isotopic-Transient Kinetics during Steady-State Reaction," *Chemical Reviews* 95 (1995) 677–695.
- [28] C.A. Mims, L.E. McCandlish, "Chain growth rates in Fischer–Tropsch synthesis on an iron catalyst: an isotopic transient study," *Journal of the American Chemical Society* 107 (1985) 696–697.
- [29] C.A. Mims, L.E. McCandlish, "Evidence for rapid chain growth in the Fischer–Tropsch synthesis over iron and cobalt catalysts," *The Journal of Physical Chemistry* 91 (1987) 929–937.
- [30] D.M. Stockwell, D. Bianchi, C.O. Bennett, "Carbon pathways in methanation and chain growth during the Fischer–Tropsch synthesis on Fe/Al₂O₃," *Journal of Catalysis* 113 (1988) 13–24.

- [31] K. Sudsakorn, J.G. Goodwin, A.A. Adeyiga, "Effect of activation method on Fe FTS catalysts: investigation at the site level using SSITKA," *Journal of Catalysis* 213 (2003) 204–210.
- [32] N. Lohitharn, J.G. Goodwin, "Impact of Cr, Mn and Zr addition on Fe Fischer–Tropsch synthesis catalysts: Investigation at the active site level using SSITKA," *Journal of Catalysis* 257 (2008) 142–151.
- [33] N. Lohitharn, J.G. Goodwin, "Effect of K promotion of Fe and FeMn Fischer–Tropsch synthesis catalysts: Analysis at the site level using SSITKA," *Journal of Catalysis* 260 (2008) 7–16.
- [34] S.H. Ali, J.G. Goodwin, "Isotopic transient kinetic Analysis of the induction phenomenon for methanol synthesis on Pd/SiO₂," *Journal of Catalysis* 170 (1997) 265–274.
- [35] S.H. Ali, J.G. Goodwin, "Analysis of sequential reactions in bifunctional catalyst systems using isotopic transient kinetics: methanol synthesis on Pd/SiO₂+Al₂O₃," *Journal of Catalysis* 171 (1997) 333–338.
- [36] S.H. Ali, J.G. Goodwin, "Impact of readsorption effects and their removal from surface reaction parameters obtained by isotopic transient kinetic analysis: Methanol synthesis on Pd/SiO₂," *Journal of Catalysis* 171 (1997) 339–344.
- [37] S.H. Ali, J.G. Goodwin, "SSITKA Investigation of palladium precursor and support effects on CO hydrogenation over supported Pd catalysts," *Journal of Catalysis* 176 (1998) 3–13.
- [38] C.A. Mims, "An oxygenated C1 intermediate in the Fischer–Tropsch synthesis on cobalt," *Catalysis Letters* 1 (1988) 293–298.
- [39] S. Vada, B. Chen, J.G. Goodwin, "Isotopic transient study of La promotion of Co/Al₂O₃ for CO hydrogenation," *Journal of Catalysis* 153 (1995) 224–231.
- [40] V. Frøseth, S. Storsæter, Ø. Borg, E.A. Blekkan, M. Rønning, A. Holmen, "Steady state isotopic transient kinetic analysis (SSITKA) of CO hydrogenation on different Co catalysts," *Applied Catalysis A: General* 289 (2005) 10–15.
- [41] J. Yang, D. Chen, A. Holmen, "Understanding the kinetics and Re promotion of carbon nanotube supported cobalt catalysts by SSITKA," *Catalysis Today* 186 (2012) 99–108.
- [42] Y.-T. Tsai, X. Mo, J.G. Goodwin, "The synthesis of hydrocarbons and oxygenates during CO hydrogenation on CoCuZnO catalysts: Analysis at the site level using multiproduct SSITKA," *Journal of Catalysis* 285 (2012) 242–250.
- [43] B. Chen, J.G. Goodwin, "Isotopic transient kinetic analysis of CO hydrogenation on Cu-modified Ru/SiO₂, *Journal of Catalysis* 158 (1996) 511–520.

