Abstract

A series of carbon-supported bimetallic PtSn catalysts having various Pt/Sn molar ratios was prepared and tested in the oxidation of 1,6-hexanediol with 1 MPa dioxygen at 343 K in aqueous solvent. The PtSn/C catalysts, which were initially reduced with sodium borohydride, did not produce Pt-Sn alloy particles. Instead, the catalysts were composed of SnO_x moieties that were well-dispersed on the surfaces of the carbon support and the Pt nanoparticles. Subsequent treatment in H₂ at 673 K induced Pt-Sn alloy formation. Whereas addition of SnO_x to the Pt nanoparticles promoted the initial 1,6-hexanediol oxidation rate by 39%, the formation of Pt-Sn alloy particles decreased the initial rate. Under 1,6-hexanediol oxidation conditions, however, the Pt-Sn alloy phase separated, leading to the recovery of the catalytic activity. No significant change of product distribution was observed on bimetallic PtSn catalysts, regardless of the composition and structure.

Key Words:

Pt; Sn; Heterogeneous bimetallic catalysts; Alcohol oxidation; Pt-Sn alloy; Pt-SnO_x interface; Catalyst restructuring.

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1. Introduction:

Bimetallic catalysts consisting of Pt and Sn have been studied extensively in 12,13 hydrogenation ¹⁻⁶, hydrocarbon reforming ⁷⁻¹¹, CO oxidation and alcohol electro-oxidation ¹⁴⁻³² because they have demonstrated enhanced activity, selectivity and/or stability, compared to monometallic Pt catalysts. The addition of Sn to Pt presumably leads to the formation of unique active sites, specifically those associated with Pt-Sn alloys and Pt-SnO_x interfaces. When Pt and Sn are in close proximity, an electronic interaction between the components and modification of Pt ensembles can alter the catalytic performance. A large body of work has reported on the promotional effects of Sn, which are attributed mainly to a change in the adsorption energy of certain molecules ^{6,12,14,20,25,27,28,33,34}, a modified rate of C-C bond cleavage reactions ^{1,20,27,30}, the efficient removal of strongly adsorbed poisons 17,25,30 and the introduction of acid sites 8,10,11 and/or O₂ adsorption site 12 . For example, in the hydrogenation of α,β -unsaturated aldehyde, the dilution of the Pt ensembles by SnO_x hindered the adsorption of C=C groups relative to C=O groups, thus favoring preferential hydrogenation of the aldehyde to produce an unsaturated alcohol with high selectivity ²⁻⁶. The added SnO_x can also act as a Lewis acid site in hydrocarbon reforming reactions, which leads to a significant increase in activity^{8,11}. In the oxidation of CO, Michalak *et al.* attributed the promoted activity over a PtSn bimetallic catalyst to the Pt-SnO_x interface 12 . The SnO_x

provides an active site for O₂ adsorption while Pt is covered with strongly adsorbed CO.

In the electro-oxidation of alcohols, supported bimetallic PtSn electro-catalysts exhibited higher activity and stability compared to monometallic Pt electro-catalysts ^{15,19,26,32}. Although the addition of Sn often increases the activity of Pt by a factor of $2 - 10^{18,19,21,24,27}$, Biallozor al. reported steady-state density with et а current а poly(3,4-dioxyethylenethiophene)-supported PtSn catalyst that was 2 orders of magnitude greater than that of Pt during the electro-oxidation of methanol¹⁵. Ishikawa *et al.* studied the oxidation of methanol on Pt-Sn alloy using density-functional theory (DFT) and suggested that the adsorption of both methanol and CO was weaker on the Pt-Sn alloy surface ¹⁴, which may account for the faster rate and greater stability of the alloy. A lower adsorption energy of methanol and ethanol on the surface of Pt-Sn alloy was also observed in a temperature-programmed desorption (TPD) study ³⁵, which is consistent with DFT results. In addition to Pt-Sn alloy formation, the presence of SnOx adjacent to Pt ensembles is also thought to play an important role in the electro-oxidation of alcohols. Castro Luna et al. report that catalysts containing the largest amount of SnO_x exhibited the best performance in ethanol oxidation ³¹. The superior activity of a SnO_x-promoted catalyst was attributed to an enhancement in the dissociative adsorption of alcohol in the low potential region ^{20,25}. Furthermore, Pergato *et al.* and Rato *et al.* proposed that SnO_x might promote the removal of adsorbed CO and other strongly-adsorbed remnants from C-C bond cleavage reaction ^{28,29}.

One potential complication with bimetallic catalysts is that their structure may change during the reaction. Whereas many studies correlate the catalytic performance of bimetallic particles to the structure of the as-prepared catalysts, changes in the structure of PtSn catalysts have been reported under both hydrogenation and oxidation conditions ^{12,15,25,36}. To understand the promotional effect of Sn on Pt catalysts, it is therefore important to examine the influence of the reaction environment on catalyst structure.

The present work explores the influence of added Sn on Pt catalysts for the selective oxidation of 1,6-hexanediol (HDO). Oxidation of HDO can produce adipic acid (DA), which is one of the top ten commodity chemicals by volume ³⁷ and is widely used in the synthesis of nylon-6,6, for carpet fibers, tire reinforcements, upholstery and apparel ³⁸. Adipic acid is currently produced from a mixture of cyclohexanol and cyclohexanone via nitric acid oxidation, which emits a considerable amount of nitrous oxide ^{39,40}. One promising environmentally-friendly route to produce adipic acid begins with hexose (glucose and fructose), derived from biomass. A high yield of 5-hydroxymethylfurfural (HMF) can be obtained from the dehydration of hexose, which can then be efficiently converted to HDO ^{41,42} and subsequently oxidized to adipic acid. Among supported metal catalysts, Au has demonstrated the highest activity for polyol oxidation under basic conditions ⁴³. The use of base, however, is not attractive because of the cost involved in neutralizing the product stream to recover the free acid. Oxidation of alcohol over Pt does not require high concentration of base for the diacid production ^{44,45}. Unfortunately, severe deactivation can be observed during the oxidation of HDO over Pt catalysts, which was tentatively attributed to strongly adsorbed species generated from C-C bond cleavage ⁴⁶. Since the addition of Sn to Pt may enhance the removal of strongly adsorbed species on the surface, PtSn bimetallic catalysts are promising candidates for the selective oxidation of HDO.

In this study, a series of carbon-supported PtSn bimetallic catalysts was prepared and

evaluated in the oxidation of HDO in liquid water by O_2 without the addition of base. Extensive characterization of the catalysts before and after reaction was performed to enable correlation of performance to catalyst structure and composition.

2. Materials and Methods

2.1. Catalyst preparation

All carbon-supported Pt and PtSn bimetallic catalysts were synthesized using a NaBH₄ reduction method. The loading of Pt was always 3 wt% while the amount of Sn was varied. The Pt and Sn precursors used were H₂PtCl₄ and Na₂SnO₃ (Sigma-Aldrich), respectively, and activated carbon (Norit, Ultra SX) was used as the support. Activated carbon (2 g) was dispersed ultrasonically in 150 cm³ of a 1 mM NaOH solution (Aldrich) for 1 h. The desired amount of Na₂SnO₃ and 0.3 mmol of the H₂PtCl₄ were dissolved separately in 25 cm³ of 1 mM NaOH and added to the carbon slurry with vigorous stirring. The Pt and Sn precursors were reduced by the rapid addition of 10 cm³ of a freshly prepared 0.3 M NaBH₄ solution (Aldrich). The slurry was left under vigorous stirring for 2 h. Finally, the slurry was filtered, washed thoroughly with distilled, deionized water and dried in air at room temperature. These catalysts are denoted as *x*PtySn/C, where *x*:*y* is the nominal molar ratio of Pt to Sn.

