# Sulfur Poisoning of Small Pore Cu-exchanged Chabazite (CHA) Catalysts for Catalytic Reduction of NOx with NH3

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#### Abstract

The main advantages of using compression ignition, diesel engines instead of gasoline spark-ignited engines are better fuel economy and the coincident lower greenhouse gas emissions. Unlike gasoline engines, diesel engines operate at air-to-fuel ratios higher than stoichiometric, known as "lean" conditions. Reducing NO<sub>x</sub> in the presence of excess oxygen is challenging and cannot be achieved using the traditional three-way catalyst technology. Selective catalytic reduction (SCR) of NO<sub>x</sub> using NH<sub>3</sub> has been widely used/studied as a promising technology for NO<sub>x</sub> abatement in mobile applications. The state-of-the-art catalysts for NH<sub>3</sub>-SCR are Cu-exchanged in small pore molecular sieves with a chabazite (CHA) structure; namely Cu-SSZ-13 and Cu-SAPO-34. Compared to other candidates, such materials have shown both better activity and thermal stability under simulated exhaust conditions. However, these materials are prone to sulfur poisoning. Even with current ultra-low sulfur diesel fuel (containing less than 15 ppm S), the cumulative lifetime exposure of catalysts to such fuel may lead to significant effects on performance/stability.

In this study, the chemistry of Cu-CHA sulfur poisoning was studied with the focus on understanding the poisoning mechanism and development of a low-temperature SCR deactivation/regeneration model.

To this end, firstly, temperature programmed desorption (TPD) and in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed to evaluate SO<sub>2</sub> poisoning effects on SCR activity and oxidation functionality of Cu-SAPO-34. The results show that SO<sub>2</sub> significantly inhibits low-temperature (< 350 °C) SCR and oxidation functionality of Cu-SAPO-34.

Secondly, studying sulfation and desulfation of Cu-SSZ-13 with different Si:Al ratios revealed that depending on the Cu active site, i.e. Z2Cu or ZCuOH, SO<sub>2</sub> interaction with Cu-CHA results in either formation of highly stable sulfite/sulfate species or ammonium sulfate depending on whether NH<sub>3</sub> is present or not. In-situ DRIFTS and transient kinetic studies revealed Z2Cu and ZCuOH have different responses to SO<sub>2</sub> exposure corresponding to different sulfur intermediates that form. Based on these findings, a low-temperature sulfur poisoning mechanism was proposed.

Finally, based on the proposed mechanism, a multi-site mechanism-based kinetic model was developed capable of describing S adsorption/desorption behavior and SCR activity on fresh, sulfated and regenerated catalyst.

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## Nomenclature

Abbreviations

SCR	selective catalytic reduction
NO <sub>x</sub>	nitrogen oxides
PM	particulate matter
EPA	environmental protection agency
NMOG	non-methane organic gas
GVWR	gross vehicle weight rating
HC	hydrocarbon
GHG	greenhouse gas
FTP	federal test procedure
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
ASC	ammonia slip catalyst
TWC	three way catalyst
NSR	NO <sub>x</sub> storage/reduction
GHSV	gas hourly space velocity
MFC	mass flow controller
TPD	temperature programmed desorption
XRD	X-ray diffraction
DRIFTS	diffusive reflectance infrared Fourier transform
FTIR	Fourier-transform infrared
XAS	X-ray absorption spectroscopy
TPR	temperature programmed reduction
XPS	X-ray photoelectron spectroscopy
SSIE	solid state ion exchange
SDA	structural directing agent
ICP	inductively coupled plasma
TOF	turn over frequency

T-O-T tetrahedral-oxygen-tehtrahedral

Symbols

А	frontal area	m <sup>2</sup>
$\psi_s$	temperature accumulation coefficient	J/(m3 k)
Ts	temperature of gas at catalyst surface	Κ
$T_x$	external temperature	Κ
Tg	temperature of bulk gas in reactor	Κ
$a_j$	active site density of reaction j	mol-site/m <sup>3</sup> washcoat
$f_{sb}$	solid fraction of substrate	
$\lambda_{sb}$	thermal conductivity of substrate	J/(m s K)
h	heat transfer coefficient	J/(m <sup>2</sup> s K)
$h_x$	external heat transfer coefficien	$J/(m^2 s K)$
$\Delta H_j$	enthalpy of reaction j (negative for exothermic reactions)	J/mol
r <sub>j</sub>	reaction rate for reaction j	mol/(mol-site s)
S	surface area per reactor volume	$m^{-1}$
$S_x$	external radial surface area of reactor/reactor volume	$m^{-1}$
$ ho_g$	density of bulk gas	kg/m <sup>3</sup>
ν	interstitial velocity	m/s
ε	void fraction of reactor	
$C_{pg}$	heat capacity of gas	J/(kg K)
$D_p$	effective particle diameter	m
$D_{i,m}$	binary diffusion coefficient of trace species i in the mixture	m <sup>2</sup> /s
$k_{m,i}$	mass transfer coefficient for species i	$kg/(m^2 s)$
Nu	Nusseldt number	
S <sub>ij</sub>	Stoichiometric coefficient of species i for reaction j	
Sh	Sherwood number	
$ heta_j$ , $ec{ heta}$	surface coverage component and vector, respectively	
$\overrightarrow{C_s}$ , $C_{s,j}$	vector and component, respectively, of concentration at catalyst surface	
$\lambda_g$	thermal conductivity of bulk gas	J/(m s K)
$\overrightarrow{W_g}, W_{g,j}$	vector and component, respectively, of mass fraction in the bulk gas	

$\overrightarrow{W_S}, W_{S,j}$	vector and component, respectively, of mass fraction at catalyst surface	
$D_{i,m}$	binary diffusion coefficient of species i in the mixture	m²/s

#### **Chapter 1 Introduction and background**

### **1.1 Introduction**

In 1982, Rudolf Diesel introduced a new fuel combustion process different from all the previously known internal combustion engines. Unlike spark-ignited engines, in his design, combustion was initiated by injecting a small amount of fuel into a cylinder containing hot compressed air. Rudolf's design is nowadays known as compression-ignited or diesel engine<sup>1,2</sup>. The diesel engine is widely accepted as the most energy efficient powerplant among all types of internal combustion engines. Better fuel economy (which translates to lower fuel consumption and higher torque at lower speed) and the coincident lower greenhouse gas emissions make the diesel engine a suitable candidate for heavy-duty trucks, buses, off-road vehicles and machinery<sup>3</sup>. However, the downside of diesel engines is the emission of hazardous gas compounds and solids/liquids (mainly soot) into the environment. In comparing diesel and gasoline exhaust gas composition, as shown in figure 1.1, diesel combustion produces significantly higher amounts of nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM)<sup>1</sup>.

According to the United States Environmental Protection Agency (EPA), the transportation sector is responsible for more than 55% of  $NO_x$  (about 8.9 million tons of  $NO_x$  per year) and 10% of PM emissions in the United States<sup>4</sup>. In the USA, such undesirable emissions are subjected to federal and state laws. After legislation of the National Environmental Policy Act and the Clean Air Act in 1970, considered a key turning point in America's

environmental awareness, the EPA published detailed regulations to limit the amount of  $NO_x$  and PM emitted<sup>4,5</sup>.



Figure 1.1 Diesel versus gasoline engines exhaust gas components during real combustion<sup>1</sup>.



Figure 1.2 Fleet average NO<sub>x</sub> + non-methane organic gas (NMOG) limits under Tier 3 standards for (A) high-duty vehicle with gross vehicle weight rating (GVWR) of 10,001-14,000 lb, (B) light-duty vehicle & truck with GVWR = Max. 8500 lb (data obtained from EPA website<sup>4</sup>).

Such regulations change with time, and as of the date of this publication, 2018, the EPA's newest standards (Tier 3) for evaporative emissions (NO<sub>x</sub> and non-methane organic gas (NMOG)) for light- and heavy-duty vehicles are shown in figure  $1.2^{4,5}$ . From figure 1.2 (B), upon completion by 2025, Tier 3 standards will result in an almost 75% reduction in
NMOG + NO<sub>x</sub> emissions. To meet such stringent emission limits, manufactures are required to provide flexible and advanced aftertreatment technologies.

# **1.2 Diesel emissions**

The regulated diesel emissions are nitrogen oxides (NO<sub>x</sub>), particulate matter (PM), carbon monoxide (CO) and unburned hydrocarbons (HC). The exhaust emission composition highly depends on the air-to-fuel ratio at which engine operates. Figure 1.3 shows NO<sub>x</sub>, CO, PM, and HC concentrations in diesel exhaust as a function of normalized air-to-fuel ratio<sup>1</sup>.



Figure 1.3 Diesel emission concentrations as a function of air/fuel ratio<sup>1</sup>.

 $NO_x$  refers to a group of nitrogen oxides including nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), nitrogen trioxide (N<sub>2</sub>O<sub>3</sub>), and nitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>)<sup>6</sup>. Among them, NO, NO<sub>2</sub> and N<sub>2</sub>O are the only regulated oxides. Note that N<sub>2</sub>O is regulated as greenhouse gas (GHG) emissions <sup>3,4</sup>. Aside from the fuel-NO<sub>x</sub>, i.e.  $NO_x$ 

formed from the nitrogen component of the fuel, thermal formation of NO from atmospheric nitrogen (i.e. Zeldovich mechanism) is the primary source of NO production<sup>2,7</sup>. The elementary reactions based on the Zeldvoich mechanism are as follows:

$$O_2 \leftrightarrow 2O$$
 (1-1)

$$0 + N_2 \leftrightarrow NO + N \tag{1-2}$$

$$N + O_2 \leftrightarrow NO + O \tag{1-3}$$

The overall reaction is:

$$N_2 + O_2 \leftrightarrow 2NO \tag{1-4}$$

The produced NO can react with O<sub>2</sub> to produce NO<sub>2</sub> via an oxidation reaction as follows:

$$NO + \frac{1}{2}O_2 \leftrightarrow NO_2 \tag{1-5}$$

The equilibrium data for these two reactions i.e. NO and NO<sub>2</sub> formation are listed in Table  $1.1^{6}$ .

	Equilibrium constants	
T [°C]	$N_2 + O_2 \leftrightarrow 2NO$	$NO + \frac{1}{2}O_2 \leftrightarrow NO_2$
27	$1.0 \times 10^{-30}$	$1.4 \times 10^{6}$
727	$7.5 \times 10^{-9}$	$1.2 \times 10^{-1}$
1227	$1.1 \times 10^{-5}$	$1.1 \times 10^{-2}$
1927	$3.5 \times 10^{-3}$	$2.6 \times 10^{-3}$

Table 1.1 NO and NO<sub>2</sub> formation equilibrium constants.

Taking only chemical equilibrium into account, at the flame temperatures (1600-2000 °C), NO<sub>x</sub> concentrations would be at around 6000 to 10,000 ppm, and the NO<sub>2</sub>/NO<sub>x</sub> ratio would be lower than 0.01. However, NO<sub>2</sub> in the diesel engine can also be formed upon NO interaction with HO<sub>2</sub> and OH radicals – also known as prompt NO<sub>2</sub><sup>1,2,6</sup>. The NO<sub>2</sub>/NO<sub>x</sub> ratio in the raw diesel exhaust is between 0.05-0.1<sup>2</sup>. Note that measured NO<sub>x</sub>

concentration in the raw diesel exhaust is different from the equilibrium values due to the rapid change in temperature and short residence time i.e. reactions are kinetically limited<sup>6</sup>.

Particulate matter (PM) is the most complex diesel emission and represents a mixture of liquid and solid pollutants including soot, lubricating oil, unburned fuel, and sulfates. Soot is produced in the diesel engine as a result of inhomogeneous combustion<sup>2</sup>. Diesel exhaust also contains greenhouse gas (GHG) emissions including carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and N<sub>2</sub>O.