- [44] D.M. Stockwell, C.O. Bennett, "An isotopic study of chain growth during the CO/H₂ reaction over Ni/Al₂O₃," *Journal of Catalysis* 110 (1988) 354–363.
- [45] D.M. Stockwell, J.S. Chung, C.O. Bennett, "A transient infrared and isotopic study of methanation over Ni/Al₂O₃," *Journal of Catalysis* 112 (1988) 135–144.
- [46] J. Gao, X. Mo, J.G. Goodwin, "Relationships between oxygenate and hydrocarbon formation during CO hydrogenation on Rh/SiO₂: Use of multiproduct SSITKA," *Journal of Catalysis* 275 (2010) 211–217.
- [47] J. Gao, X. Mo, J.G. Goodwin, "Evidence of strong metal-oxide interactions in promoted Rh/SiO₂ on CO hydrogenation: Analysis at the site level using SSITKA," *Catalysis Today* 160 (2011) 44–49.
- [48] R. Burch, M.I. Petch, "Investigation of the synthesis of oxygenates from carbon monoxide/hydrogen mixtures on supported rhodium catalysts," *Applied Catalysis A: General* 88 (1992) 39–60.
- [49] B.C. McClaine, R.J. Davis, "Isotopic transient kinetic analysis of Cs-promoted Ru/MgO during ammonia synthesis," *Journal of Catalysis* 210 (2002) 387–396.
- [50] B.C. McClaine, R.J. Davis, "Importance of product readsorption during isotopic transient analysis of ammonia synthesis on Ba-promoted Ru/BaX catalyst," *Journal of Catalysis* 211 (2002) 379–386.
- [51] J.T. Calla, M.T. Bore, A.K. Datye, R.J. Davis, "Effect of alumina and titania on the oxidation of CO over Au nanoparticles evaluated by ¹³C isotopic transient analysis," *Journal of Catalysis* 238 (2006) 458–467.
- [52] J.T. Calla, R.J. Davis, "Oxygen-exchange reactions during CO oxidation over titania- and alumina-supported Au nanoparticles," *Journal of Catalysis* 241 (2006) 407–416.
- [53] T.W. Birky, J.T. Kozlowski, R.J. Davis, "Isotopic transient analysis of the ethanol coupling reaction over magnesia," *Journal of Catalysis* 298 (2013) 130–137.
- [54] N. Lohitharn, J.G. Goodwin, "An investigation using SSITKA of chain growth on Fe and FeMnK Fischer–Tropsch synthesis catalysts," *Catalysis Communications* 10 (2009) 758–762.
- [55] X.-R. Shi, J. Wang, K. Hermann, "CO and NO adsorption and dissociation at the β-Mo₂C(0001) surface: A density functional theory study," *The Journal of Physical Chemistry C* 114 (2010) 13630–13641.
- [56] J.W. Han, L. Li, D.S. Sholl, "Density functional theory study of H and CO adsorption on alkali-promoted Mo₂C Surfaces," *The Journal of Physical Chemistry C* 115 (2011) 6870–6876.