The *x*PtySn/C catalysts were then heated to 673 K at 1 K min⁻¹ under 100 cm³ min⁻¹ of flowing dihydrogen (GT&S 99.999%) and reduced for 2 h. These catalysts are denoted as *x*PtySn/C-H. To study the potential structural and compositional changes of *x*PtySn/C-H, catalysts were recovered after HDO oxidation, washed with distilled and deionized water and dried at room temperature. The used catalyst after reaction was denoted as *x*PtySn/C-H-R. In

addition, the 3Pt3Sn/C catalyst was also heated to 473 K at 1 K min⁻¹ under 100 cm³ min⁻¹ of flowing dihydrogen and treated for 4 h, giving a sample denoted as 3Pt3Sn/C-473H.

2.2. Catalyst characterization

The fraction of available Pt on the surface of a catalyst was estimated by H_2 chemisorption using a Micromeritics ASAP 2020 automated adsorption analyzer. The catalysts were heated to 473 K at 4 K min⁻¹ under flowing H₂ (GT&S 99.999%) and reduced for 2 h. The samples were then evacuated for 2 h at 473 K before being cooled to 308 K for analysis in the pressure range of 1.33 – 59.9 KPa. The amount of exposed Pt was evaluated by the total amount of H₂ adsorbed, extrapolated to zero pressure, assuming a stoichiometry (H/Pt_{surf}) equal to unity.

The X-ray diffraction (XRD) patterns were recorded using a PANalytical X'Pert Pro MPD (Multi-Purpose Diffractometer) instrument with Cu K α radiation (45 kV, 40 mA) and scanning of 2 θ from 20 ° to 80 ° with a step size of 0.0025 ° at a rate of 0.125 ° min⁻¹.

Transmission electron microscopy (TEM) was performed on a JEOL 2000 operating at 200 kV to obtain the metal particle size distribution of the catalysts. The high-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) were performed on an FEI Titan 80-300 operating at 300 kV that is equipped with a Gatan 794 Multi-scan Camera (EFTEM) and an energy dispersive spectrometer for elemental X-ray analysis. To prepare a sample, ~1 mg of catalyst was suspended in 10 cm³ of ethanol by agitating the mixture for 30 min in a sonication bath. A copper grid with a holey carbon film was dipped into the solution to capture the particles and the ethanol was thoroughly

evaporated before microscopy.

The X-ray photoelectron spectroscopy (XPS) was carried out at the Nanomaterials Core Characterization Facility of the Virginia Commonwealth University (Richmond, VA), utilizing a Thermo Scientific ESCALAB 250 spectrometer equipped with a focused monochromatic Al Ka X-ray radiation source (1486.6 eV) and a hemispherical analyzer with a 6-element multichannel detector. The incident X-ray beam was 45 ° off normal to the sample while the X-ray photoelectron detector was normal to the sample. A large area magnetic lens with a 500 µm spot size in constant analyzer energy mode was utilized with a pass energy of 20 eV for region scans. Charge compensation was employed during data collection with an internal electron flood gun (2 eV) and a low energy external Ar ion flood gun. All spectra were deconvoluted with a curve fitting routine in CasaXPS software. The background was corrected using the linear method and the binding energy of the C 1s peak assigned at 284.5 eV, which is attributed to the support, was used to reference the peak positions ¹⁹. The integral of each peak was calculated after subtracting the background and fitting with a combination of Lorentzian asymmetric curves of variable proportion. The Pt:Sn surface atomic ratios were calculated from peak areas normalized by atomic subshell photoionization cross sections of the corresponding element ⁴⁷. The detailed XPS curve fitting parameters are listed in Table **1**.

Table 1. XPS curve fitting parameters used in Casa XPS(Version 2.3.16)

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Species	Pt(0)	Pt(II)	Sn(0)	Sn(II,IV)
Position (eV)	70.5 - 71.5	71.5 - 73.0	484.5 - 486.0	486.0 - 487.5
FWHM	0.3 – 1.5	1 - 2.5	0.3 – 1.5	1 – 2.5
Line shape	LA(1.2,85,70)	LA(1.2,85,70)	LA(1.2,1.5,5)	LA(1.2,1.5,5)

Elemental analysis was used to determine some of the Pt and Sn weight loadings on the supported PtSn bimetallic catalysts and the concentration of leached Pt and Sn in the reaction solution after 4 h of HDO oxidation. Elemental analysis was performed by Galbraith Laboratories (2323 Sycamore Drive, Knoxville, TN 37921) using inductively coupled plasma – atomic emission spectroscopy (ICP-AES).

2.3. 1,6-Hexanediol (HDO) oxidation reactions

Semi-batch alcohol oxidation reactions were performed in a 50 cm³ Parr Instrument Company 4592 batch reactor with a 30 cm³ glass liner. An aqueous 1 mM HDO solution and 0.0132 g catalyst were added to the glass liner. The glass liner was inserted into the reactor, sealed, purged with He (GT&S, 99.999%), heated to 343 K and held for 20 min. The reaction was initiated by pressurizing the reactor with 1 MPa of O₂ (GT&S, 99.993%). Liquid samples were periodically removed and the catalyst was filtered using a 0.2 µm PTFE filter before product analysis with a Waters e2695 high performance liquid chromatograph (HPLC). The HPLC was equipped with refractive index detector. Product separation in the HPLC was accomplished on an Aminex HPX-87H column (Bio-Rad) operating at 318 K with an aqueous 5 mM H₂SO₄ solution as mobile phase flowing at 5 cm³ min⁻¹. The retention times and calibration curves were determined by injecting known concentrations of standards. Carbon balances were always greater than 90%.

The maximum O_2 transport rate from the gas phase to the aqueous phase in the pressurized reaction system was determined by the sulfite oxidation method ⁴⁸. The amount of catalyst added to the reactor was chosen so that the alcohol oxidation rate would not be

limited by O_2 mass transfer from the gas to the liquid. Selectivity to a specific product is defined as moles of that product formed divided by moles of all products produced. The initial turnover frequency (TOF) [mol alcohol converted (mol metal_{surface})⁻¹ s⁻¹] was calculated from the initial conversion of the alcohol, usually within the first 15 min of the reaction. Because Sn is not active for oxidation catalysis, some estimate of surface Pt is needed to calculate a turnover frequency. As a first approximation, we normalized the initial TOF of HDO conversion to the estimated fraction of Pt atoms that can be exposed to the surface, which is determined from the inverse of surface weighted average metal diameter by TEM ^{49,50}.