## **1.3 Diesel emission standards in United States**

Both diesel and gasoline emissions are directly regulated by the EPA. In accordance with the U. S. federal law, i.e. the Clean Air Act Amendments (CAAA) of 1990, the EPA regulates the maximum degree of emission control for different classes of vehicles<sup>5</sup>. The emissions for heavy-duty trucks, for instance, are measured using a standardized Federal Test Procedure (FTP)<sup>8</sup>. Figure 1.4 shows the variation in vehicle speed during the FTP cycle<sup>4</sup>. Based on the FTP, the vehicle undergoes cold start, cold stabilized and hot start phases and the emitted gaseous emissions are collected and reported in the units of g/bhp-h for trucks and g/mile or g/km for passenger cars<sup>8</sup>. For on-road light-duty vehicles (defined as vehicles of GVWR (gross vehicle weight rating) of maximum 8,500 lbs), there are two standards in the federal law, namely Tier 1 and 2. Upon completion of Tier 2, the EPA published the Tier 3 regulations which are being implemented from 2017-2025. Such regulations report the limits for CO, PM, NMOG + NO<sub>x</sub> and formaldehyde (HCHO). For on-road heavy-duty vehicles (GVWR  $\geq$  8,500), the standards are based on US GHG regulations developed by the EPA and the National Highway Traffic Safety Administration

(NHTSA). GHG standards include  $CO_2$  emission standards, as well as emission standards for N<sub>2</sub>O and CH<sub>4</sub><sup>3,4</sup>.



EPA Federal Test Procedure (FTP) Duration = 1874 seconds, Distance = 11.04 miles, Average Speed = 21.19 mph

Figure 1.4 EPA federal test procedure (FTP) for on road heavy-duty trucks<sup>4</sup>.

# 1.4 Diesel exhaust aftertreatment system

To meet regulations, modern diesel engines are equipped with exhaust aftertreatment systems. The diesel aftertreatment system contains subsystems located downstream of the engine. These include sensors, catalytic converters and particulate filters<sup>1</sup>. An example of a commercial Johnson Matthey Diesel Exhaust Gas treatment SCRT<sup>®</sup> system is shown in figure 1.5. This system includes a diesel oxidation catalyst (DOC), diesel particulate filter (DPF), selective catalytic reduction (SCR) catalyst with urea delivery system and ammonia slip catalyst (ASC).



Figure 1.5 Johnson Matthey diesel exhaust gas aftertreatment SCRT<sup>®</sup> system. (the schematic of the aftertreatment system is taken from Johnson Matthey website.)

### **1.5 Diesel oxidation catalyst**

Typically located in the upstream of the diesel aftertreatment system, the DOC is responsible for two primary functions: oxidation of CO and unburned hydrocarbons (HC). Oxidation of these also provides heat via the generated exotherms to regenerate downstream filters, to be discussed below, and NO oxidation to form NO<sub>2</sub> promoting low temperature activity of a downstream SCR catalyst<sup>9</sup>. The DOC can also, in an unwanted side reaction, oxidize SO<sub>2</sub> to SO<sub>3</sub>. Having SO<sub>3</sub> can significantly affect the durability of downstream catalysts.

Structurally similar to that of a gasoline three way catalyst (TWC), current DOCs are in the form of a ceramic monolithic honeycomb as shown in figure 1.6<sup>8</sup>. Having high oxidation activity along with thermal durability, platinum metal groups (PGMs), specifically platinum (Pt) and palladium (Pd), have been widely used as the active DOC sites. To increase the surface area, active metals are deposited on alumina (the most common support), silica or zeolites as a support<sup>10</sup>. Compared to Pt- and Pd-only monometallic catalysts, using bimetallic Pt-Pd catalysts enhances HC oxidation activity and stability towards thermal aging and sulfur poisoning<sup>10,11</sup>. Modern DOCs use several washcoat layers containing various Pt-Pd ratios together with HC storage materials like a zeolite in order to trap the HC during cold start<sup>11</sup>.



Figure 1.6 Diesel oxidation catalyst (DOC).

### **1.6 Diesel particulate filter**

Highly efficient with excellent thermal stability, diesel particulate filters (DPFs) are the current technology used in diesel vehicles to physically trap and remove particulates<sup>12,13</sup>. Structurally, DPFs, as shown in figure 1.7, are in the form of monolithshaped reactors and primarily made of ceramic. The channels are alternatively closed at each end forcing the gas to flow throw the porous walls where the separation occurs<sup>14,15</sup>. DPFs can accumulate a certain amount of soot. When the filter has trapped some predetermined amount, regeneration is needed to oxidize the deposited particulate.



Corning® Ceramic Particulate Filters

Figure 1.7 Diesel particulate filter structure (pictures are taken form Corning website).

There are two types of DPF regeneration: "passive" regeneration occurs at low temperature when there is NO<sub>2</sub> available as the oxidant. NO<sub>2</sub> oxidation of soot can occur at temperatures as low as 300 °C. In this case, regeneration is highly dependent on duty-cycle and insufficient exhaust temperature over a long period of time can result in slow soot oxidation. "Active" regeneration, on the other hand, is used when passive is insufficient. Here, the oxidant is O<sub>2</sub> and soot oxidation via O<sub>2</sub> occurs at temperatures higher than 500 °C, however diesel exhaust gas temperature is generally between 200-300 or 300-450 °C for light- and heavy-duty engines, respectively<sup>10,15</sup>. To achieve the higher than normal temperatures, heat from an external source like a burner or electrical heater can be provided, but more often extra fuel is added to the exhaust stream upstream of the DOC,

and the generated exothermic heat from the oxidation reaction increases the exhaust temperature<sup>3,13–16</sup>.

### **1.7 NOx reduction technologies**

Diesel combustion is "lean" meaning that it operates at higher than stoichiometric air-to-fuel ratios. This translates to very low concentrations of NO<sub>x</sub> - on the order of ppm - compared to O<sub>2</sub> (% levels) present in diesel exhaust gas <sup>17,18</sup>. In gasoline engines, significant reductions in NO<sub>x</sub> can be achieved using three-way catalysts (TWC). A 14.5:1 ratio is the normal/stoichiometric air-to-fuel ratio for gasoline, producing exhaust gas containing enough CO, H<sub>2</sub> and HC to reduce NO<sub>x</sub> and O<sub>2</sub><sup>19</sup>. The NO<sub>x</sub> reductions reactions on a TWC are as follows:

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$
 (1-6)

$$C_x H_y + \left(2x + \frac{y}{2}\right) NO \rightarrow xCO_2 + \frac{y}{2}H_2O + \left(x + \frac{y}{4}\right)N_2$$

$$(1-7)$$

$$H_2 + NO \to H_2O + \frac{1}{2}N_2$$
 (1-8)

But, removal of NO<sub>x</sub> under fuel lean (or oxygen rich) conditions, which is the case in diesel engine exhaust, is not feasible using the conventional TWC method due to a selectivity challenge, all the reductants would react with the O<sub>2</sub> instead of NO<sub>x</sub><sup>20</sup>. To overcome this challenge, many technologies have been evaluated/developed for the control of NO<sub>x</sub> under lean exhaust conditions. Such technologies are based on two approaches. One uses a catalytic reaction to selectively reduce NO<sub>x</sub> in an oxidizing environment. This method is referred to as selective catalytic reduction (SCR) and includes urea (NH<sub>3</sub>)-SCR, hydrocarbon-SCR, and H<sub>2</sub>-SCR. The second is storing NO<sub>x</sub> under lean conditions, followed by the reduction of stored NO<sub>x</sub> under rich conditions. This method is known as NO<sub>x</sub> storage/reduction (NSR) or also called the lean NO<sub>x</sub> trap (LNT)<sup>21</sup>.

### **1.7.1 NO<sub>x</sub> storage/reduction (NSR)**

Figure 1.8 shows the cycles involved in the NO<sub>x</sub> adsorption/reduction mechanism together with the NO<sub>x</sub> breakthrough and release profile over a Pt/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst. The overall catalytic cycle can be described using the following five steps: (1) NO oxidation to form NO<sub>2</sub> whose adsorption is more effective compared to that of NO, (2) NO or NO<sub>2</sub> adsorption in the form of nitrites or nitrates, (3) switching from lean to rich conditions meaning that the exhaust oxygen concentration is dropped, (4) NO<sub>x</sub> desorption from the nitrite or nitrate sites, and (5) NO<sub>x</sub> reduction to N<sub>2</sub> in the presence of a reductant like H<sub>2</sub>, CO and HC<sup>21</sup>.

NSR catalysts usually consist of an alkali or alkaline-earth material together with precious metals components such as platinum and rhodium, all deposited on the support, e.g. Pt/Ba/Al<sub>2</sub>O<sub>3</sub><sup>17,18,21</sup>. The advantage of using NSR is that there is no additional reducing agent needed<sup>18</sup>. However, the NO<sub>x</sub> reduction efficiency can be significantly negatively impacted by sulfur and high temperature exposure<sup>18,22</sup>. Sulfur can interact with NSR catalysts via two different pathways; (1) SO<sub>2</sub> can be oxidized to SO<sub>3</sub> over precious metals and react with the support forming stable sulfate species, (2) SO<sub>x</sub> can react with the storage component and form compounds like barium sulfate blocking nitrate formation sites<sup>22</sup>.



**Figure 1.8** Effluent NO<sub>x</sub> concentration during the adsorption/release experiment. Experimental procedure: the catalyst, Pt/Ba/Al<sub>2</sub>O<sub>3</sub>, was exposed to 250 ppm NO, 8% H<sub>2</sub>O, 8% CO<sub>2</sub>, 8% O<sub>2</sub>, balanced with N<sub>2</sub> for 10 minutes, followed by 2000 ppm H<sub>2</sub>, 8% H<sub>2</sub>O, 8% CO<sub>2</sub>, and a balance of N<sub>2</sub>. (data is taken from Epling et al.<sup>21</sup> and the schematic is from dieselnet.com).

## 1.7.2 Selective catalytic reduction

After having been used for several years in stationary power plants, in 1990 the use of NH<sub>3</sub> SCR for NO<sub>x</sub> abatement in mobile sources was proposed. Before then, using NH<sub>3</sub> in vehicles was not entertained due to difficulties associated with its storage and distribution<sup>18</sup>. However, in 1990, Held et al.<sup>23</sup> suggested using urea as the NH<sub>3</sub> source, making this technology viable for mobile applications. A lot of research has since focused on improving the activity and stability of NH<sub>3</sub>-SCR catalysts in order to be efficiently applied in diesel aftertreatment systems<sup>24</sup>. Along with NH<sub>3</sub>-SCR, HC- and H<sub>2</sub>-SCR have been studied due to the reductant's availability in diesel exhaust<sup>18,24</sup>. However, higher de $NO_x$  activity, a wider temperature window, lower cost, lower fuel penalty and lower GHG emissions make  $NH_3$ -SCR a better candidate than HC- and  $H_2$ -SCR<sup>3,17</sup>.