- [57] A.J. Medford, A. Vojvodic, F. Studt, F. Abild-Pedersen, J.K. Nørskov, "Elementary steps of syngas reactions on $\text{Mo}_2\text{C}(0\ 0\ 1)$: Adsorption thermochemistry and bond dissociation," *Journal of Catalysis* (2012).
- [58] J. Ren, C.-F. Huo, J. Wang, Y.-W. Li, H. Jiao, "Surface structure and energetics of oxygen and CO adsorption on $\alpha\text{-Mo}_2\text{C}(0\ 0\ 1)$," *Surface Science* 596 (2005) 212–221.
- [59] J.R. Kitchin, J.K. Nørskov, M.A. Barteau, J.G. Chen, "Trends in the chemical properties of early transition metal carbide surfaces: A density functional study," *Catalysis Today* 105 (2005) 66–73.
- [60] J.A. Schaidle, "carbide and nitride based catalysts for synthesis gas conversion," Ph.D., University of Michigan, 2011.
- [61] S. Wang, B. Temel, J. Shen, G. Jones, L.C. Grabow, F. Studt, T. Bligaard, F. Abild-Pedersen, C.H. Christensen, J.K. Nørskov, "Universal Brønsted–Evans–Polanyi relations for C–C, C–O, C–N, N–O, N–N, and O–O dissociation reactions," *Catalysis Letters* 141 (2011) 370–373.
- [62] J. Raskó, J. Kiss, "Infrared study of the adsorption of CO and CH_3 on silica-supported MoO_3 and Mo_2C catalysts," *Applied Catalysis A: General* 253 (2003) 427–436.
- [63] W. Wu, Z. Wu, C. Liang, X. Chen, P. Ying, C. Li, "In Situ FT-IR spectroscopic studies of CO adsorption on fresh $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst," *The Journal of Physical Chemistry B* 107 (2003) 7088–7094.
- [64] W. Wu, Z. Wu, C. Liang, P. Ying, Z. Feng, C. Li, "An IR study on the surface passivation of $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst with O_2 , H_2O and CO_2 ," *Physical Chemistry Chemical Physics* 6 (2004) 5603–5608.
- [65] H. Tominaga, M. Nagai, "Density functional theory of water-gas shift reaction on molybdenum carbide," *The Journal of Physical Chemistry B* 109 (2005) 20415–20423.
- [66] M. Nagai, K. Matsuda, "Low-temperature water–gas shift reaction over cobalt–molybdenum carbide catalyst," *Journal of Catalysis* 238 (2006) 489–496.
- [67] J.A. Schaidle, A.C. Lausche, L.T. Thompson, "Effects of sulfur on Mo_2C and $\text{Pt}/\text{Mo}_2\text{C}$ catalysts: Water gas shift reaction," *Journal of Catalysis* 272 (2010) 235–245.
- [68] N.M. Schweitzer, J.A. Schaidle, O.K. Ezekoye, X. Pan, S. Linic, L.T. Thompson, "High activity carbide supported catalysts for water gas shift," *Journal of the American Chemical Society* 133 (2011) 2378–2381.

- [69] J.S. Lee, S. Kim, K.H. Lee, I.-S. Nam, J.S. Chung, Y.G. Kim, H.C. Woo, "Role of alkali promoters in K/MoS₂ catalysts for CO-H₂ reactions," *Applied Catalysis A: General* 110 (1994) 11–25.
- [70] J.S. Lee, S.T. Oyama, M. Boudart, "Molybdenum carbide catalysts: I. Synthesis of unsupported powders," *Journal of Catalysis* 106 (1987) 125–133.
- [71] H.H. Hwu, J.G. Chen, "Surface Chemistry of Transition Metal Carbides," *Chemical Reviews* 105 (2005) 185–212.
- [72] J.A. Schaidle, N.M. Schweitzer, O.T. Ajenifujah, L.T. Thompson, "On the preparation of molybdenum carbide-supported metal catalysts," *Journal of Catalysis* 289 (2012) 210–217.
- [73] J. Sehested, C.J.H. Jacobsen, S. Rokni, J.R. Rostrup-Nielsen, "Activity and stability of molybdenum carbide as a catalyst for CO₂ reforming," *Journal of Catalysis* 201 (2001) 206–212.
- [74] H.C. Woo, I.S. Nam, J.S. Lee, J.S. Chung, Y.G. Kim, "Structure and Distribution of Alkali Promoter in K/MoS₂ Catalysts and Their Effects on Alcohol Synthesis from Syngas," *Journal of Catalysis* 142 (1993) 672–690.

Chapter 7.