3. Results

3.1. Characterization of bimetallic PtSn catalysts

The mean particle sizes of bimetallic PtSn catalysts are reported in Table 2. The bright field TEM images for PtSn/C and PtSn/C-H showed a fairly narrow size distribution of nanoparticles on the carbon support (Figures. 1 and 2). Although some large nanoparticles were observed (~10 nm), the vast majority of particles was in the range of 2 to 5 nm (Fig. 2). The number average particle diameter of catalysts with different Pt to Sn ratio and various treatments ranged from 2.9 nm to 3.8 nm, as summarized in Table 2. The similarity of the particle sizes in this study enabled us to eliminate particle size as a factor that might influence the observed catalytic performance. A surface-weighted average metal particle diameter of PtSn bimetallic catalysts is also presented in Table 2. The surface-weighted average diameter was used to estimate the potential fraction of exposed Pt metal sites on the surface, which

was subsequently used to calculate a lower bound on the turnover frequency (TOF) and the number of catalytic turnovers. For monometallic Pt catalysts, the fraction of exposed metal atoms, or dispersion, can also be determined by H_2 chemisorption. As summarized in Table 2, the dispersion of Pt (H/Pt) was 0.33 and 0.31 for 3Pt/C and 3Pt/C-H, respectively. The calculated Pt surface fraction of 3Pt/C and 3Pt/C-H, determined from TEM, was 0.20, which is slightly lower than the dispersion determined by chemisorption. This discrepancy is probably the result of small nanoparticles (< 1 nm) that were not counted by TEM, which is limited by the resolution of method, whereas H_2 chemisorption includes all nanoparticles.



Figure 1. Bright field TEM images of PtSn/C and PtSn/C-H.



Figure 2. Particle size distributions obtained from TEM of PtSn/C and PtSn/C-H.

Table 2. Summary of results from H_2 chemisorption and electron microscopy of carbon supported bimetallic PtSn catalysts.

	D+a	Sma		Avg	Surface-weighted	Fraction of
Catalysts		SII	H/Pt ^b	diameter ^c	Avg diameter ^d	surface
	(wt%) (wt			(nm)	(nm)	atoms ^e
3Pt/C ^f	3.0	_	0.33	3.8 ±0.9	4.9	0.20
3Pt1Sn/C ^f	3.0	0.6	0.19	2.9 ± 0.9	4.7	0.21
3Pt3Sn/C ^f	3.0	1.8	0.16	3.7 ± 1.0	6.1	0.16
3Pt6Sn/C ^f	3.0	3.7	0.11	3.1 ± 0.7	4.2	0.24
3Pt/C-H ^f	3.0	_	0.31	3.7 ± 1.1	5.0	0.20
3Pt1Sn/C-H ^f	3.0	0.6	0.16	2.8 ± 0.8	5.0	0.20
3Pt3Sn/C-H ^f	3.0	1.8	0.13	3.8 ± 1.0	7.4	0.14
3Pt6Sn/C-H ^f	3.0	3.7	0	3.2 ± 0.9	5.6	0.18
3Pt3Sn/C-H-R ^g	3.0	1.8	N/A	3.6 ±0.9	6.6	0.15
3Pt6Sn/C-H-R ^g	3.0	3.7	N/A	3.1 ±0.9	4.9	0.20

a: Nominal weight loading.

b: Determined from H₂-chemisorption, assuming a nominal loading of Pt.

c: Fitted from TEM using Cauchy-Lorentz distribution.

d: Obtained from TEM by calculating $\Sigma d^3 / \Sigma d^2$.

f: Catalysts prior to reaction.

g: Catalysts collected after 4 h of 1,6-hexanediol oxidation reaction.

The X-ray diffraction patterns of PtSn/C are shown in Fig. 3a. The peak at 26.6° was attributed to graphitic carbon (JCPDS 23-0064) while the peaks at 39.6°, 45.9° and 67.5° were attributed to the (111), (200) and (220) features of Pt (JCPDS 04-802). As an increasing amount Sn was added, there was no obvious shift in the XRD patterns compared to monometallic Pt catalyst (Fig. 3a). Evidently, Pt-Sn alloys were not formed when the bimetallic samples were prepared by NaBH₄ reduction, without additional treatment in H₂. Because the diffraction patterns of Sn (JCPDS 04-0673), SnO (JCPDS 06-0395) and SnO₂ (JCPDS 21-1250) were not observed, we conclude that Sn species were well dispersed over the carbon support and/or Pt nanoparticles. The XRD patterns of the PtSn/C-H, shown in Fig. 3b, indicate alloy formation from Pt and Sn (Pt₃Sn and PtSn) resulting from treatment in H₂ at 673 K. With a small amount of added Sn, the Pt (111), (200) and (220) peaks shifted to lower angle for 3Pt1Sn/C-H. In particular, the (220) feature moved from 67.5° for 3Pt/C-H to 65.9° for 3Pt1Sn/C-H catalyst, indicating the formation of a Pt₃Sn alloy (JCPDS 35-1360). Because the XRD patterns exhibited features that appeared between the diffraction patterns of Pt and Pt₃Sn alloy, we propose that 3Pt1Sn/C-H contained a mixture of Pt, Pt₃Sn and other Sn species ^{19,21}. When the ratio of Sn to Pt was equal to or greater than one, diffraction features of the 1:1 PtSn alloy were observed. For 3Pt3Sn/C-H and 3Pt6Sn/C-H, new peaks appeared at 41.8° and 44.1°, which were attributed to the PtSn alloy (JCPDS 25-614). The significant difference between the XRD patterns in Fig 3a and Fig 3b clearly demonstrate the importance

of H_2 treatment at elevated temperature to enhance Pt-Sn interaction and to form Pt-Sn alloy nanoparticles. The crystallite size of the monometallic Pt particles can also be calculated from XRD results using the Scherrer equation. For 3Pt/C and 3Pt/C-H, the crystallite sizes were estimated to be 4.7 nm and 5.2 nm, respectively, which were slightly larger than the average diameters evaluated from TEM because the crystallite size determined by XRD is a volume-weighted average diameter ⁴⁹ that is usually shifted to higher value. Nevertheless, the size of Pt nanoparticles determined from H₂ chemisorption, TEM and XRD was relatively consistent.

To probe the surface composition of the bimetallic nanoparticles, H₂ chemisorption and XPS were utilized. The H/Pt ratios for bimetallic PtSn catalysts determined by chemisorption are listed in Table 2. For both PtSn/C and PtSn/C-H, the ratio of adsorbed hydrogen atoms to total platinum atoms decreased significantly, with increasing amounts of Sn. The H/Pt ratio of 3Pt/C and 3Pt/C-H were 0.33 and 0.31, whereas the H/Pt ratio decreased to 0.11 for 3Pt6Sn/C and 0 for 3Pt6Sn/C-H. As revealed by TEM, the drop in H₂ chemisorption on the samples was not the result of larger particles being formed. Instead, Sn species (Sn metal or Sn oxide) were present on the surfaces of Pt-Sn nanoparticles and block Pt sites from the uptake of hydrogen, a phenomenon that has also been observed by others with bimetallic PtSn catalysts ^{2,5}.



Figure 3. XRD patterns of a) PtSn/C and b) PtSn/C-H.