# **1.8 NH<sub>3</sub>-Selective Catalytic Reduction**

# 1.8.1 Basics of NH<sub>3</sub>-SCR chemistry

Used as a reducing agent in the SCR reaction,  $NH_3$  is supplied through urea decomposition in automotive applications. Urea solution decomposes at around 180 °C to  $NH_3$  and  $CO_2$  based on the reaction below<sup>25</sup>:

$$CO(NH_3)_2 + H_2O \to CO_2 + 2NH_3$$
 (1-8)

As mentioned earlier, NO<sub>x</sub> in the raw diesel exhaust is primarily in the form of NO and the NO<sub>2</sub>/NO<sub>x</sub> ratio is small (5-10% NO<sub>2</sub>).<sup>24</sup> However, the DOC can oxidize NO (i.e. reaction 1-5) increasing the NO<sub>2</sub>/NO<sub>x</sub> ratio. The main, basic NH<sub>3</sub>-SCR reactions are as follows<sup>24–28</sup>:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{Standard-SCR} \tag{1-9}$$

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$$
 Fast-SCR (1-10)

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$
 NO<sub>2</sub>-SCR (1-11)

Responsible for low-temperature SCR activity, fast-SCR proceeds when NO<sub>2</sub>/NO is at a 1/1 ratio. This reaction, as the name implies, happens at a faster rate compared to the standard- and slow-SCR<sup>24,26</sup>. In the case of NO<sub>2</sub>/NO ratios higher than 1:1, the slow-SCR or NO<sub>2</sub>-SCR becomes active. An excess amount of NO<sub>2</sub> in the feed can result in undesired N<sub>2</sub>O production, which is a potent greenhouse gas. This side reaction happens as follows<sup>25</sup>:

$$NH_3 + NO_2 \rightarrow \frac{1}{2}N_2 + \frac{1}{2}N_2O + \frac{3}{2}H_2O$$
 (1-12)

The main three SCR reactions are also accompanied by non-selective  $NH_3$  oxidation by  $O_2$  as follows<sup>24–28</sup>:

$$4NH_3 + 5O_2 \to 4NO + 6H_2O \tag{1-13}$$

$$4NH_3 + 3O_2 \to 2N_2 + 6H_2O \tag{1-14}$$

# **1.9 NH<sub>3</sub>-SCR Catalysts**

In 2005, Daimler AG commercialized urea-SCR catalyst for heavy-duty diesel engines under the trademark Blue TEK. Similar to what had been used in stationary power plants,  $V_2O_5$ -WO<sub>3</sub>-TiO<sub>2</sub> was chosen as the catalyst<sup>25,29</sup>. The operational temperature window for V-based catalysts was reported to be in the range of 300-400 °C<sup>29</sup>. Using Vbased catalysts for more widespread vehicular applications failed due to drawbacks such as low activity and selectivity at high temperatures, oxidation of SO<sub>2</sub> to SO<sub>3</sub> and the toxicity of vanadia if it sublimes at high temperatures<sup>30</sup>. As an alternative to vanadia-based catalysts, a variety of zeolites with different frameworks have been studied, such as ZSM-5, mordenite, beta, ferrierite, Y-zeolite. Such zeolites are generally promoted by transition metals, such as Fe and Cu in order to increase the  $NO_x$  reduction activity<sup>25</sup>. Dealumination and issues associated with unburned hydrocarbons in medium- and large-pore zeolites led to the advent of metal exchanged small pore molecular sieves with a chabazite structure (e.g. SSZ-13 and SAPO-34)<sup>28</sup>. Johnson Matthey, Inc. (in  $2008^{31}$ ) and BASF (in  $2009^{32}$ ) patented the commercial Cu-SSZ-13 and Cu-SAPO-34 catalysts for NH<sub>3</sub>-SCR applications. Having high hydrothermal stability and activity, Cu-SSZ-13 and Cu-SAPO-34 became the best candidates for commercial application<sup>33,34</sup>. Both SSZ-13 and SAPO-34 have the same crystallographic framework, which is called chabazite (CHA). SSZ-13 is

a zeolite containing primarily  $[SiO_4]^{4-}$  and a minor amount of  $[AIO_4]^{5-}$  tetrahedral forming a series of Si-O-Si and Si-O-Al bonds. SAPO-34, on the other hand, is a zeotype material containing nearly equimolar amounts of Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>, with a minor amount of SiO<sub>2</sub><sup>25</sup>. A CHA framework, as shown in figure 1.9, consists of two main building units: (1) doublesix-membered rings (d6r) connected through tilted 4-membered rings, and (2) large pore eight-membered rings (CHA cages). Connecting these units results in a 3-dimentional network of small pores (~ 3.7 Å) as shown in figure 1.9<sup>26,35</sup>.



Figure 1.9 Topology of CHA framework<sup>35</sup>.

## 1.10 NH<sub>3</sub>-SCR Mechanistic Aspects

There has been significant interest in understanding the SCR mechanism, and developing a comprehensive model that mimics the stoichiometry of the standard-SCR reaction (i.e. reaction 1-9). Today, it is generally agreed that NH<sub>3</sub> reacts with a (N, O) species on isolated Cu sites (i.e. Cu<sup>2+</sup> and [Cu<sup>II</sup>(OH)]<sup>+</sup>) to form N<sub>2</sub> via a redox cycle (Cu<sup>2+</sup>  $\leftrightarrow$  Cu<sup>+</sup>)<sup>36-41</sup>. Exploiting kinetic rate measurements, many studies reported a reproducible local minimum at around in 350 °C in NO<sub>x</sub> conversion light-off curve as shown in figure

1.10. This "seagull" shape conversion has been attributed to the presence of two kinetic regimes for NH<sub>3</sub>-SCR over Cu-CHA<sup>27,38</sup>.



Figure 1.10 NO<sub>x</sub> conversion data for NH<sub>3</sub>-SCR over a Cu/SSZ-13 catalyst (taken form Gao et al.<sup>38</sup>). Cu:Al = 0.13, Si:Al = 12, experimental procedures:350 ppm NO, 350 ppm NH<sub>3</sub>, 14% O<sub>2</sub>, and 2.5% H<sub>2</sub>O balanced with N<sub>2</sub>, Gas hour space velocity (GHSV)= 400,000 h<sup>-1</sup>.

At high temperatures, i.e. temperatures above ~350 °C, SCR rates were found to increase linearly with Cu loading (figure 1.11) showing that each Cu site is catalyzing the SCR reaction independently<sup>36</sup>. High temperature SCR kinetics can be explained by the mechanism proposed by Janssens et al.<sup>41</sup>. This reaction scheme, shown in figure 1.12, successfully explains the SCR mechanism on a single Cu site and it is consistent with the total stoichiometry of the standard-SCR reaction.

The key step here is the formation of NO<sub>2</sub> by NO oxidation. During adsorption and desorption, only stable molecules were assumed (O<sub>2</sub>, NO, NH<sub>3</sub>). In other words, fragments like  $\frac{1}{2}$  O<sub>2</sub> or isolated OH<sup>-</sup>, H<sup>+</sup>, or O<sup>2-</sup> were not considered as reactants.



**Figure 1.11** SCR rates, within the differential regime and at temperatures near 350 °C, plotted as a function of the Cu loading (taken form Gao et al.<sup>36</sup>). Experimental conditions: 350 ppm NO, 350 ppm NH<sub>3</sub>, 14% O<sub>2</sub>, 2.5% H<sub>2</sub>O balanced with N<sub>2</sub>. GHSV = 1,200,000 h<sup>-1</sup>.

The reaction starts with a NO molecule (in the presence of oxygen) being adsorbed on  $Cu^+$  in the form of a nitrate (step 1). Formation of nitrate species was proposed to be the rate determining step (RDS). Reaction of another NO molecule with the adsorbed nitrate leaves a gas phase NO<sub>2</sub> and a nitrite species on the Cu atom (step 2). Produced NO<sub>2</sub> reacts with another Cu<sup>+</sup> and leaves an identical nitrite species (step 8). These two nitrites react with NH<sub>3</sub> and NO releasing water and nitrogen as the SCR products. This results in reduction of Cu<sup>2+</sup>–OH<sup>-</sup> species to Cu<sup>+</sup> sites which can be oxidized by NO + O<sub>2</sub> or NO<sub>2</sub> to form nitrate species and closes the cycle<sup>41</sup>. This mechanism might not be suitable for lowtemperature SCR because of the low reactivity of nitrate species.



**Figure 1.12** SCR reaction mechanism over Cu-CHA proposed by Janssens et al.<sup>41</sup>. Blue cycle represents the fast SCR, and black cycle shows NO activation. Standard-SCR reactants are shown in red, and products are in black, and the NO<sub>2</sub> intermediate is displayed in green.

Exploiting kinetic measurements under differential conditions, Gao et al.<sup>36</sup> reported a linear correlation between SCR rate and [Cu loadings]<sup>2</sup> at temperatures lower than 300 °C as shown in figure 1.13. They concluded that the dimeric Cu species might be catalyzing low temperature SCR.

Utilizing DFT calculations combined with operando spectroscopic experiments, Paolucci et al.<sup>39</sup> found that at low-temperatures, NH<sub>3</sub>-solvated Cu ions are the most abundant Cu species present under SCR conditions. Taking both Z2Cu and ZCuOH sites into account, it was predicted that  $Z[Cu^{II}(OH)(NH_3)_3] \leftrightarrow Z[Cu^{I}(NH_3)_2]$  and  $Z2[Cu^{II}(NH_3)_4] \leftrightarrow ZNH_4/Z[Cu^{I}(NH_3)_2]$  are the redox couples with the lowest free energies at 200 °C and in the presence of 2% H<sub>2</sub>O, 300 ppm NH<sub>3</sub> and 10% O<sub>2</sub>.



**Figure 1.13** SCR rates, within the differential regime and at temperatures lower than 300 °C, plotted as a function of the (Cu loading)<sup>2</sup> (taken form Gao et al.<sup>36</sup>). Experimental conditions: 350 ppm NO, 350 ppm NH<sub>3</sub>, 14% O<sub>2</sub>, 2.5% H<sub>2</sub>O balanced with N<sub>2</sub>. GHSV = 1,200,000 h<sup>-1</sup>.

Probing  $Cu^{II}$  and  $Cu^{I}$  under the reaction conditions (using X-ray absorption spectroscopy (XAS) and DFT), Paolucci et al.<sup>39</sup> proposed a SCR mechanism successfully explaining the reduction half-cycle at low temperatures. Based on this mechanism, as shown in figure 1.14, the SCR reaction starts with a NO molecule attacking NH<sub>3</sub>-solvated Cu ions forming an N–N bond. The key here is the formation of H<sub>2</sub>NNO as the intermediate, which can be decomposed to H<sub>2</sub>O and N<sub>2</sub>. During this process, an electron is transferred to Cu, and a proton to either a Cu–OH ligand (in the case of ZCuOH) or framework oxygen (O<sub>f</sub>) (in the case of Z2Cu)<sup>39</sup>.

According to Paolucci et al.<sup>39</sup>, the reduction half-cycle consists of  $NH_3$  adsorption,  $H_2NNO$  formation simultaneous with  $Cu^{II}$  reduction to  $Cu^{I}$  and finally  $N_2$  and  $H_2O$ 

desorption. The oxidation half-cycle, however, was less clear. It was suggested that for low-temperature oxidation, dimeric copper sites were needed but how these sites can form under SCR conditions was not fully understood.



Figure 1.14 Proposed SCR mechanism by Paolucci et al.<sup>39</sup> for NH<sub>3</sub>-solvated Z2Cu (green) and ZCuOH (black) sites.

Very recently, Gao et al.<sup>38</sup> and Paolucci et al.<sup>40</sup> demonstrated that NH<sub>3</sub>-solvated Cu ions could be mobile. Mobile Cu ions can travel through zeolite channels and form dimeric Cu sites that can participate in the oxidation reaction. More specifically, two  $[Cu^{I}(NH_{3})_{2}]^{+}$  migrate to the vicinity of another, forming  $[Cu^{I}(NH_{3})_{2}]^{+}-O_{2}-[Cu^{I}(NH_{3})_{2}]^{+}$ . This intermediate can be used to explain the oxidation half-cycle involved in low-temperature SCR chemistry. In the presence of NO,  $2Cu^{I}$  ions can be oxidized to  $2Cu^{II}$ , and form a  $[Cu^{II}(NH_{3})_{2}]^{2+}-O-[Cu^{II}(NH_{3})_{2}]^{2+}$  intermediate. This intermediate can be hydrolyzed by a

 $H_2O$  molecule forming two  $[Cu^{II}(OH)(NH_3)_2]$  active sites and thereby closing the SCR cycle.