Conclusions and future work

7.1 Conclusions

Molybdenum carbide nanoclusters (1-3 nm) were synthesized on various supports (MgO, α -Al₂O₃ and γ -Al₂O₃) using incipient wetness impregnation, followed by drying, calcination and temperature-programmed carburization with a mixture of H₂ and CH₄ (or C₂H₆). The high dispersion of the molybdenum carbide domains was verified by the lack of a diffraction pattern in XRD, the direct observation in electron microscopy and the coordination number of Mo–Mo derived from EXAFS.

The CO hydrogenation reactions were conducted in a fixed-bed reactor at typical conditions of 573 K, 30 bar and H₂/CO = 1. The supported-Mo₂C catalysts without co-existing Rb promoter typically demonstrated high selectivity towards hydrocarbons in CO hydrogenation. If not passivated, the unpromoted Mo₂C/ α -Al₂O₃ catalyst also demonstrated the capacity for alcohol formation, the rate of which was comparable to those on Rb-promoted Mo₂C/ α -Al₂O₃. Passivation with dilute O₂ introduced surface acidity on Mo₂C and decreased the activity of unpromoted Mo₂C/ α -Al₂O₃ in CO hydrogenation by about 40%. Passivation did not significantly affect the activity of the Rb-promoted Mo₂C/ α -Al₂O₃ catalyst. The acidity on the Mo₂C catalyst (introduced by the surface passivation) or on the support (like γ -Al₂O₃) substantially decreased the apparent alcohol formation rate on Mo₂C by catalyzing secondary dehydration reactions of alcohols to form ethers or hydrocarbons. The addition of Rb promoter to Mo₂C/Al₂O₃ gradually shifted the selectivity of the syngas reaction toward alcohols, primarily by

inhibiting hydrocarbon and ether formation. In addition, the added Rb promoted the formation of higher alcohols over methanol. Due to its basicity, MgO support also increased the alcohol selectivity on Mo₂C to some extent. Moreover, the alcohol selectivity over Mo₂C catalysts decreased significantly with CO conversion, suggesting that alcohols were probably the primary products in CO hydrogenation. In all cases, the selectivity of CO₂ was nearly the stoichiometric maximum, indicating the water-gas shift reaction is very favored at syngas reaction conditions.

X-ray absorption near edge spectroscopy followed the partial reduction of passivated supported Mo₂C at reaction conditions (573 K, 30 bar), confirmed the presence of partially oxidized Mo during reaction and observed structural modification of Rb₂CO₃ caused by Mo₂C. Also, the *ex situ* XANES of air-free Mo₂C/ α -Al₂O₃ samples (prepared in glovebox) directly confirm the partial oxidation of oxophilic Mo₂C caused by passivation with 1% O₂.

The IR spectrum of adsorbed CO revealed features at 2105 cm⁻¹ and 2014 cm⁻¹ on the unpromoted 2 wt.% Mo₂C/ γ -Al₂O₃ catalyst pretreated by 30 bar syngas at 573 K. With added Rb₂CO₃, the IR features of adsorbed CO on Mo₂C nanoclusters shifted substantially to lower frequencies (~200 cm⁻¹ shift from an unpromoted sample to a 10 wt.% Rb-promoted sample), which correlated with the enhanced alcohol selectivity. Results from DFT qualitatively reproduced the trends observed by IR spectroscopy and were used to interpret the various features (Mo-top and C-top CO adsorption). The interaction of the Rb promoter and the Mo₂C catalyst was facilitated by H₂O added during catalyst pretreatment, and presumably by *in situ* formation of H₂O during syngas reaction. According to DFT calculation, water can easily dissociate on the representative

Mo₂C surface, forming OH groups, which probably possess decent acidity. The basic Rb₂CO₃ promoter may interact with Mo₂C by neutralizing the surface acidity, and hence preventing the potential secondary reaction paths and preserving the alcohols as primary products in CO hydrogenation, which can be reflected in the corresponding changes of product distribution in catalytic syngas conversion.