Figure 4. a) XRD pattern of 3Pt3Sn/C-473H and b) reaction profile of 1,6-hexanediol oxidation over 3Pt3Sn/C-473H with 1 MPa O2 at 343 K.

For H₂ chemisorption measurements, the catalysts were first pretreated in H₂ at 473 K, which might have altered the structure of PtSn/C, compared to those prepared only by reduction of NaBH₄. To investigate the potential influence of pretreatment during the H₂ chemisorption experiment, 3Pt3Sn/C was exposed to flowing H₂ at 473 K for 4 h, characterized by XRD and tested in HDO oxidation reaction (the results are presented in Fig. 4). The XRD pattern revealed that the structure of 3Pt3Sn/C-473H was similar to that of 3Pt3Sn/C before H₂ treatment. No indication of Pt-Sn alloy formation was observed by XRD. In addition, the reaction profile during HDO oxidation over 3Pt3Sn/C was unaffected by the H₂ treatment at 473 K (Fig. 4b and Fig. 5b). We therefore conclude that the 473 K pretreatment for H₂ chemisorption did not significantly influence the morphology of PtSn/C in the way that treatment at 673 K in H₂ did.



Figure 5. Reaction profiles for 1,6-hexanediol oxidation with 1 MPa oxygen at 343 K over carbon supported bimetallic PtSn catalysts in the range of a) 0 - 60 min and b) 0 - 4 h and over Pt-Sn/C-H in the range of c) 0 - 60 min and d) 0 - 4 h.

The XPS analysis of 3Pt3Sn/C and 3Pt3Sn/C-H revealed the enrichment of Sn species on the surface, which is consistent with the H₂ chemisorption results. As shown in Table 3, the ratio of Sn to Pt was 1.3 and 2.1 for 3Pt3Sn/C and 3Pt3Sn/C-H, respectively. The increase in the ratio of Sn to Pt after H₂ treatment may suggest an enhanced interaction of Sn and Pt atoms. The XPS analysis also provides information on the oxidation states of Pt and Sn. The Pt 4f_{7/2} and Sn 3d_{5/2} spectra of 3Pt3Sn/C and 3Pt3Sn/C-H are shown in Fig. 6, and the fitting results are summarized in Table 3. The Pt 4f_{7/2} features were fitted with two oxidation states: Pt(0) and Pt(II) at ~71 eV and ~73 eV, respectively. The Sn $3d_{5/2}$ spectra were fitted with Sn(0) and Sn (II, IV) at ~486 eV and ~487 eV, respectively. Because the difference in the binding energy of Sn(II) and Sn(IV) is only 0.2 eV⁵, it was not possible to differentiate between them by curve fitting. Thus, only one peak was fitted in the analysis of the oxidized Sn. For 3Pt3Sn/C, 83% of the Pt was metallic. Conversely, the majority of Sn (78%) was oxidized to Sn(II) or Sn(IV). After the treatment in H₂ (3Pt3Sn/C-H), the small contribution from Pt(II) disappeared so that nearly all of the Pt was metallic. The metallic Sn(0) content increased from 22% to 32% by treatment of the sample in the H₂. Evidently, treatment in H₂ at 673 K reduced all of the Pt but only partially reduced the Sn, which is consistent with results reported by Ruiz-Mart nez et al.⁵. The reduction of Pt and Sn oxides at 673 K in H₂ is correlated to the formation Pt-Sn alloy observed by XRD. Chang et al. reported that the reduction of bimetallic Pt-Sn occurs below 600 K while the reduction of Sn oxide alone requires over 700 K²⁰. Because the catalysts were treated in H₂ at 673 K, it is quite likely that Sn species adjacent to Pt were reduced to form a Pt-Sn alloy whereas isolated Sn oxide on the support remained unreduced.



Figure 6. The Pt $4f_{7/2}$ X-ray photoemission spectra of a) 3Pt3Sn/C, c) 3Pt3Sn/C-H and e) 3Pt3Sn/C-H-R (collected after 4 h of HDO oxidation) and the Sn $3d_{5/2}$ spectra of b) 3Pt3Sn/C, d) 3Pt3Sn/C-H and f) 3Pt3Sn/C-H-R (collected after 4 h of 1,6-hexanediol oxidation). The grey dots are the actual data points and the red solid lines are the results from peak fitting.

	Binding Energy (eV)				$\mathbf{D}_{\mathbf{f}}(0)$	D 4(II)	$\mathbf{S}_{m}(0)$	Sn(II,	Sn/Pt ^d
Catalysts	Pt(0)	Pt(II)	Sn(0)	Sn(II,IV) ^c	PI(0)	Pt(II)	Sn(0)	IV)	(atomic
	4f _{7/2}	$4f_{7/2}$	3d _{5/2}	3d _{5/2}	(%)	(%)	(%)	(%)	ratio)
3Pt3Sn/C ^a	70.8	72.7	485.8	486.8	83	17	22	78	1.3
3Pt3Sn/C-H ^a	71.0		485.8	486.8	100	0	32	68	2.1
3Pt3Sn/C-H-R ^b	70.5		485.8	487.1	100	0	13	87	2.4

Table 3. XPS binding energies (Pt,Sn) and surface compositions of 3Pt3Sn/C, 3Pt3Sn/C-H and 3Pt3Sn/C-H-R

a: Catalyst prior to reaction.

b: Catalyst collected after 4 h of 1,6-hexanediol oxidation.

c: The difference in binding energy of Sn(II) and Sn(IV) is only 0.2 eV, which could not be reliably differentiated.

d: Corrected by atomic subshell photoionization cross sections of corresponding element ⁴⁷.

Both the XRD and XPS results suggest that treatment in H₂ at 673 K promoted the interaction of Pt and Sn atoms and the formation of alloy nanoparticles. To further investigate the composition of catalysts, PtSn/C and PtSn/C-H were examined by EDS in the electron microscope before and after thermal treatment in H₂. The composition of individual particles was determined with an EDS spot size of approximately 100 nm², whereas the overall composition was measured by EDS using a ~2500 nm² probe size. Figure 7 and Table 4 present the regions analyzed by EDS and the resulting metal compositions of 3Pt3Sn/C and 3Pt3Sn/C-H. Areas that contain relatively large nanoparticles (a1, a2, a3, a4, b1, b2, b5) and small nanoparticles (a5, b3, b4) were measured. The overall composition evaluated by EDS of 3Pt3Sn/C and 3Pt3Sn/C-H confirmed an atomic ratio of Pt:Sn close to unity, which is consistent with the nominal atomic ratio of the sample. Individual nanoparticles examined with the small probe size revealed a wide distribution of metal compositions on 3Pt3Sn/C.