# 1.11 Deactivation Mechanisms of Cu-CHA Catalysts for SCR applications

Under practical conditions, Cu-CHA catalysts undergo hydrothermal aging and sulfur poisoning. These two are considered the main Cu-CHA deactivation mechanisms responsible for loss in de-NO<sub>x</sub> activity<sup>42–44</sup>. During DPF regeneration, the temperature in the SCR catalyst can surpass 600 °C. Exposure to such high temperatures in the presence of water can result in structural collapse, also known as dealumination<sup>25</sup>. Measuring NO<sub>x</sub> conversions for hydrothermally aged Cu-SSZ-13 and Cu-SAPO-34 at 700, 750 and 800 °C for 16 h, Wang et al.<sup>44</sup> found that both materials were stable up to 750 °C, after which a significant decrease was observed in Cu-SSZ-13 SCR activity. Cu-SAPO-34, however, maintained its activity even after 800 °C<sup>44</sup>. Studying the hydrothermal stability of Cu-SSZ-13 catalysts with different Cu/Al ratios, Kim et al.<sup>45</sup> reported that Cu species inside the CHA cage agglomerate more readily compared to Cu ions occupying d6r sites. Very recently, combining spectroscopic techniques with DFT calculations, Song et al.<sup>46</sup> showed that the hydrolysis activation barrier for ZCuOH sites are less than that of Z2Cu making these sites more susceptible to agglomeration<sup>46</sup>.

## 1.11.1 Sulfur poisoning in Cu-CHA for NH<sub>3</sub>-SCR applications

Diesel fuel and lubricating oil are the main sources of sulfur present in the exhaust. The diesel lube oils contain about 4000 to 10,000 ppm sulfur. After 2010, based on EPA's diesel standards, all highway diesel vehicles must use ultra-low sulfur diesel (ULSD) fuel, i.e. fuel with a maximum sulfur level of 15 ppm. Raw diesel exhaust contains mostly SO<sub>2</sub> and about 2-4% SO<sub>3</sub>. SO<sub>2</sub>, however, can be oxidized to SO<sub>3</sub> over the DOC at temperatures above 300 °C<sup>47</sup>. Both SO<sub>2</sub> and SO<sub>3</sub> can act as a catalyst poison affecting catalytic performance through blocking the active sites, changes in morphology, and electronic properties<sup>10</sup>. The exhaust SO<sub>2</sub> concentration is linearly proportion to the fuel sulfur level. Even with ultra-low sulfur diesel fuel, the cumulative lifetime exposure of catalysts to such fuel may lead to significant effects on performance.

In an early work on sulfur poisoning on Cu-CHA, researchers at Ford motor company investigated the effects of SO<sub>2</sub> and SO<sub>3</sub> on Cu-Zeolite catalysts for SCR applications<sup>48</sup>. In their study, Cu-zeolite samples were exposed to either 40 ppm  $SO_2$  or SO<sub>3</sub> in the presence of H<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub> at 200, 300, and 400 °C for 1.5 h corresponding to 500 sulfur-equivalent miles with 350 ppm sulfur fuel. Note that they did not feed NH<sub>3</sub> during the sulfation procedure. The loss of SCR activity was reported to be more considerable for SO<sub>3</sub>-aged samples compared to that of SO<sub>2</sub>. They reported formation of highly dispersed CuSO<sub>4</sub> in the zeolite as the main sulfur poisoning mechanism. Kumar et al. <sup>49</sup> investigated the effect of different sulfur feeds such as SO<sub>2</sub>, SO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> in NH<sub>3</sub>-SCR over the Cu-SAPO-34. They reported that sulfur poisoning on Cu-SAPO-34 happens not only through  $SO_2$  and  $SO_3$  adsorption, but also through some temperature-activated chemical reaction with the catalyst. Comparing SCR conversions in the presence and absence of SO<sub>2</sub>, Zhang et al. <sup>43</sup> reported a decrease in NO<sub>x</sub> reduction activity of Cu-SAPO-34 (as shown in figure 1.15) at temperatures lower than 300 °C due to formation of ammonium sulfate.

They also showed larger amounts of S adsorbed when  $NH_3$  and  $SO_2$  are co-fed. Very recently, Wijayanti et al.<sup>50</sup> studied effect(s) of gas compositions on  $SO_2$  poisoning over Cu/SSZ-13 for SCR applications. They showed that  $SO_2$  exposure under dry conditions results in a higher amount of sulfate formation compared to that under wet conditions. Compared to the other types of sulfur species, the rate of ammonium sulfate formation was found to be highest. Today, it is generally agreed that low temperature SCR (< 350 °C) activity over Cu-CHA is adversely influenced by  $SO_x$ .

High- temperature SCR activity, on the other hand, is found to be less sensitive to sulfur poisoning. Fortunately, the SCR activity of sulfated samples can be satisfactory recovered by treating at high temperatures (> 600 °C) and under lean conditions. This process is commonly known as de-SO<sub>x</sub> or desulfation. Zhang et al.<sup>43</sup>, as shown in figure 1.16, reported that de-SO<sub>x</sub> at 500 °C can result in 90% recovery of low-temperature SCR due to the decomposition of ammonium sulfate species. However, higher temperatures were needed to remove more stable copper sulfate species<sup>43</sup>. Recently, Kumar et al.<sup>51</sup> reported lower de-SO<sub>x</sub> temperatures using a "chemical de-SO<sub>x</sub>" protocol. Chemical de-SO<sub>x</sub> involves exposing poisoned samples to reductants such as NH<sub>3</sub>, C<sub>3</sub>H<sub>6</sub>, and n-C<sub>12</sub>H<sub>26</sub>. Such exposures can possibly change the oxidation state of Cu resulting in sulfur removal at lower temperatures compared to conventional deSO<sub>x</sub> temperatures.



**Figure 1.15** NO<sub>x</sub> conversion of Cu-SAPO-34 in the absence and presence of SO<sub>2</sub><sup>43</sup>. Experimental conditions: 500 ppm NH<sub>3</sub>, 500 ppm NO, 0, 50 or 200 ppm SO<sub>2</sub>, 10% O<sub>2</sub> and a balance of N<sub>2</sub>.



**Figure 1.16** NO<sub>x</sub> conversion of Cu-SAPO-34 with and without SO<sub>2</sub> and after a high temperature desulfation/regeneration exposure. Experimental conditions: 500 ppm NH<sub>3</sub>, 500 ppm NO, 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub> in a balance of N<sub>2</sub>. High temperature deSO<sub>x</sub> at 600, 700, or 735 °C in 10% O<sub>2</sub>/N<sub>2</sub> and overnight.

### 1.12 NH<sub>3</sub>-SCR kinetic modeling for Cu-zeolite catalysts

Both global and detailed kinetic models have been developed for NH<sub>3</sub>-SCR on different commercial, as well as model zeolites such as H-ZSM-5<sup>52,53</sup>, Fe-ZSM-5<sup>54,55</sup>, and Cu-faujasite <sup>56</sup>. For NH<sub>3</sub>-SCR over Cu-ZSM-5, Olsson et al.<sup>57,58</sup> developed global as well as detailed kinetic models. Metkar et al.<sup>59</sup> also developed kinetic models for NH<sub>3</sub>-SCR on Cu-CHA and Fe-ZSM-5, and included the effect of washcoat diffusivities on NH<sub>3</sub>-SCR transient behavior<sup>59</sup>.

Very recently, Olsson et al.<sup>60</sup> developed a kinetic model for sulfur poisoning and regeneration of NH<sub>3</sub>-SCR on Cu-SSZ-13. However, formation/decomposition of S intermediates i.e. copper sulfate and ammonium sulfate, the effect of S on different active sites and S adsorption/desorption were not included in this model.

# 1.13 Research objectives and dissertation outline

The cumulative exposure to ppm levels of sulfur present in the ultra-low sulfur diesel fuel can severely influence the performance of aftertreatment catalysts. A large body of research, therefore, has been directed at sulfur poisoning of Cu-CHA catalysts for NH<sub>3</sub>-SCR applications over the past years. Despite significant success, a molecular level understanding of the Cu/SSZ-13 sulfur poisoning mechanism is still missing. This seems crucial for manufacturing more stable SCR catalysts as well as the design of effective de-SO<sub>x</sub> procedures. Therefore, in the present dissertation, I aimed to first experimentally study the chemistry of Cu-CHA sulfur poisoning with the focus on development of a low-temperature SCR deactivation/regeneration mechanism. Then, this mechanism was used as the basis for the kinetic model development.

This dissertation is organized as follows. Chapter 2 describes the experimental setup and procedures used for catalyst performance testing and spectroscopic characterization. The experimental study of the effect of SO<sub>2</sub> on NH<sub>3</sub> oxidation over a Cu-SAPO-34 SCR catalyst is provided in chapter 3. In this study, exploiting temperatureprogrammed-desorption (TPD) and kinetic analysis, the impact of  $SO_2$  on  $NH_3$  oxidation, an undesired SCR side reaction was studied. Chapter 4 describes the study of SO<sub>2</sub> poisoning on NH<sub>3</sub>-SCR over a Cu-SAPO-34 catalyst, focusing on the forms/states of stored S and the effect of such species on low-temperature  $NO_x$  reduction activity. In this study, micro-reactor experiments, TPD and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) of NO adsorption were used to characterize/distinguish the forms of S species that formed upon SO<sub>2</sub> interaction with Cu-SAPO-34. Chapter 5 provides results of the study of the effect(s) of SO<sub>2</sub> on the two types of active sites in Cu-SSZ-13, namely Z2Cu and ZCuOH. In this study, by varying Si:Al ratios, two model catalysts with different distributions of these two active sites were prepared. Combining experimental analysis with DFT calculations, responses of Z2Cu and ZCuOH to SO<sub>2</sub> were investigated and a low-temperature sulfur poisoning mechanism was proposed. Based on experimental results, a kinetic model capable of describing sulfur storage and desorption behavior as well as NO<sub>x</sub> conversion over sulfated samples was developed and is presented in chapter 6. Finally, chapter 7 describes the conclusions of the dissertation and recommendations for the future work.

### **Chapter 2 Experimental methods**

In this Chapter, details of the experimental setup used in this dissertation are presented. Two main reactor systems were used: (1) reactor tests along with temperature programmed desorption (TPD) experiments were conducted in a bench-scale micro-reactor system equipped with MultiGas<sup>TM</sup> Fourier transform infrared (FTIR) spectrometry, (2) surface adsorption and reaction studies were done in an *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reactor system. The details of these two systems are described in this chapter. Other experimental apparatus used include X-ray diffraction (XRD) and inductively coupled plasma optical emission spectroscopy (ICP-OES). H<sub>2</sub> temperature programmed desorption (H<sub>2</sub>-TPR) experiments were conducted using a Micromeritics AutoChem II analyzer. The details of these instruments will be introduced in the following chapters where used.

## 2.1 Bench scale microreactor system

The process flow diagram of the micro-reactor system is shown in figure 2.1. The actual setup is shown in figure 2.2. The micro-reactor configuration can be divided into the three subsystems: (1) gas injection manifolds, including gas cylinders, mass flow controllers (MFC), filters, water and  $SO_2/SO_3$  injection systems, (2) micro-reactor system, which consists of the quartz tube reactor, tube furnace with temperature control, thermocouples and bypass, and (3) FTIR spectrometer and data acquisition system.

### 2.1.1 Gas injection manifolds

Table 2.1 lists the specifications of the gases used in the micro-reactor system. MKS mass flow controllers (MFC) (model: 1179C Mass-Flo<sup>®</sup>) were used to control the



Figure 2.1 Bench-scale micro-reactor system used in this study.

inlet gas flow rates. To display and control flow meters, MKS 4-channel power supply/readout units (model: MKS 247D) were used. The flow rate set points were calibrated using a Bios Definer digital flow meter. Three main manifolds were designed to control the inlet gases: (1) main manifold, including MFCs for N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, NO and NO<sub>2</sub>, (2) water was fed using a Bronkhorst evaporated liquid delivery system, and (3) SO<sub>2</sub>/SO<sub>3</sub> and NH<sub>3</sub> were introduced using separate manifolds to minimize the response time of the system and avoid contamination of the main inlet lines. The water injection system used was a Bronkhorst controlled evaporator mixer (CEM) equipped with El-FLOW MFC for

the  $N_2$  carrier gas and a Bronkhorst LIQUI-FLOW MFC for liquid water. All the gas lines were



Figure 2.2 The micro-reactor setup used in this study. This reactor setup is located at University of Houston.

kept heated at 200 °C to avoid water condensation and sulfur deposition. To this end, Cole-Parmer insulated heating tapes were used (shown in red lines in Fig. 2.1).