Bimetallic Co-Mo₂C/ α -Al₂O₃ catalysts were prepared by co-precipitation of the Co and Mo precursors, followed by drying, calcination, carburization and passivation. The addition of Co to Rb-promoted Mo₂C/ α -Al₂O₃ enhanced the overall reactivity of Mo₂C catalysts, promoted the formation of higher alcohols over methanol, and effectively reduced the loss of alcohol selectivity at high CO conversion. The results from X-ray absorption spectroscopy revealed that the Co metal and Mo carbide domains on alumina, although very highly dispersed, were more reduced than their corresponding monometallic samples. Although direct interactions between Co and Mo were not observed spectroscopically, the reactivity patterns reported here clearly suggest a molecular-level interaction between Co and Mo.

The multi-product SSITKA revealed that the intrinsic TOF on the relatively “slow” Mo₂C catalysts was in fact comparable to those on other active elements in CO hydrogenation such as Fe and Rh. Consequently, the small coverage of the reactive intermediates on Mo₂C surface was found to be the reason for its low apparent activity in CO hydrogenation. The addition of Rb₂CO₃ did not change the intrinsic rate of CO hydrogenation on Mo₂C, but substantially reduced the coverage of the reactive intermediates, which provided direct evidence for the previously-speculated site-blockage mechanism of the alkali metal promoter on the Mo₂C catalyst. The SSITKA also

demonstrated that the rate of the water-gas shift reaction on Mo_2C was naturally faster than that of CO hydrogenation, which is consistent with the ever-present CO_2 selectivity that was close to the stoichiometric maximum in Mo_2C -catalyzed syngas reaction.

In summary, given the abundant fundamental understanding on the nature of Mo_2C catalyst obtained from this study, promoted Mo_2C is perhaps not among the optimal choices for catalytic conversion of syngas towards higher alcohols because of:

1. Limited higher alcohol selectivity (< 50 % on a CO_2 -free basis);
2. A low coverage of active sites in CO hydrogenation;
3. Rapid water-gas shift compared to CO hydrogenation (which unproductively consumes CO)

Figure 7.1 Syngas conversion (via methanol) towards C2-C4 olefins and ethanol.

7.2 Future Work

Given the difficulty in suppressing methanation and water-gas shift reactions, the direct syngas conversion towards desirable C2+ products on Mo-based catalysts is still problematic. In fact, the competitive processes via a methanol intermediate, although multi-step, are able to give almost 100% carbon efficiency from syngas, such as UOP's MTO [1] and Celanese's TCX [2], as shown in Figure 7.1.

Indeed, it is difficult to obtain an as high carbon efficiency in an alternative process, but there is room to improve the design of the Mo-based catalysts for selective conversion of syngas, as are suggested below.

7.2.1 Single-phase molybdenum-based bimetallic carbide catalysts for CO hydrogenation

Since the mixed-phase Co–Mo₂C did not significantly improve Mo₂C in higher alcohol synthesis [1], a reasonable alternative would be to use Mo₂C as catalyst support for selective syngas conversion. In fact, Mo₂C-supported Co and Ru catalysts have been explored for Fischer–Tropsch synthesis [3]. Since Thompson and co-workers had reported superior activity of Pt/Mo₂C in the water-gas shift reaction compared to Mo₂C [4], such synergy may also occur in CO hydrogenation. Unfortunately, according to Schaidle [5], Mo₂C-supported metal catalysts were not bifunctional in nature for CO hydrogenation, where the reaction seemed to take place on the supported metal sites and Mo₂C sites independently.

Single-phase Co–Mo and Fe–Mo bimetallic carbides, however, may be worth exploring. The phase-pure bulk and supported Co₃Mo₃C (Fe₃Mo₃C) can be synthesized by one-step [6,7] or two-step [8,9] topotactic methods from the mixed oxide via Co₃Mo₃N (Fe₃Mo₃N), or by carbothermal hydrogen reduction from carbon-supported mixed oxide [10]. The catalytic conversion of syngas on alkali-metal-promoted Mo₂C always produces substantial undesired C1 products (CH₄, CH₃OH and CO₂). The Co (or Fe) component may shift the selectivity towards C2+ products, given its stronger chain growth capacity and lower water-gas-shift activity than Mo₂C. Also, the phase uniformity may bring the synergetic effect between the two metals.