For example, the metal in region a3 (Fig. 7a) was nearly all Pt whereas the metal in region a5 (Fig. 7a) was mostly Sn. After treatment of the sample in H₂ at 673 K, the distribution of metals appeared to be more uniform. As shown in Fig. 7b and Table 4, the relative percentages of Pt and Sn were close to 50/50 for both large or small nanoparticles on 3Pt3Sn/C-H. Similar results were also observed on 3Pt6Sn/C and 3Pt6Sn/C-H (Fig. 8 and Table 5). In an effort to quantify the distribution of the particle compositions for bimetallic PtSn catalyst before and after thermal treatment in H₂, 20 nanoparticle regions for each sample were analyzed and the compositions are listed in Table 6. For both 3Pt3Sn/C and 3Pt6Sn/C, the standard deviation in the measured Pt content was 20% and 28%, respectively, indicating a fairly broad distribution of compositions. After the treatment in H₂ at 673 K, however, the standard deviation decreased to 6% and 7%, respectively, indicating a more uniform distribution in particle composition. The broad distribution in composition of PtSn/C suggests that the Sn species were dispersed randomly on both the carbon support and on the platinum nanoparticles. After thermal treatment in H₂, the interaction between Pt and Sn was enhanced and the resulting bimetallic nanoparticles were fairly uniform in composition.



Figure 7. Regions for EDS analysis of a) 3Pt3Sn/C and b) 3Pt3Sn/C-H and 3Pt3Sn/C-H-R catalysts collected after c) 15 min and d) 4 h of 1,6-hexanediol oxidation. The corresponding compositions are shown in Table 4.

Table 4. Elemental compositions nom EDS of 51 (55%)C, 51 (55%)C-11 and 51 (55%)C-11-K								
Sampla Area	Pt	Sn	Sampla	Aroo	Pt	Sn		
Sample	Alta	(mole%)	(mole%)	Sample	Alta	(mole%)	(mole%)	
	a1	65	35		b1	49	51	
	a2	67	33		b2	45	55	
3Pt3Sn/C	a3	91	9	3Pt3Sn/C	b3	46	53	
	a4	68	32	-H	b4	56	44	
	a5	31	69		b5	51	49	
	overall	54	46		overall	48	52	
	c 1	42	58		d1	97	3	
	c2	52	48		d2	81	19	
3Pt3Sn/C	c3	53	47	3Pt3Sn/C	d3	5	95	
-H-R ^b	c4	56	44	-H-R ^c	d4	54	46	
	c5	53	47		d5	23	67	
	overall	54	46		overall	50	50	

Table 4. Elemental compositions from EDS of 3Pt3Sn/C. 3Pt3Sn/C-H and 3Pt3Sn/C-H-R^a

a: The corresponding regions for EDS analysis are shown in Fig. 7.

b: Catalyst collected after 15 min of 1,6-hexanediol oxidation.

c: Catalyst collected after 4 h of 1,6-hexanediol oxidation.



Figure 8. Regions for EDS analysis of a) 3Pt6Sn/C and b) 3Pt6Sn/C-H catalyst. The corresponding compositions are shown in Table 5.

Sample	Area	Pt (%)	Sn (%)	Sample	Area	Pt (%)	Sn (%)
	al	55	45		b1	31	69
	a2	11	89		b2	34	66
	a3	40	60		b3	30	70
3PtoSn/C	a4	28	72	3PtoSn/C-H	b4	31	69
					b5	41	59
	overall	31	69		overall	31	69

Table 5. Elemental compositions from EDS of the 3Pt6Sn/C and 3Pt6Sn/C-H^a

a: The corresponding regions for EDS analysis are shown in Fig. 8.

Table 6. Statistical elemental compositions from EDS of PtSn/C and PtSn/C-H ^a									
	3Pt3Sn/C		3Pt3S	n/C-H	3Pt6	6Sn/C 3Pt6S		n/C-H	
	Pt %	Sn %	Pt %	Sn %	Pt %	Sn %	Pt %	Sn %	
1	100	0	50	50	88	12	31	69	
2	80	20	36	64	89	11	40	60	
3	53	47	60	40	30	70	33	67	
4	83	17	47	53	85	14	50	50	
5	75	25	50	50	25	75	32	68	
6	52	47	47	53	83	17	26	74	
7	20	80	53	47	96	4	23	77	
8	50	50	40	60	49	51	31	69	
9	77	23	51	49	30	70	37	63	
10	35	65	44	56	25	75	35	65	
11	51	48	53	47	30	70	31	69	
12	53	47	66	34	24	76	31	69	
13	50	50	41	59	45	55	35	64	
14	68	32	47	53	27	73	31	69	
15	73	27	49	51	8	92	32	68	
16	65	35	49	51	33	67	31	69	
17	67	33	45	55	55	45	34	66	
18	91	9	46	53	11	89	30	70	
19	68	32	56	44	40	60	31	69	
20	31	69	51	49	28	72	41	59	
Average	62	38	49	51	45	55	33	67	
Standard deviation	20	20	7	7	28	28	6	6	

Table 6 Statistical elemental compositions from EDS of PtSn/C and PtSn/C-H^a

a: The EDS were collected from a circle area of which the diameter is about 10 nm.

Additional characterization by STEM-EDS was also performed. Figure 9 shows the STEM-EDS line-scan results of 3Pt3Sn/C and 3Pt3Sn/C-H with the scanning region indicated by the red line. For 3Pt3Sn/C, the Pt was easily detected by EDS. Although Sn signals were also observed, they were less intense and appeared to be dispersed more evenly along the scan line. This result is consistent with the idea that Pt nanoparticles were formed during the NaBH₄ reduction step and the Sn was deposited on both the Pt and carbon support. After the thermal treatment in H₂, Sn and Pt appear together in the EDS line scan, as shown in Fig. 9b, and the intensities of metal EDS signals were similar, which is consistent with the nominal 1:1 molar ratio of Pt:Sn in the sample.



Figure 9. STEM-EDS line scans of a) 3Pt3Sn/C and b) 3Pt3Sn/C-H and 3Pt3Sn/C-H-R collected after c) 15 min and d) 4 h of 1,6-hexanediol oxidation.

The nature of the catalyst was different in the presence of excess Sn relative to Pt. The major diffraction features of 3Pt6Sn/C-H are attributed to the equimolar PtSn alloy (Fig 3b). The excess Sn appears to be associated with the bimetallic nanoparticles since single particle EDS revealed the appropriate composition of Pt and Sn. The micrographs in Fig. 10 reveal a core-shell structure of the bimetallic particles on this sample. It needs to be mentioned that no core-shell structures were observed for the other bimetallic PtSn catalysts. The contrast

differences in bright field TEM (Fig. 10a) and dark field STEM (Fig. 10b) suggest the Pt or PtSn alloy was present in the core of the particles whereas amorphous Sn oxide was the primary component of the shell ³⁶. This core-shell model explains why the H/Pt ratio of 3Pt6Sn/C-H measured by H₂ chemisorption was below the detection limit. The Pt sites capable of chemisorbing H atoms were covered by a Sn shell, likely SnO_x, that is not able to chemisorb H₂.



Figure 10. a) Bright field TEM and b) dark field STEM image of 3Pt6Sn/C-H.

In summary, the PtSn/C and PtSn/C-H have different compositions and structures resulting from overall metal loading and thermal treatment in H₂. Without the H₂ treatment, negligible alloy formation was observed. Evidently, the Sn species were well dispersed on the support and the surfaces of Pt nanoparticles. After the thermal treatment in H₂, the presence of Pt-Sn alloys was detected by XRD and STEM-EDS and the bimetallic particles were more uniform in composition. For 3Pt6Sn/C-H containing excess Sn relative to Pt, a core-shell

nanoparticle was observed, which was composed of a Pt or Pt-Sn alloy core surrounded by SnO_x species shell that could not chemisorb dihydrogen.