# 2.1.2 Micro-reactor system

The schematic of the packed-bed micro-reactor system is shown in figure 2.3. This reactor system consists of a 50 cm long quartz tube with 4 mm inner diameter (ID). A pair of Swagelok Ultra-Torr fittings together with Swagelok rubber ferrules were used as the end caps of the reactor. Two K-type thermocouples were placed upstream and downstream of

the catalyst bed to monitor the inlet and outlet temperatures. The temperature differences between inlet and outlet did not exceed 5 °C during all reactor experiments.

Gas	Description	Purity
N <sub>2</sub>	On-Site Nitrogen generator system (N-30-TGN model), used as the diluent for reactive feed gas	99.999%
$O_2$	Praxair Inc., pure	99.993%
NO	Praxair Inc., balanced with N <sub>2</sub>	5 %, certified standard
NO <sub>2</sub>	Praxair Inc., balanced with N <sub>2</sub>	5000 ppm, certified standard
NH <sub>3</sub>	Praxair Inc., balanced with N <sub>2</sub>	5 %, certified standard
$SO_2$	Praxair Inc., balanced with N <sub>2</sub>	1%, certified standard

 Table 2.1 Specifications of the gases used in the monolith reactor system.

The powder catalysts (250–425  $\mu$ m sizes) were held in place using quartz wool on both ends. The packed-bed micro-reactor was placed inside a Lindberg Minimite temperature-controlled furnace.



Figure 2.3 The schematic of packed-bed micro-reactor system.

For the purpose of lab safety, four Detcon gas sensors (model: DM-700) were used and placed near the micro-reactor gas supply systems to detect SO<sub>2</sub>, NO, NH<sub>3</sub> and H<sub>2</sub>. These sensors were controlled and monitored using a MX 32 digital controller (Oldham). To detect any possible CO leaks, portable CO alarms (Kidde model) were also placed throughout the lab.

### 2.1.3 FTIR spectrometer and data acquisition system

A MKS MultiGas MG-2030 FTIR spectrometer, capable of simultaneous analysis and display of more than 30 gases, equipped with a LN<sub>2</sub>-cooled MCT detector was used to measure the reactor effluent gas compositions. The analyzer is equipped with a digital temperature controller keeping the gas cell temperature at 191°C. The gas cell volume was 200 ml with a 5.11 m effective path length. In this thesis, the species concentrations measured by the FTIR included SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, CO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub>. Before each run, a background spectrum was taken, averaging 16 scans. The gas sampling cell was being purged when no measurements were taken, with a flow of pure N<sub>2</sub> (> 200 ml/min). CO<sub>2</sub>-free clean dry air with the maximum pressure of 20 psig was used to purge the instrument optical parts.

Sulfur measurements were done in a modified sulfur-resistant cell provided by MKS. The inside of the gas sampling cell was coated using corrosion resistant materials under the trademark Dursan<sup>®</sup>. The mirrors were coated using MgF<sub>2</sub>, and ZnSe windows equipped with Kalrez O-rings were used to prevent possible sulfur damage.

For recording concentration data taken from the FTIR, MKS MG2000® software was used. The data acquisition frequency was set to be 0.5 seconds with a resolution of 0.5 cm<sup>-1</sup>. The temperature data measured by thermocouples were measured using National Instruments modules, i.e., Field point controller and Labview® software. The temperature data collected by the software were then saved and analyzed using Microsoft Excel.

## 2.2 Diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS)

### **2.2.1 Introduction**

The advantage that diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) has over transmission IR techniques is the ability to study non-transparent materials for *in-situ* measurements at reaction temperatures. As the name implies, DRIFTS is based on radiations that undergo diffusive reflection from the catalyst surface. Having travelled through the particles, such reflected radiations provide useful information on the absorption characteristics of the catalyst<sup>61</sup>. However, unlike transmission IR, in DRIFTS, quantitative measurement of adsorbate concentrations is extremely difficult and highly dependent on the experimental conditions. The Lambert-Beer law, which relates absorbance to adsorbate concentration using the absorption coefficient (k), is not applicable in DRIFTS. However, for semi-quantitative analyses, the Kubelka-Munk equation can be used to convert the measured reflectance spectrum into the absorbance spectrum. Assuming a sample of infinite thickness, K-M expression can be simplified as follows:

$$f(r_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} = \frac{k}{s}$$
(2-1)

Where  $f(r_{\infty})$  is the K-M function,  $R_{\infty}$  is the measured spectrum, k is the absorption coefficient, s is the scattering coefficient which depends on particle size and and packing density of the sample. Similarly to the Lambert-Beer law, k can be replaced by  $2.303 \times \varepsilon(\nu) \times c$ , in which  $\varepsilon$  and c are the absorptivity and adsorbate concentration, respectively<sup>61</sup>. This gives:

$$f(r_{\infty}) = 2.303 \times \varepsilon(\nu) \times c/s \tag{2-2}$$

which resembles the Lambert-beer law used in the transmission IR spectroscopy.

### 2.2.2 Reactor system

Similar to the micro-reactor setup described in previous section, MKS mass flow controllers together with MKS 4-channel control boxes were used to control and display the gas flows. Specifications of gases used in the DRIFTS rector systems were similar to that of micro-reactor system except for the carrier gas. He was used as the carrier gas and the total flow was set to 50 cm<sup>3</sup>/min (STP). All the gas cylinders were purchased from Praxair, Inc. All the feed gases were mixed before being injected to the reaction chamber. A three-way switching valve placed close to the inlet of the reactor chamber was used to feed NH<sub>3</sub> and SO<sub>2</sub> from their separate manifolds. Using Cole Parmer heating tapes, all the inlet lines were heated to 150 °C to prevent water condensation and sulfur deposition.

The Praying Mantis<sup>™</sup> (DRP) accessory together with the high temperature reaction chamber (HVC), purchased form Harrick Scientific Products, Inc., was used to perform insitu measurements at high temperatures. The schematic of the Praying Mantis<sup>™</sup> and HVC are shown in figure 2.4 and 2.5, respectively<sup>62</sup>. Praying Mantis<sup>™</sup> includes a series of mirrors to collect/separate the specularly reflected radiations form the diffusive radiations. The mirrors are optically arranged so that the infrared beam is focused on the surface of sample, which is placed inside the HVC. Diffusive reflected radiations then are collected using other mirrors and sent to the detector<sup>62</sup>.



Figure 2.4 Front view of Praying Mantis<sup>™</sup> accessory used in DRIFTS setup<sup>62</sup>.

As shown in Fig. 2.5, the HVC chamber is equipped/sealed with a dome with three windows: two zinc selenium (SeZn) windows for the spectrometer radiation, and a transparent window for viewing the sample. The feed gases enter through the inlet and pass through the sample form the top and leave from underneath the sample. Even though the HVC is designed for operation up to 910 °C in vacuum, ZnSe windows can withstand a maximum temperature of 200 °C<sup>61</sup>. The HVC chamber is thermally controlled using a cartridge heater and K-type thermocouple connected to a Harrick Scientific temperature controller. To control the temperature of the outer surface of the HVC and protect the windows, a water-cooling jacket was designed underneath the chamber.



Figure 2.5 High temperature reaction chamber (HVC) used in DRIFTS.

# 2.2.3 Spectrometer and data acquisition system

The Thermo Scientific Nicolet<sup>TM</sup> iS<sup>TM</sup>50 FTIR spectrometer was used. Praying Mantis<sup>TM</sup> is installed and used in the spectrometer sample compartment. Thermo Scientific OMNIC software was used for recording and analyzing DRIFTS data. Watlow EZ-Zone<sup>®</sup> Configurator software was used to control and program the temperature. The DRIFTS data were collected/presented in Kubelka-Munk (K-M) units. Before each run, background spectra were taken in the range of 4000 to 600 cm<sup>-1</sup> (with a resolution of 4 cm<sup>-1</sup>) under a flow of He and 10% O<sub>2</sub>.

### Chapter 3 Effect of SO<sub>2</sub> on NH<sub>3</sub> oxidation over a Cu-SAPO-34 SCR catalyst

Note: The material presented in this chapter has been published (Jangjou et al., Catalysis Science & Technology, 2016, 6 (8), 2679-2685). The introduction and experimental methods material have been summarized to avoid redundancy with Chapters 1 and 2. Reference and figure numbers also changed for dissertation consistency.

# **3.1 Introduction**

Currently, selective catalytic reduction of NO<sub>x</sub> using ammonia (NH<sub>3</sub>-SCR) is widely used for NO<sub>x</sub> abatement in diesel aftertreatment systems <sup>25</sup>. The state-of-the-art SCR catalyst is a small pore metal-exchanged zeolite with a chabazite (CHA) structure, such as Cu-SSZ-13 and Cu-SAPO-34 <sup>63</sup>. Compared to medium pore zeolites such as Cu-ZSM-5, the CHA family has shown better hydrothermal stability and a wider operating temperature window for deNO<sub>x</sub> activity <sup>33,64</sup>.

However, it has been reported that even with Ultra-Low Sulfur Diesel (ULSD), the catalyst's cumulative exposure to sulfur over time will result in a loss of NH<sub>3</sub>-SCR activity, especially at low temperatures (i.e. under 300 °C) <sup>43,48,49</sup>. In terms of sulfur species in the exhaust gas, it is primarily SO<sub>2</sub>. But with oxidation catalysts often placed upstream of SCR catalysts, SO<sub>2</sub> can be converted to SO<sub>3</sub> <sup>65</sup>. In recent years, many research groups have studied the effects of sulfur species on NH<sub>3</sub>-SCR activity over Cu-CHA <sup>43,48,49,66-69</sup>. Cheng et al. <sup>48</sup> observed a significant loss in SCR activity over Cu-zeolite catalysts pre-exposed to SO<sub>2</sub> or SO<sub>3</sub>. In comparing the SCR activity of sulfated samples with SO<sub>2</sub> and SO<sub>3</sub>, the SO<sub>3</sub> poisoning effect was more severe than SO<sub>2</sub>. It was also reported that CuSO<sub>4</sub> formed upon SO<sub>2</sub> and SO<sub>3</sub> adsorption on Cu-zeolite catalysts. Zhang et al. <sup>43</sup> studied the impact of

SO<sub>2</sub> on NH<sub>3</sub>-SCR performance over a commercial Cu-SAPO-34 sample, and focused on the SO<sub>2</sub> poisoning mechanism. The authors concluded that deNO<sub>x</sub> activity at low temperature (<300 °C) was inhibited primarily due to formation of ammonium sulfate. It was, however, observed that the inhibition effect became insignificant at higher temperatures under the conditions of their tests, and activity was completely recovered after a high temperature thermal treatment in an O<sub>2</sub>/N<sub>2</sub> mixture. Most recently, Brookshear et al. <sup>69</sup> examined and characterized Cu-CHA catalysts after being exposed to 500 ppm SO<sub>2</sub> at 250 and 400 °C. A decrease in surface area and NO<sub>x</sub>/nitrate adsorption were observed after S exposure, possibly due to Cu sites being blocked. Overall, prior studies have illustrated losses in standard NH<sub>3</sub>-SCR performance after sulfur exposure due to formation of ammonium sulfate and sulfate species that can block active Cu sites, and the poisoning effect can be reversed by thermal treatment at higher temperatures.