Figure 7.2 Product distribution predicted by the Anderson–Schulz–Flory model [11].

7.2.2 Direct conversion of syngas to C2-C4 olefins

As an alternative resource of C2-C4 olefins (typically from fluid catalytic cracking), methanol-to-olefin technology first produces methanol from syngas, then converts methanol into olefins [1]. Since syngas may have the potential for the direct production of olefins, there is still space to simplify the process from syngas to olefins. Recently, de Jong and co-workers reported an effective Fe-based catalyst for this process [11], where they claimed that the maximum selectivity achievable for the C2-C4 fraction is approximately 50 wt.%, with a chain growth probability (α) between 0.4 and 0.5, as shown in Figure 7.2. In fact, alkali metal promoted Mo₂C has been studied for selective syngas conversion towards light olefins at ambient pressure [12]. Moreover, with cobalt being added to Mo₂C, the chain growth probability on Mo₂C in CO hydrogenation can be increased from about 0.35 to about 0.5, and the water-gas shift activity can be suppressed too some extent, as described earlier in Chapter 5. Given that cobalt and molybdenum were not optimally incorporated, there is still great potential to optimize the synthesis of bimetallic carbides and the reaction conditions that would lead to better selectivity of C2-C4 olefins and to reduce formation of C1 products (CH₄ and CO₂) in CO hydrogenation.

References of Section 7.2

- [1] M. Stöcker, “Methanol-to-hydrocarbons: catalytic materials and their behavior,” *Microporous and Mesoporous Materials* 29 (1999) 3–48.
- [2] A.H. Tullo, “Celanese takes an ethanol plunge,” *Chemical & Engineering News* 89 (2011) 20–21.
- [3] A. Griboval-Constant, J.-M. Giraudon, G. Leclercq, L. Leclercq, “Catalytic behavior of cobalt or ruthenium supported molybdenum carbide catalysts for FT reaction,” *Applied Catalysis A: General* 260 (2004) 35–45.
- [4] N.M. Schweitzer, J.A. Schaidle, O.K. Ezekoye, X. Pan, S. Linic, L.T. Thompson, “High activity carbide supported catalysts for water gas shift,” *Journal of the American Chemical Society* 133 (2011) 2378–2381.
- [5] J.A. Schaidle, “Carbide and nitride based catalysts for synthesis gas conversion,” Ph.D., University of Michigan, 2011.
- [6] X.-H. Wang, M.-H. Zhang, W. Li, K.-Y. Tao, “A simple synthesis route and characterisation of $\text{Co}_3\text{Mo}_3\text{C}$,” *Dalton Transactions* (2007) 5165–5170.
- [7] X.-H. Wang, M.-H. Zhang, W. Li, K.-Y. Tao, “Synthesis and characterization of cobalt–molybdenum bimetallic carbides catalysts,” *Catalysis Today* 131 (2008) 111–117.
- [8] S. Korlann, B. Diaz, M.E. Bussell, “Synthesis of bulk and alumina-supported bimetallic carbide and nitride catalysts,” *Chemistry of Materials* 14 (2002) 4049–4058.
- [9] S. Alconchel, F. Sapiña, E. Martínez, “From nitrides to carbides: topotactic synthesis of the η -carbides $\text{Fe}_3\text{Mo}_3\text{C}$ and $\text{Co}_3\text{Mo}_3\text{C}$,” *Dalton Transactions* (2004) 2463–2468.
- [10] C. Liang, W. Ma, Z. Feng, C. Li, “Activated carbon supported bimetallic CoMo carbides synthesized by carbothermal hydrogen reduction,” *Carbon* 41 (2003) 1833–1839.
- [11] H.M. Torres Galvis, J.H. Bitter, C.B. Khare, M. Ruitenbeek, A.I. Dugulan, K.P. de Jong, “Supported iron nanoparticles as catalysts for sustainable production of lower olefins,” *Science* 335 (2012) 835–838.
- [12] K.Y. Park, W.K. Seo, J.S. Lee, “Selective synthesis of light olefins from syngas over potassium-promoted molybdenum carbide catalysts,” *Catalysis Letters* 11 (1991) 349–356.