3.2. HDO oxidation over bimetallic PtSn catalysts

The differences in structure and composition of the PtSn/C and PtSn/C-H catalysts were accompanied by differences in catalyst performance in the selective oxidation of 1,6-hexanediol. The turnover frequencies (TOF) and number of turnovers were normalized by the Pt content in the sample and the fraction of surface atoms calculated from the surface weighted average diameter from TEM (Table 2). The reactivity results for the series of bimetallic PtSn catalysts are shown in Fig. 5 and Tables 7 and 8. The performance of the bimetallic PtSn catalysts without H₂ treatment will be discussed first. As indicated in Table 7, the conversion of HDO at 15 min increased only slightly with the addition of Sn, from 20% for 3Pt/C to 26% for 3Pt6Sn/C CIN. These results correspond to a slight increase in TOF, from 0.44 s⁻¹ for 3Pt/C to 0.50 s⁻¹ for 3Pt6Sn/C. The conversion of HDO after 4 h of reaction over the PtSn/C exhibited a similar trend. For example, the 4 h conversion of HDO was 60% for 3Pt6Sn/C compared to 47% for 3Pt/C. The number of turnovers, which is based on the conversion after 4 h, was the highest for 3Pt3Sn/C and was 1.6 times that of monometallic Pt/C. Evidently, the addition of Sn had a modest promotional influence on the initial activity and the number of turnovers after 4 h of reaction, and the deactivation behavior of the bimetallic PtSn catalysts was comparable to the monometallic Pt catalyst, as shown in Fig. 5b. The product distributions at relatively low conversion ($\sim 20\%$) and higher conversion ($\sim 50\%$) listed in Tables 7 and 8 revealed no significant change with Sn loading.

Catalyst	Conversion		TOF $(s^{-1})^c$			
	(%)	ALD	HA	AA	DA	
3Pt/C	20	89	11	0	0	0.44
3Pt1Sn/C	21	82	16	2	0	0.45
3Pt3Sn/C	22	84	14	2	0	0.61
3Pt6Sn/C	26	80	17	3	0	0.50
3Pt/C-H	22	86	13	1	0	0.49
3Pt1Sn/C-H	14	83	17	0	0	0.30
3Pt3Sn/C-H	12	84	16	0	0	0.38
3Pt6Sn/C-H	6	88	12	0	0	0.14

Table 7. Initial rate of selective oxidation of 1,6-hexanediol over PtSn/C and PtSn/C-H^a.

a: Reaction conditions: 10 cm³ 0.1M 1,6-hexanediol aqueous solution, 0.0132 g catalyst
(Pt:HDO = 1:500) 1 MPa O₂, 343 K, reaction time is 15 min.

- b: Selectivity to ALD (6-hydroxyhexanal), HA (6-hydroxyhexanoic acid), AA (6-oxohexanoic acid) and DA (adipic acid).
- c: TOF is normalized by the Pt content in the sample and the fraction of surface atoms revealed by TEM (Table 2).

Catalyst	Conversion	S	Selectivi	ty (%) ^b	Number of	
	(%)	ALD	HA	AA	DA	turnovers ^c
3Pt/C	47	69	24	4	2	0.9×10^{3}
3Pt1Sn/C	56	61	29	7	4	1.1×10^{3}
3Pt3Sn/C	56	61	29	7	4	1.4×10^{3}
3Pt6Sn/C	59	55	31	9	5	1.0×10^{3}
3Pt/C-H	58	59	30	8	4	1.0×10^{3}
3Pt1Sn/C-H	62	53	32	12	4	1.3×10^{3}
3Pt3Sn/C-H	59	55	31	9	5	2.0×10^{3}
3Pt6Sn/C-H	66	55	30	9	5	1.5×10^{3}

Table 8. Catalytic performance of PtSn/C and PtSn/C-H at higher conversion of 1.6-hexanediol^a

a: Reaction conditions: 10 cm³ 0.1M 1,6-hexanediol aqueous solution, 0.0132 g catalyst
(Pt:HDO = 1:500) 1 MPa O₂, 343 K, reaction time is 4 h.

b: Selectivity to ALD (6-hydroxyhexanal), HA (6-hydroxyhexanoic acid), AA (6-oxohexanoic acid) and DA (adipic acid).

c: Number of turnovers is normalized by the Pt content in the sample and the fraction of surface atoms revealed by TEM (Table 2).

The catalysts were also evaluated after thermal treatment in H_2 to test the effect of alloy formation on reactivity. As discussed above, XRD revealed that 3Pt1Sn/C-H contains Pt_3Sn alloy whereas 3Pt3Sn/C-H and 3Pt6Sn/C-H contains the PtSn alloy. As shown in Table 7, the initial conversion of HDO on monometallic 3Pt/C-H after 15 min was 22%, which is approximately the same as untreated 3Pt/C catalyst (20%). The initial conversion of HDO decreased significantly when Sn was added to the catalyst and subsequently treated in H_2 to form alloy nanoparticles. The conversion after 15 min was 14%, 12% and 6% for 3Pt1Sn/C-H, 3Pt3Sn/C-H and 3Pt6Sn/C-H, respectively. Although the initial activity decreased with Sn addition, the rate was recovered during the HDO oxidation reaction. As shown in Fig. 5c, the rate of reaction increased over 3Pt3Sn/C-H and 3Pt6Sn/C-H in the first 30 min of reaction and then gradually decreased. After 4 h of reaction, the conversion and number of turnovers for the PtSn/C-H bimetallic catalysts were ultimately higher than those determined with the monometallic 3Pt/C-H. The number of turnovers (after 4 h) was 2.0×10^3 for 3Pt3Sn/C-H, which is twice that for 3Pt/C-H. The product distribution at low and high conversion is summarized in Tables 7 and 8. As observed with non-alloyed PtSn/C catalysts, no significant change in product distribution was observed with the PtSn/C-H catalysts.

3.3. Characterization of PtSn/C-H after reaction

The initially low rate of conversion of HDO over the PtSn/C-H catalysts relative to a monometallic Pt catalyst indicates an induction period for catalyst activity followed by the usual deactivation. A change in the active sites during reaction can be ascribed to sintering ^{51,52}, leaching ^{51,53}, over-oxidation ⁵⁴, adsorption of by-products ^{46,51,55–64} and modification of the nanoparticle composition or structure ^{15,25,36}. To probe the potential influence of metal leaching, fresh 3Pt3Sn/C-H and used 3Pt3Sn/C-H-R catalysts were analyzed by ICP-AES and the elemental analysis results are summarized in Table 9. As a reference, the nominal molar loading of each metal was 0.15 mmol/g. As indicated in Table 9, the molar loading of Pt and Sn was slightly lower on the catalyst recovered from 4 h HDO oxidation, the molar ratio of Pt to Sn remained constant at 1.2. The recovered reaction

medium was also tested for leached metals after 4 h of reaction. The concentration of Pt and Sn were below 6.3 ppm (the detection limit of ICP-AES), confirming less than 2% of available Pt or Sn leached into the solution. We attribute the slight decrease of Pt and Sn loading on the used catalyst to adsorbed species on the solid rather than the leaching of Pt and Sn into the solution, a conclusion also reached by Wörz *et al.* ⁶⁵.