In this study, we examined SO<sub>2</sub> poisoning of NH<sub>3</sub> oxidation over Cu-SAPO-34. Ammonia oxidation is an important side reaction, as its non-selective oxidation by O<sub>2</sub>, called parasitic oxidation, results in less NH<sub>3</sub> to react with NO<sub>x</sub>, and some of the NH<sub>3</sub> can be oxidized to NO, furthering an apparent loss in activity. It is generally accepted that CuO particles/clusters present in Cu-CHA are active toward NH<sub>3</sub> oxidation <sup>70,71</sup>. Also, the active site types apparently vary as function of temperature; at high temperatures (> 300 °C), Cu-ion monomers were found to be active for NH<sub>3</sub> oxidation. However, dimeric Cu formed under reaction conditions was reported to be the low temperature active center <sup>36</sup>. In terms of sulfur poisoning on NH<sub>3</sub> oxidation, Kumar et al. <sup>49</sup> and Brookshear et al.<sup>69</sup> have reported that sulfur inhibits NH<sub>3</sub> oxidation at low temperatures, and as was noted above, standard SCR is also inhibited in this same temperature range.

## 3.2 Experimental methods

### **3.2.1** Catalyst preparation and characterization

A solid-state ion-exchange (SSIE) method <sup>71,72</sup> was used to prepare Cu-SAPO-34 samples with various Cu loadings. Briefly, four different Cu-SAPO-34 samples (0.2, 0.5, 1.5 and 2.5 wt.% Cu-SAPO-34) were prepared by mixing various amounts of CuO (purchased from Sigma-Aldrich) with H-SAPO-34 (purchased from ACS Materials). For each sample, 1 g of H-SAPO-34 was thoroughly mixed with the desired amount of CuO and homogenized with an ultrasound mixer for 45 min. After mixing, the sample was placed in a cylindrical furnace that had 130 sccm of air flowing through it. Subsequently, the temperature was increased to 120 °C and held for 4 hr to dehydrate the sample. This was followed by two temperature ramps: one from 120 to 600 °C at 2 °C/min followed by the temperature being maintained at 600 °C for 6 hr in order to remove the impurities, and from 600 to 800 °C at 2 °C/min followed by a hold for 16 hr. Migration of copper into the pores of the H-form SAPO-34 happens in the final stage.

A Rigaku SmartLab X-ray diffractometer equipped with Cu Ka radiation was used for powder X-ray diffraction (XRD) measurements. XRD data were collected with  $2\theta$ ranging from 5 to 50° and a step size of 0.02. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of NO adsorption was used to characterize the Lewis acidity of Cu-SAPO-34 samples. In each run, 60 mg of powder sample were placed in the sample cup inside a high temperature reaction chamber (Harrick Praying Mantis) equipped with ZnSe windows. Before each run, samples were pretreated at 500 °C in 10% O<sub>2</sub> for 2 hr. The temperature was then set to 35 °C and a background spectrum was taken after the
system became stable. NO adsorption was performed by flowing 500 ppm of NO for 20 min in the presence of 10%  $O_2$  balanced with He, which was enough for complete NO saturation. The data were collected in the spectral range of 4000-650 cm<sup>-1</sup> using a Nicolet 6700 IR spectrometer equipped with a MCT detector.

## 3.2.2 Standard NH<sub>3</sub>-SCR and NH<sub>3</sub> oxidation reaction tests

NH<sub>3</sub> oxidation and standard NH<sub>3</sub>-SCR kinetic experiments were carried out in a micro-reactor system. In each run, 60 mg of Cu-SAPO-34 sample (250-425 µm sizes) were put into a 4 mm ID  $\times$  500 mm L quartz tube. The quartz tube was then placed inside a Lindberg Minimite temperature-controlled furnace. Two k-type thermocouples were placed in the system, upstream and downstream of the catalyst bed, to monitor the inlet and outlet temperatures. The gas lines were heated to >150 °C to prevent sulfur deposition and water condensation. A MKS MultiGas MG-2030 FT-IR analyzer was used to measure the effluent gas concentration. Before each run, the catalyst was pretreated in 10%  $O_2/N_2$  for 4 hr at 550 °C. For standard NH<sub>3</sub>-SCR tests, the inlet gas contained 500 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, and was balanced with N<sub>2</sub>. A similar feed composition was used for NH<sub>3</sub> oxidation experiments except that NO was removed from the feed. Sulfur poisoning reactions were conducted in an identical manner but with 50 ppm SO<sub>2</sub> in the feed. The total gas flow was 400 sccm and kept constant for all the experiments. The corresponding gas hourly space velocity (GHSV) was estimated to be 50,000 hr<sup>-1</sup>. NO<sub>x</sub> and NH<sub>3</sub> conversions were calculated based on the following equations:

$$NO_{x} Conversion \% = \frac{(NO+NO_{2})_{inlet} - (NO+NO_{2}+N_{2}O)_{outlet}}{(NO+NO_{2})_{inlet}} \times 100$$
(3-1)

$$NH_3 Conversion \% = \frac{(NH_3)_{inlet} - (NH_3)_{outlet}}{(NH_3)_{inlet}} \times 100$$
(3-2)

NH<sub>3</sub> oxidation rates were calculated using the following equation:

$$r_{NH_3 \text{ oxidation}} = \frac{X_{NH_3} \times F_{NH_3}}{W}$$
(3-3)

where  $X_{NH3}$  is the NH<sub>3</sub> conversion (%),  $F_{NH3}$  is the NH<sub>3</sub> flow rate (moles of NH<sub>3</sub> per s), W is the mass of the catalyst (g), and  $r_{NH3-oxidation}$  is the NH<sub>3</sub> oxidation reaction rate (moles of NH<sub>3</sub> per g<sub>cat</sub> per s).

Temperature-programmed desorption (TPD) experiments were conducted by first exposing the sample to 50 ppm SO<sub>2</sub>, 500 ppm NH<sub>3</sub>, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> using the same reactor described above. The adsorption phase was performed at 150 °C and with a total flow rate of 400 sccm. This was followed by a purge phase in N<sub>2</sub> for 1 hr, and then the temperature was ramped from 200 to 800 °C at a rate of 10 °C/min and held at 800 °C for 10 min.

#### 3.3 Results and discussion

#### 3.3.1 Catalyst characterization

XRD patterns were evaluated to verify the crystal structure of the Cu-SAPO-34 samples and to determine if Cu clusters formed during the synthesis. As shown in Figure 3.1, the XRD patterns obtained from the Cu-containing samples are similar to that obtained from H-SAPO-34, confirming that the CHA framework structure was maintained during synthesis, which included a treatment at 800 °C during the solid-state ion-exchange procedure. According to Feng et al. <sup>72</sup>, aging SAPO-34 can lead to some framework decomposition, which can be identified by the presence of a weak X-ray diffraction peak

at 21.3°, assigned to a tridimite (SiO<sub>2</sub>) dense phase. The absence of such peak in our samples confirms that the CHA framework was maintained after the solid-state ion-exchange procedure. However, as shown in Fig.3.1, two peaks at 35.6° and 38.7° were observed in the XRD patterns obtained from the 1.5 and 2.5 wt.% Cu-SAPO-34 samples, indicating that some unexchanged CuO was present in/on the crystal structure <sup>71,72</sup>. Note that these peaks were absent in the samples with low Cu loading, i.e. 0.2 and 0.5 wt.%.



**Figure 3.1** XRD patterns from the Cu-SAPO-34 and H-SAPO-34 samples. The inset shows the CuO phases (35.6° and 38.7°).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) during and after NO adsorption on Cu-SAPO-34 was used to characterize the Lewis acidity. Previous studies have shown that IR spectroscopy of NO adsorption can be used to identify the oxidation state and location of Cu species in Cu-CHA <sup>63</sup>. Zhang et al. <sup>73</sup> reported that NO adsorption on Cu-CHA resulted in the formation of NO<sup>+</sup> (~2170-2160 cm<sup>-1</sup>), Cu<sup>2+</sup>-NO (~1950-1850 cm<sup>-1</sup>), Cu<sup>+</sup>-NO (~1808-1770 cm<sup>-1</sup>), and [Cu(II)OH]<sup>+</sup>-NO species (~1870-1915cm<sup>-1</sup>). However, it has also been reported that formation of these species is highly 41

dependent on pretreatment conditions <sup>63</sup>. Moreover, two distinct NO vibration frequencies, corresponding to NO adsorption on Cu<sup>2+</sup> in two different cationic



**Figure 3.2** DRIFTS spectra obtained after exposing the samples to NO at 35 °C. The inset shows a magnified range, 1975-1850 cm<sup>-1</sup>, of the NO adsorption data with the 0.2 and 0.5 wt.% Cu-SAPO-34 samples. Experiment conditions: 35 °C exposure to 400 ppm NO balanced with He, total flow rate 50 mL/min, adsorption time: 20 min.

positions, have been observed <sup>74</sup>. Based on these data, IR bands observed at 1914 cm<sup>-1</sup> and 1948 cm<sup>-1</sup> were assigned to NO chemisorbed on Cu<sup>2+</sup> sites located in the CHA cage and six-membered ring, respectively. The DRIFTS spectra obtained during NO adsorption on our Cu-SAPO-34 samples are shown in Figure 3.2. The IR band at 1948 cm<sup>-1</sup>, accompanied by a feature at 1917 cm<sup>-1</sup>, was present in the DRIFTS spectra for all samples. This feature has been previously assigned to monomeric Cu<sup>++</sup> located in the six-membered ring position <sup>74</sup>. An IR feature at 1904 cm<sup>-1</sup> was present in the spectra obtained from the 0.5, 1.5, and 2.5 wt.% Cu samples, and its intensity increased as Cu content increased. This peak is assigned to Cu<sup>++</sup> located inside the CHA cages. Note that this peak was not observed in 0.2 wt.%

Cu sample. Overall, these observations confirm the presence of monomeric  $Cu^{++}$  in two distinct cationic positions for the 0.5, 1.5 and 2.5 wt.% Cu samples.

#### 3.3.2 Steady-State NH<sub>3</sub>-SCR activity in presence and absence of SO<sub>2</sub>

The standard NH<sub>3</sub>-SCR reaction performance was measured in the absence and presence of SO<sub>2</sub>, and the NO<sub>x</sub> and NH<sub>3</sub> conversions are plotted versus temperature in Figure 3.3. Similar NO<sub>x</sub> and NH<sub>3</sub> conversions to those observed previously were obtained  $^{71}$ . In the low temperature region (here defined as 100-250  $^{\circ}$ C), and in the absence of SO<sub>2</sub>, both NO and NH<sub>3</sub> conversions monotonically increased as the Cu loading increased. In the high temperature region (250-500 °C) and with higher Cu loadings (i.e. 1.5 and 2.5 wt.% Cu), the NO<sub>x</sub> conversion dropped with increasing temperature due to increasing parasitic ammonia oxidation. Note that in the low temperature region (100-250 °C) and with low Cu loading, the  $NO_x$  and  $NH_3$  conversion curves overlapped, demonstrating no overconsumption of NH<sub>3</sub> and thus no oxidation of NH<sub>3</sub> by O<sub>2</sub>. Surprisingly however, with higher Cu loading, 1.5 and 2.5 wt.% Cu, there was some NH<sub>3</sub> overconsumption observed even in the low temperature region. As shown in figure 3.3, the presence of SO<sub>2</sub> severely inhibited low temperature SCR performance for all the samples. However, with increasing temperature there was less impact. This trend is consistent with recently published work that evaluated sulfur poisoning of NH<sub>3</sub>-SCR over Cu-CHA catalysts <sup>43,49,69</sup>. In terms of parasitic NH<sub>3</sub> oxidation, no overconsumption of NH<sub>3</sub> was observed in the presence of SO<sub>2</sub> in the low temperature region, which was not the case for the higher Cu loaded samples in the absence of SO<sub>2</sub>. Therefore, SO<sub>2</sub> inhibited NH<sub>3</sub> oxidation at low temperature.