Appendix A.

Upgrade of steady-state isotopic transient kinetic analysis system for the multi-product purpose

The information of the construction of multi-product SSITKA is summarized in

Table A.1.

Table A.1 Upgrades of conventional SSITKA for multi-product purposes

Part	Quant.	Brand (part number)	Specification
34-port valve	1	Valco (EMT2CST16MWE)	N/A
Sample loop	16	Valco (SL250CSTP)	250 μ L
Back-up sample loop	16	Valco (SL50CSTP)	50 μ L
Gas chromatography	1	SRI (8610C)	Self-modified sampling valve Max T: 220 $^{\circ}$ C FID, TCD
GC packed column	1	HayeSep-D	3.8 mm ID, 1.8 m length
GC PLOT column	2	Restek (79716-273)	SS PLOT 3.5'' coil Max T: 250 $^{\circ}$ C
Methanizer	1		3/8'' OD
Methanation catalyst	5 g	Sigma-Aldrich (311324)	5 wt.% Pt/ Al_2O_3 40-100 mesh, pelletized

Appendix B.

List of Publications at University of Virginia

- [1] H. Shou, R.J. Davis, “Multi-product steady-state isotopic transient kinetic analysis of CO hydrogenation over supported molybdenum carbide,” to be submitted to *Journal of Catalysis*.
- [2] H. Shou, L. Li, D. Ferrari, D.S. Sholl, R.J. Davis, “Use of infrared spectroscopy and density functional theory to study the influence of rubidium on alumina-supported molybdenum carbide catalyst for higher alcohol synthesis from syngas,” *Journal of Catalysis* 299 (2013) 150–161.
- [3] H. Shou, D. Ferrari, D.G. Barton, C.W. Jones, R.J. Davis, “Influence of passivation on the reactivity of unpromoted and Rb-promoted Mo₂C nanoparticles for CO hydrogenation,” *ACS Catalysis* 2 (2012) 1408–1416.
- [4] H. Shou, R.J. Davis, “Reactivity and *in situ* X-ray absorption spectroscopy of Rb-promoted Mo₂C/MgO catalysts for higher alcohol synthesis,” *Journal of Catalysis* 282 (2011) 83–93.
- [5] K. Yin ^[+], H. Shou ^[+], D. Ferrari, C.W. Jones, R.J. Davis, “Influence of cobalt on rubidium-promoted alumina-supported molybdenum carbide catalysts for higher alcohol synthesis from syngas,” *Topics in Catalysis* (2013), accepted. ^[+] Equal contribution.
- [6] M.R. Morrill, N.T. Thao, H. Shou, R.J. Davis, D.G. Barton, D. Ferrari, P.K. Agrawal, C.W. Jones, “Origins of unusual alcohol selectivities over mixed MgAl oxide supported K/MoS₂ catalysts for higher alcohol synthesis from syngas,” *ACS Catalysis* (2013), in review.
- [7] L. Li, M.R. Morrill, H. Shou, D.G. Barton, D. Ferrari, R.J. Davis, P.K. Agrawal, C.W. Jones, D.S. Sholl, “On the relationship between Mo *K* edge energies and DFT computed partial charges,” *The Journal of Physical Chemistry C* 117 (2013) 2769–2773.
- [8] M.R. Morrill, N.T. Thao, P.K. Agrawal, C.W. Jones, R.J. Davis, H. Shou, D.G. Barton, D. Ferrari, “Mixed MgAl oxide supported potassium promoted molybdenum sulfide as a selective catalyst for higher alcohol synthesis from syngas,” *Catalysis Letters* 142 (2012) 875–881.