	Pt	Sn	Pt	Sn	Pt:Sn	
Sample	(wt%)	(wt%)	(mmol/g catalyst)	(mmol/g catalyst)	(molar ratio)	
3Pt3Sn/C-H	3.3	1.7	0.17	0.14	1.2	
3Pt3Sn/C-H-R ^b	2.7	1.4	0.14	0.12	1.2	

Table 9. Elemental analysis of 3Pt3Sn/C-H and 3Pt3Sn/C-H-R^a.

a: Analyzed by ICP-AES method.

b: Catalyst was collected after 4 h of 1,6-hexanediol oxidation

The 3Pt3Sn/C-H-R and 3Pt6Sn/C-H-R catalysts collected after 4 h of reaction were further analyzed by TEM to determine whether or not sintering of nanoparticles occurred during the reaction. The TEM images of the used catalysts and corresponding particle size distributions are shown in Fig. 11 and the statistical analyses of the nanoparticle sizes are presented in Table 2. The mean particle diameters (determined from a Cauchy-Lorentz distribution) of 3Pt3Sn/C-H-R and 3Pt6Sn/C-H-R was 3.6 ± 0.9 nm and 3.1 ± 0.9 nm, respectively, which are quite similar to the mean diameters of the catalysts prior to reaction (3.8 ± 1.0 nm and 3.2 ± 0.9 nm, respectively). Likewise, the surface average diameters, which are related to the fractions of exposed metal sites, are also similar for PtSn/C-H and PtSn/C-H-R catalysts. Prior work by Ide *et al.* has also shown that a monometallic Pt/C catalyst does not sinter during the selective oxidation of alcohols under similar conditions ⁴⁶.



Figure 11. TEM image and particle size distribution of a) 3Pt3Sn/C-H-R and b) 3Pt6Sn/C-H-R collected after 4 h of 1,6-hexandediol oxidation.

To investigate the oxidation state of Pt and Sn after reaction, the 3Pt3Sn/C-H-R collected after 4 h of HDO oxidation was analyzed by XPS and compared to 3Pt3Sn/C-H prior to reaction. The Pt 4f_{7/2} and Sn 3d_{5/2} core level spectra of 3Pt3Sn/C-H-R are shown in Figs. 6 e,f and the analysis of the spectra is summarized in Table 3. For both 3Pt3Sn/C-H and 3Pt3Sn/C-H-R, the Pt detected by XPS remained in the metallic state. Evidently, the Pt sites were not deactivated by over-oxidation during the reaction. Since the Pt sites are believed to be the active sites for β -hydrogen elimination, which is proposed to be a kinetically significant step in the alcohol oxidation reaction ⁴⁴, we do not suspect that over-oxidation of Pt sites in the presence of Sn was the reason for the low initial activity of the hydrogen-treated bimetallic catalysts. In contrast to Pt, the percentage of oxidized Sn increased from 68% for 3Pt3Sn/C-H catalyst to 87% for 3Pt3Sn/C-H-R. The small fraction of Sn to be accompanied by compositional and structural change of nanoparticles, which might account for the induction period observed with the alloy catalyst.

For fresh 3Pt3Sn/C-H, TEM-EDS shows that nanoparticles have a relatively uniform

composition of metals and Pt-Sn alloy formation was detected by XRD and STEM-EDS. After 15 min of reaction, the relatively uniform composition of Pt and Sn in 1:1 ratio in the individual nanoparticles was maintained, as indicated in Table 4. The statistical analysis of EDS results of twenty regions of 3Pt3Sn/C-H-R (after 15 min) is presented in Table 10 and reveals a standard deviation of 15% for the Pt and Sn content, which is larger than the observed deviation of the Pt and Sn content of the fresh catalyst (7%). The larger deviation in particle composition of a used catalyst (after 15 min of reaction) suggests a change in the composition of the nanoparticles. After 4 h of reaction, the compositional and structural changes of 3Pt3Sn/C-H are more evident. The compositional variations presented in Table 4 and the statistical analysis of 20 regions of nanoparticles in Table 10 both confirm a broader distribution of metal composition of the used catalyst compared to those prior to reaction. The STEM-EDS results in Figures 9 c and d show that although Pt and Sn appear together in the same particles, the relative intensity of the Sn contribution relative to Pt decreased at longer reaction time.

$\frac{able 10. \text{ Statistical elemental compositions from EDS of PtSn/C-H-R^{\circ}}{3Pt3Sn/C-H-R^{\circ}} = 3Pt3Sn/C-H-R^{\circ}$							-
	Pt %	Sn %	Pt %	Sn %	Pt %	Sn %	
1	40	60	93	6	100	0	-
2	-10 51	46	22	67	100	0	
2	50	40 50	33 79	07	100	0	
5	30	30	78	22	05	57	
4	30	70		23	62	38	
5	52	48	33	67	60	40	
6	93	7	35	65	57	43	
7	53	46	30	70	73	27	
8	84	15	54	46	56	44	
9	43	57	30	70	58	42	
10	73	27	68	32	20	80	
11	43	57	43	57	70	30	
12	50	50	78	22	46	54	
13	58	42	63	37	19	81	
14	42	58	70	30	39	61	
15	49	51	44	56	28	72	
16	42	58	97	3	88	12	
17	52	48	81	19	58	42	
18	53	47	5	95	45	55	
19	56	44	54	46	44	56	
20	53	47	23	67	33	67	
Average	54	46	54	45	56	44	
Standard deviation	15	15	25	25	23	23	

Table 10. Statistical elemental compositions from EDS of PtSn/C-H-R^a

a: The EDS were collected from a circle area of which the diameter is about 10 nm.

b: Catalyst were collected after 15 min of 1,6-hexanediol oxidation.

c: Catalyst were collected after 4 h of 1,6-hexanediol oxidation.

The 3Pt3Sn/C-H-R catalyst (after 15 min and 4 h of reaction) was also interrogated by XRD. The XRD patterns of 3Pt3Sn/C-H-R and 3Pt3Sn/C-H in Fig. 12 indicate a significant decrease in the peaks attributed to PtSn alloy as a result of HDO oxidation reaction. Although the XRD indicates that dealloying of Pt and Sn occurred during reaction, no XRD peaks corresponding to Sn or Sn oxides were observed. Evidently, dealloyed Sn species remained well dispersed on the carbon support or Pt surface, since leaching of Sn was not observed. Evidence from TEM, XPS and XRD indicates that alloyed PtSn nanoparticles phase-separated under HDO oxidation conditions and formed a highly dispersed Sn oxide phase on the support.



Figure 12. XRD patterns of 3Pt3Sn/C-H and 3Pt3Sn/C-H-R collected after 15 min and 4 h of 1,6-hexanediol oxidation.