Figure 3.3 SCR of NO<sub>x</sub> conversion as a function of temperature in the absence and presence of 50 ppm SO<sub>2</sub> over (A) 0.2 wt.% Cu-SAPO-34, (B) 0.5 wt.% Cu-SAPO-34, (C) 1.5 wt.% Cu-SAPO-34, and (D) 2.5 wt.% Cu-SAPO-34. Reaction conditions: 400 ppm NH<sub>3</sub>, 400 ppm NO, 0 or 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub> and a balance of N<sub>2</sub>, total flow rate 400 cc/min, SV = 50,000 hr<sup>-1</sup>.

# 3.3.3 Steady-State NH<sub>3</sub> oxidation activity in presence and absence of SO<sub>2</sub>

Steady-state NH<sub>3</sub> oxidation data obtained in the presence and absence of SO<sub>2</sub> are shown in Figure 3.4. In the absence of SO<sub>2</sub>, NH<sub>3</sub> oxidation was observed with all samples, and light off temperature decreased with increasing Cu content. And since NH<sub>3</sub> oxidation activity has been reported to be negligible on H-SAPO-34 <sup>37</sup>, Cu is what catalyzes NH<sub>3</sub> oxidation over these samples. NH<sub>3</sub> oxidation in the presence of SO<sub>2</sub>, Figure 3.4, showed two distinct trends in two different temperature regions. At temperatures below 350 °C,

SO<sub>2</sub> clearly inhibited NH<sub>3</sub> oxidation. This inhibition effect was more obvious at higher Cu loading samples (Fig. 3.4 (C) and (D)).



Figure 3.4 NH<sub>3</sub> oxidation conversion as a function of temperature in the absence and presence of 50 ppm SO<sub>2</sub> over (A) 0.2 wt.% Cu-SAPO-34, (B) 0.5 wt.% Cu-SAPO-34, (C) 1.5 wt.% Cu-SAPO-34, and (D) 2.5 wt.% Cu-SAPO-34. Reaction conditions: 400 ppm NH<sub>3</sub>, 0 or 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub> and a balance of N<sub>2</sub>, total flow rate 400 cc/min, SV = 50,000 hr<sup>-1</sup>.

As an example, at 275 °C with the 2.5% Cu-SAPO-34 sample, NH<sub>3</sub> conversion was 10% in the absence of SO<sub>2</sub> and 2% when SO<sub>2</sub> was present. These results are in good agreement with those obtained by Brookshear et al. <sup>69</sup>. At temperatures higher than 350 °C no SO<sub>2</sub> inhibition was noted.

#### **3.3.4** NH<sub>3</sub> + SO<sub>2</sub> + O<sub>2</sub> Temperature-Programmed-Desorption (TPD)

The measured SO<sub>2</sub> concentrations during a temperature programmed desorption experiment, after the catalysts were exposed to NH<sub>3</sub>, SO<sub>2</sub> and O<sub>2</sub> at 200  $^{\circ}$ C, are shown in

Figure 3.5. A desorption peak at around 350 °C was observed with all samples. This has been previously assigned to the decomposition of ammonium sulfate <sup>43</sup>. Note that this peak, as shown in Fig. 3.5, was not observed with the H-SAPO-34 sample.



**Figure 3.5** Temperature-programmed desorption (TPD) results after sample exposure to SO<sub>2</sub> + NH<sub>3</sub> + O<sub>2</sub> at 200 °C. Experimental conditions: 400 ppm NH<sub>3</sub>, 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub> and a balance of N<sub>2</sub> at 200 °C, purged by N<sub>2</sub>, then TPD from 200 to 800 °C with a heating rate of 10 °C/min in N<sub>2</sub>.

Furthermore, the intensity of the desorption peak monotonically increased with increased Cu loading. Ammonium sulfate formed upon exposure of the Cu-SAPO-34 samples to  $NH_3 + SO_2 + O_2$  and its formation was catalyzed by the Cu. In comparing these TPD and steady-state  $NH_3$  oxidation data, it is apparent that the formation of ammonium sulfate is a  $NH_3$  oxidation poisoning mechanism at temperatures below 350 °C.

## 3.3.5 Kinetic analysis of NH<sub>3</sub> oxidation in presence and absence of SO<sub>2</sub>

Kinetic analysis was conducted to further investigate the effect of SO<sub>2</sub> on NH<sub>3</sub> oxidation. The NH<sub>3</sub> oxidation rates in the absence and presence of SO<sub>2</sub> were calculated

using steady-state data and plotted versus temperature in Figures 3.6 and 3.7. The Arrhenius plots are shown in Figure 3.8.

Two distinct kinetic trends as a function of temperature were observed with the 1.5 and 2.5 wt.% samples, as was also observed by Gao et al.<sup>37</sup> over Cu-SSZ-13. Gao et al.<sup>37</sup> explained this observation by the existence of two distinct apparent activation energies due to intra-particle diffusion at higher temperature or changes in coordination of the active catalytic centers. However, since two distinct kinetic regimes were observed in all the samples with different Cu loadings, the possibility of having two distinct active centers was neglected. The steady-state data used in evaluating the Arrhenius plots in Figure 3.8 are free from internal and external mass transfer limitations, as the Koros-Nowak criterion (Figure 3.9) holds in both kinetic regions. Interestingly, in the first kinetic region, all samples resulted in the same rates and apparent activation energies ( $E_{0.2\%}=84$ ,  $E_{0.5\%}=85$ ,  $E_{1.5\%}=86$ ,  $E_{2.5\%}=85$  kJ/mol). This strongly suggests that there is an identical type of active site in/on all samples that catalyzes NH<sub>3</sub> oxidation in this temperature region. With the 1.5 and 2.5 wt.% samples, a distinct change in the kinetic behavior was observed, with an activation energy of ~30 kJ/mol.

It is generally accepted that as Cu loading is increased, at some point Cu clusters will form rather than singly exchanged Cu in the zeolite framework. Furthermore, based on the XRD data presented in Section 3.3.1, there are some CuO particles in/on the samples with higher Cu loading.



Figure 3.6 NH<sub>3</sub> oxidation rate in the absence of SO<sub>2</sub> as a function of temperature on Cu-SAPO-34 samples with different Cu loadings. Experiment conditions: 400 ppm NH<sub>3</sub>, 10% O<sub>2</sub> balanced with N<sub>2</sub> at a GHSV of  $50,000 \text{ h}^{-1}$ .



**Figure 3.7** NH<sub>3</sub> oxidation rate in the presence of 50ppm SO<sub>2</sub> as a function of temperature on Cu-SAPO-34 samples with different Cu loadings. Experiment conditions: 50 ppm SO<sub>2</sub>, 400 ppm NH<sub>3</sub>, 10% O<sub>2</sub> balanced with N<sub>2</sub> at a GHSV of 50,000 h<sup>-1</sup>.

We therefore attribute the change in slope in the Arrhenius plot for the 1.5 and 2.5 wt% Cu-SAPO-34 samples to the presence of two  $NH_3$  oxidation active sites, one that is only active at high temperatures and one that is active in a larger temperature range, i.e. lower temperature, but is overall less active.



Figure 3.8 Arrhenius plots for NH<sub>3</sub> oxidation on Cu-SAPO-34 with different Cu loadings in the absence (solid lines) and presence of SO<sub>2</sub> (dashed lines).

The latter is assigned to some form of Cu cluster, and the former to exchanged Cu ions. The existence of two kinetic regions cannot be related to Cu<sup>++</sup> in two different cationic positions since the NO adsorption data discussed in Section 3.1 demonstrated that Cu<sup>++</sup> was present in two cationic positons for 0.5, 1.5 and 2.5% samples, and therefore the 0.5 wt.% Cu sample should have shown the same trend. Overall, these findings are consistent with the literature. Monomeric copper, i.e. isolated Cu<sup>++</sup>, has been reported as an NH<sub>3</sub> oxidation active site <sup>36</sup>. Gao et al. <sup>36</sup> also concluded there was a change in the dominant NH<sub>3</sub> oxidation catalytic site as a function of temperature when evaluating Cu-SSZ-13.

More specifically, at temperatures below 300 °C, dimeric copper species were responsible for NH<sub>3</sub> oxidation. However, at higher temperatures, isolated Cu-ion monomers were the main active sites.



**Figure 3.9** NH<sub>3</sub> oxidation rates in the absence of SO<sub>2</sub> as function of Cu loading at 277 and 324 °C. Experiment conditions: 400 ppm NH<sub>3</sub>, 10% O<sub>2</sub> balanced with N<sub>2</sub> at a GHSV of 50,000 h<sup>-1</sup>.

In the presence of SO<sub>2</sub>, there was a loss in NH<sub>3</sub> oxidation at low temperature, whereas high temperature performance was intact. In analyzing these data, only one kinetic region is therefore observed. SO<sub>2</sub> inhibited the active site that catalyzed the low temperature NH<sub>3</sub> oxidation. This was correlated to the Cu clusters/particles and therefore these sites are poisoned by SO<sub>2</sub>, at least at temperatures below 350 °C. Since above 350 °C identical activation energies were calculated and NH<sub>3</sub> oxidation conversions are unaffected by SO<sub>2</sub>, the monomeric Cu was active for NH<sub>3</sub> oxidation even though SO<sub>2</sub> was present. However, this does not suggest that the exchanged Cu ions were unaffected by SO<sub>2</sub>, only that at higher temperatures there was no evidence for it when only analyzing NH<sub>3</sub> oxidation. At low temperatures, i.e. below 350 °C, SCR performance was lost (Figure 3.8)

demonstrating that the Cu<sup>++</sup> sites were indeed poisoned as well. The temperature at which there is a change in kinetic regimes coincides with the onset temperature of ammonium sulfate decomposition. Therefore, the low temperature NH<sub>3</sub> oxidation is inhibited through the formation of ammonium sulfate, and with its decomposition NH<sub>3</sub> oxidation is again observed. We attribute this to poisoning of the Cu clusters, but since SCR was similarly inhibited by SO<sub>2</sub> at low temperature, Cu<sup>++</sup> ions were also poisoned. At temperatures above 350 °C, where the ammonium sulfate has decomposed, both NH<sub>3</sub> oxidation and SCR performances were recovered.

# **3.4 Conclusions**

The effect of SO<sub>2</sub> on NH<sub>3</sub> oxidation over a series of Cu-SAPO-34 catalysts with different Cu loadings was investigated in this study. Two kinetic regions were observed when evaluating samples with higher Cu loadings (1.5 and 2.5 wt.%). The apparent activation energy of the first kinetic region was similar to that observed in evaluating samples with lower Cu loading, i.e. 0.2 and 0.5 wt.% Cu. Based on these data, and TPD and XRD results, monomeric Cu<sup>++</sup> is an active site for NH<sub>3</sub> oxidation and catalyzes NH<sub>3</sub> oxidation in all samples. Cu clusters also catalyze NH<sub>3</sub> oxidation, and in a lower temperature range than the monomeric sites. Steady-state NH<sub>3</sub> oxidation experiments were then repeated in presence of SO<sub>2</sub> to study its poisoning effect. At temperatures below 350 °C, SO<sub>2</sub> severely inhibited NH<sub>3</sub> oxidation and SCR activity. However, SO<sub>2</sub> poisoning was negligible at higher temperatures. Kinetic and characterization analysis clearly demonstrate that SO<sub>2</sub> inhibited monomeric copper through formation of ammonium sulfate.

# Chapter 4 SO<sub>2</sub> poisoning of the NH<sub>3</sub>-SCR reaction over Cu-SAPO-34: Impact of ammonium sulfate versus other S-containing species

Note: The material presented in this chapter has been published (Jangjou et al., ACS Catalysis, 2016, 6 (10), 6612-6622). The introduction and experimental methods material have been summarized to avoid redundancy with Chapters 1 and 2. Reference and figure numbers also changed for dissertation consistency.