The 3Pt6Sn/C-H, which is proposed to have a SnO_x @ PtSn alloy core-shell structure, is a unique case. The reaction profile in Fig. 5 shows the longest induction time for 3Pt6Sn/C-H and the catalyst had an H/Pt ratio of 0 (Table 2), indicating that initially all of the Pt was covered. Thus, the increase in activity observed during the first 30 min of reaction suggests that active Pt surface sites were recovered during the reaction. To study the change during the reaction, the 3Pt6Sn/C-H-R, which was collected after 4 h of reaction, was characterized by TEM and EDS. The TEM images and the regions for EDS analysis of the used catalyst are shown in Figures 11 and 13, respectively. The shell surrounding the core of Pt or PtSn alloy revealed in Fig. 10 has disappeared, suggesting the migration of the SnO_x shell under reaction conditions, which explains the recovery of HDO oxidation activity during aqueous phase reaction. As discussed for 3Pt3Sn/C-H, the standard deviation of the individual particle compositions of 3Pt6Sn/C-H increased significantly after reaction, which is consistent with a compositional change of the catalyst during reaction.



Figure 13. Regions for EDS analysis of 3Pt6Sn/C-H-R collected after 4 h of 1,6-hexanediol oxidation. The corresponding compositions are shown in Table 11.

Area	Pt (%)	Sn (%)
1	100	0
2	100	0
3	46	54
4	45	55
5	44	56
6	39	61
overall	41	59

Table 11. Elemental compositions from EDS of 3Pt6Sn/C-H-R^a

a: The corresponding regions for EDS analysis are shown in Fig. 13; Catalyst were collected after 4 h of 1,6-hexanediol oxidation.

4. Discussion

4.1. Structural change of PtSn bimetallic catalysts

A significant structural and compositional change of PtSn bimetallic catalyst was observed after hydrogen treatment and oxidation of HDO. Based on the extensive characterization including (S)TEM, EDS, XRD, ICP-AES and XPS, we propose a model for the evolution of PtSn/C, PtSn/C-H and PtSn/C-H-R catalysts, as shown in Scheme 1. For the PtSn/C catalysts prepared by NaBH₄ reduction, SnO_x species were well dispersed on the carbon support and on Pt nanoparticles (Scheme 1a), with negligible formation of Pt-Sn alloy. After the H₂ treatment at 673 K, Pt-Sn alloy particles were observed on PtSn/C-H (Scheme 1b), which could be explained by the enhanced interaction between adjacent Pt and Sn species in H₂ under high temperature ^{20,66}. During the oxidation of HDO in liquid water over PtSn/C-H, however, a phase segregation of the Pt-Sn alloy particles occurred (Scheme 1a), which was also observed by Michalak *et al.* in CO oxidation at around 500 K over a PtSn bimetallic catalyst ¹².



Scheme 1. Illustration of restructuring between a) separate Pt and SnO_x domains (PtSn/C and PtSn/C-H-R catalysts) and b) Pt-Sn alloy (PtSn/C-H catalysts). Pt and Sn species are grey and pink, respectively (see online article for color).

4.2. Quantification of active sites

To study the activity of different catalysts, a comparison of turnover frequencies is commonly employed. The ambiguity of this comparison arises from a lack of clarity regarding the active sites available for reaction. Because a monometallic Sn catalyst showed no activity in alcohol oxidation, we conclude that the exposed Pt atoms are the active sites. The observed changes in the structure and composition of the PtSn bimetallic catalysts during the reaction prevented the common use of H₂ chemisorption as a method to quantify the active Pt sites. Thus, as a first approximation, we estimated the fraction of active sites to be the inverse of the surface-weighted average diameter of Pt nanoparticles determined from TEM (Table 2), assuming that the fraction of Pt sites that can be eventually exposed to the surface is the same as the fraction of surface atoms from TEM. This assumption is reasonable for both PtSn/C and PtSn/C-H catalysts for the following reasons. First, the SnO_x species are well dispersed and mobile on PtSn/C, so the nanoparticles observed by TEM are likely composed primarily of Pt. For alloyed particles in PtSn/C-H, the fraction of exposed Pt and the fraction of exposed metal (Pt+Sn) are assumed to be similar. Finally, there was a negligible change in particle size during reaction (Table 2).

4.3. Role of Sn addition on alcohol oxidation

The impact of adding Sn to Pt on the catalysis of HDO oxidation depends on the structure of the catalyst. Whereas addition of Sn to Pt modestly increased the initial activity of PtSn/C catalysts relative to Pt, thermal treatment of those same catalysts in H₂ to produce PtSn/C-H actually decreased the initial activity relative to Pt. The results from characterization suggest that the Pt-SnO_x interface in PtSn/C promotes oxidation activity while alloying Sn with Pt inhibits activity. Although the exact relationship between the structure and oxidation activity of PtSn bimetallic catalysts is still not clear, the modest promotional effect of the Pt-SnO_x interface might be related to a change of exposed Pt ensembles ⁶⁷, the introduction of O₂ adsorption sites ¹² and/or the enhanced ability to remove

strongly-adsorbed species ^{28,29}. As discussed in the literature, changes in electron density ^{19,26} and/or modified lattice spacing ^{14,33,35} upon Pt-Sn alloy formation might account for the negative impact on activity. Although the initial rate over the alloyed nanoparticles on PtSn/C-H was low, the activity was recovered throughout the initial stages of the reaction (1 h). Accordingly, recovery of activity was accompanied by dealloying of nanoparticles on PtSn/C-H and the subsequent formation of SnO_x near the active Pt particles.

5. Conclusions

Bimetallic PtSn/C catalysts, which were initially reduced with sodium borohydride, formed nanoparticles of Pt and a dispersed phase of SnO_x . The presence of SnO_x promoted the turnover frequency of 1,6-hexanediol oxidation, presumably a consequence of the Pt-SnO_x interface. Treatment of a PtSn/C catalyst in H₂ at 673 K resulted in the formation of alloyed Pt-Sn nanoparticles that were initially less active than Pt for 1,6-hexanediol oxidation. During the alcohol oxidation reaction over the alloyed catalysts, the Sn dealloyed from the nanoparticles and formed SnO_x species, leading to the recovery of the oxidation activity with time in the reactor. This work presents evidence for severe restructuring of PtSn catalysts under the relatively mild conditions of aqueous-phase alcohol oxidation and illustrates the importance of characterizing the structure and composition of bimetallic catalysts after exposure to reactive environments.

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Appendix: HPLC Analysis

Sample Chromatograms



Figure 14. Sample HPLC chromatogram with RI (refractive index) detector for 1,6-hexanediol oxidation using Bio-Rad Aminex column. Reproduced from the thesis, "Ide, M.(2013). Diol Oxidation to Diacids over Supported Metal Catalysts. Retrieved from http://libra.virginia.edu/catalog/libra-oa:3654"



Figure 15. Sample HPLC chromatogram with UV-VIS detector at 290 nm for 1,6-hexanediol oxidation using Bio-Rad Aminex column. Reproduced from the thesis, "Ide, M.(2013). Diol Oxidation to Diacids over Supported Metal Catalysts. Retrieved from http://libra.virginia.edu/catalog/libra-oa:3654"

Sample Calibrations



Figure 16. Calibration curve of 1,6-hexanediol with the refractive index detector.



Figure 17. Calibration curve of 6-hydroxyhexanoic acid with the refractive index detector.



Figure 18. Calibration curve of adipic acid with the refractive index detector.