# 4.1 Introduction

Selective catalytic reduction of NO<sub>x</sub> using ammonia (NH<sub>3</sub>-SCR) has been extensively used/studied for NO<sub>x</sub> abatement in both mobile and stationary applications<sup>25</sup>. Recently discovered small-pore ion-exchanged zeolites, such as Fe- and Cu-CHA catalysts, have shown high hydrothermal stability and improved N<sub>2</sub> selectivity for SCR applications when compared to previously used metal exchanged zeolite systems such as Cu- or Feexchanged ZSM-5 or Beta<sup>24,33,34</sup>. Under actual exhaust conditions, the activity and stability of Cu-CHA SCR catalysts can be prone to hydrothermal aging and sulfur poisoning<sup>48,75,76</sup>. Sulfur can accumulate on the catalyst and ultimately result in decreased SCR performance, especially at low temperatures (< 350 °C)<sup>43,48,49</sup>.

Over the past few years, sulfur's impact on SCR performance and the associated chemistry/mechanism, as well as catalyst regeneration (deSO<sub>x</sub>) have been investigated. Key findings include the following:

(1) SO<sub>x</sub> severely inhibits low temperature NH<sub>3</sub>-SCR (< 350 °C) over both Cu-SAPO-34 and Cu-SSZ-13, whereas high temperature SCR activity seemed to be unaffected, or at least less sensitive to  $S^{43,48,49,69}$ .

- (2) Comparing SO<sub>2</sub> and SO<sub>3</sub>, SO<sub>3</sub> impacts were found to be more significant and difficult to reverse<sup>48,49</sup>. It was suggested that this is due to the ease of sulfate formation by interaction of SO<sub>3</sub> with Cu/zeolites compared to SO<sub>2</sub><sup>48</sup>. It was also reported that available active sites in Cu-CHA react with SO<sub>2</sub> and SO<sub>3</sub> via different mechanisms. The authors suggested that SO<sub>3</sub> poisoning involved some temperature-activated reactions rather than just simple adsorption of S-containing species<sup>49</sup>.
- (3) Cu-SSZ-13 and Cu-SAPO-34 oxidation functionality (i.e. NO and NH<sub>3</sub> oxidation reactions) at lower temperatures were substantially inhibited by low temperature sulfur exposures. At higher temperatures, however, SO<sub>2</sub> had no significant impact on NH<sub>3</sub> oxidation over Cu-CHA which corresponds to the lack of S poisoning in the standard SCR reaction in the same temperature range<sup>42,49,60,69,77</sup>.
- (4) NH<sub>3</sub> storage capacity was reportedly higher on sulfated Cu-SSZ-13 compared to the sample not exposed to  $S^{42}$ . However, there has been controversy on the effect of sulfur on NH<sub>3</sub> storage capacity over Cu-SAPO-34; Kumar et al.<sup>49</sup> and Wijayanti et al.<sup>66</sup> observed no significant impact on total NH<sub>3</sub> storage capacity over pre-sulfated samples, whereas Zhang et al.<sup>43</sup> reported an increase in ammonia storage after SO<sub>2</sub> + NH<sub>3</sub> co-adsorption relative to just NH<sub>3</sub> adsorption. This difference is due to the differences in the sulfation procedures used; co-adsorption led to significantly more ammonium sulfate formation.

- (5) Recently, using NH<sub>3</sub> adsorption as a probe, Luo et al.<sup>42</sup> concluded that monomeric copper density (Cu<sup>++</sup>), more specifically Cu<sup>++</sup> and [CuOH]<sup>+</sup>, were significantly decreased upon sulfur exposure.
- (6) In almost all cases, the SCR performance of poisoned Cu-SSZ-13 and Cu-SAPO-34 could be recovered with a high temperature (> 550 °C) treatment, and under lean conditions<sup>43,48,49,66,67,77–79</sup>. Recently, Kumar et al.<sup>51</sup> were able to successfully regenerate SCR activity of S-poisoned samples at lower temperatures using a "chemical deSO<sub>x</sub>" protocol. In this method, poisoned Cu-zeolites were treated by reductants such as NO<sub>x</sub> + NH<sub>3</sub>, NH<sub>3</sub>, C<sub>3</sub>H<sub>6</sub> or n-C<sub>12</sub>H<sub>26</sub>. Such exposures, according to the authors, changed the oxidation state of Cu which resulted in sulfur removal at lower temperatures compared to conventional deSO<sub>x</sub> temperatures<sup>51</sup>.

In terms of a deactivation mechanism, in early studies, Cheng et al.<sup>48</sup> reported formation of stable and highly dispersed CuSO<sub>4</sub>-like species in Cu-SSZ-13 upon exposure to SO<sub>x</sub>. Based on such observations, formation of CuSO<sub>4</sub> compounds was then claimed to be the main deactivation mechanism and reason for loss in low temperature SCR activity. At higher temperatures (> 350 °C), the authors concluded that these CuSO<sub>4</sub> species became unstable and catalyst performance was completely recovered after being treated at temperatures higher than 500 °C<sup>48,78,79</sup>. It should be noted that in these studies, an effect of ammonium sulfate was not considered since NH<sub>3</sub> was not used in the sulfation procedure. More recently, Zhang et al.<sup>43</sup> observed formation of ammonium sulfate as a result of SO<sub>2</sub> and NH<sub>3</sub> co-adsorption over Cu-SAPO-34. Their NH<sub>3</sub> + SO<sub>2</sub> temperature programmed desorption analysis showed that ammonium sulfate started decomposing at temperatures as low as 300 °C. The reversible nature of the poisoning behavior, with a threshold at around 350 °C, was simply explained by formation/decomposition of ammonium sulfate<sup>43</sup>.

Proposed ammonium and copper sulfate formation and decomposition scenarios, together with observations such as chemical deSO<sub>x</sub>, suggest that the sulfur poisoning mechanism/chemistry over Cu-CHA is still not well understood. For example, can ammonium sulfate formation be neglected if NH<sub>3</sub> is not used in the sulfation process; or if a pre-sulfated sample is exposed to  $NH_3$  is it possible to form ammonium sulfate? If ammonium sulfate is the primary low temperature SCR poison and decomposes at 300-350 °C, why are temperatures higher than 500 °C needed to recover low temperature SCR activity? Can we distinguish between the impact of ammonium sulfate and other sulfate species on NH<sub>3</sub>-SCR? Then, what are the effects of non-ammonium sulfate S species on SCR performance? In this study, we evaluated the possible forms/states of S-containing species on Cu-SAPO-34 and the effect(s) of such species on SCR performance. We were experimentally able to distinguish sulfur poisoning caused by ammonium sulfate and other S-containing species. DRIFTS was used to study the effect of S-containing species on active Cu centers, and similarly the progression of the surface species during desulfation experiments. With these results, we evaluated simulated low temperature  $deSO_x$  on SCR performance and its recovery.

## 4.2 Experimental methods

#### 4.2.1 Reaction tests

The Cu-SAPO-34 (with Si/(Al + P) = 0.16) sample was prepared in-house using a solid-state ion-exchange method described by Wang et al.<sup>80</sup>. The Cu content was measured

using ICP-OES (Galbraith Laboratories, Inc.) and was 0.95 wt.% (Cu/Al: 0.022). All the reaction tests were carried out in a micro-reactor described previously<sup>77</sup>. A MKS MultiGas 2030 FTIR was used to analyze the effluent gas composition, which included SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. In all the reaction tests the base feed composition was 10% O<sub>2</sub> with a balance of N<sub>2</sub>, and the total gas flow was 400 sccm, for a gas hourly space velocity (GHSV) of 270,000 hr<sup>-1</sup>. Before each test, the catalyst was pre-treated in 10% O<sub>2</sub> balanced with N<sub>2</sub> at 550 °C for 4 hr. NO<sub>x</sub> conversion was calculated using the equation below:

$$NO_{\chi} Conversion \% = \frac{(NO+NO_2)_{inlet} - (NO+NO_2 + N_2O)_{outlet}}{(NO+NO_2)_{inlet}} \times 100$$
(4-1)

To evaluate the effect of feed composition on S storage capacity, a series of temperature programmed desorption (TPD) experiments were carried out after the catalyst was exposed to  $SO_2 + NH_3 + NO + O_2$ ,  $SO_2 + NH_3 + O_2$ , or  $SO_2 + O_2$ . The adsorption phase was run at 210 °C until saturation. This was followed by purging in a N<sub>2</sub> flow for 1 hr, and finally heating the sample from 210 to 830 °C at 10 °C/min and holding at 830 °C for 10 min.

Two sets of experiments were designed to form sulfate species, one to form ammonium sulfate + Cu sulfate and one to form only Cu sulfate species. These are discussed below with details in Table 4.1.

#### 4.2.2 Cu<sub>x</sub>SO<sub>y</sub> formation and associated experiments

First, we designed an experiment to examine whether ammonium sulfate plays a role as a SCR reactant in the presence of NO +  $O_2$ , in other words, to determine if ammonium sulfate can be used to reduce NO<sub>x</sub>. Then by deliberately removing ammonium

sulfate, we were also able to form only  $Cu_xSO_y$  on the surface and in such a way, the role of the remaining S was explored.

#1.Cu <sub>x</sub> SO <sub>y</sub> forming experiment (Figure 4.2)			#2. (NH <sub>4</sub> ) <sub>x</sub> Cu <sub>y</sub> SO <sub>z</sub> forming experiment (Figure 4.3)	
Cu <sub>x</sub> SO <sub>y</sub> deposition	Stage 1	Co-adsorption of NH <sub>3</sub> and SO <sub>2</sub> : 55 ppm SO <sub>2</sub> (120 min), 425 ppm NH <sub>3</sub> (90 min), 10% O <sub>2</sub> , T=210 °C	Stage 1-4	Same as left column
	Stage 2	Purging in N <sub>2</sub> for 120 min, T=210 °C	Stage 5	Exposing stored S to NH <sub>3</sub> : 425 ppm NH <sub>3</sub> and 10% O <sub>2</sub> for 120 min , T=210 °C
	Stage 3	Ammonium-Sulfate removal: 425 ppm NO and 10% O <sub>2</sub> for 120 min, T=210 °C	Stage 6	Purging in N <sub>2</sub> for 60 min, T=210 °C
	Stage 4	Purging in N <sub>2</sub> for 30 min, T=210 °C		
	Stage 5	TPD in N <sub>2</sub> : Heating up from 210 to 830 °C at 10 °C/min (100 min)	Stage 7	TPD in N <sub>2</sub> : Heating up from 210 to 830 °C at 10 °C/min (100 min)

Table 4.1 Experimental conditions used in the experiments used to form the two distributions of S.

This experiment consisted of multiple stages:

- The sample was pre-exposed to 55 ppm SO<sub>2</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 30 min. After this, the sample was exposed to 422 ppm NH<sub>3</sub> and 55 ppm SO<sub>2</sub> for 90 min in the same base feed. The pre-exposure to SO<sub>2</sub> allows quantitative analysis of ammonium sulfate formation as NH<sub>3</sub> is injected.
- A purge phase followed at the same temperature with only N<sub>2</sub> flowing, for 120 min.
- Subsequently, the catalyst was exposed to 425 ppm NO and 10% O<sub>2</sub> at 210 °C for 120 min.

- 4) The sample then underwent a final purge phase in N<sub>2</sub> at 210 °C for 30 min. Based on the lack of NH<sub>3</sub> desorption in the TPD stage described below, and the absence of S desorption in any of the previous stages, upon completion of stage 4, the state/form of the remaining S species following this procedure was Cu<sub>x</sub>SO<sub>y</sub>.
- 5) Finally, a TPD was performed by heating the catalyst from 210 to 830 °C at 10 °C/min and then holding the temperature at 830 °C for 10 min.

#### 4.2.3 (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> and Cu<sub>x</sub>SO<sub>y</sub> formation and associated experiments

The second type of experiment aimed to evaluate the possibility of re-formation of ammonium sulfate from surface sulfur species that remained after an initial ammonium sulfate decomposition. Here, the first 4 stages were similar to that of the experiment described in section 4.2.2. However, in stage 5, unlike the previous experiment, the catalyst was exposed to 425 ppm NH<sub>3</sub> and 10% O<sub>2</sub> in N<sub>2</sub> at 210°C. Subsequently, the catalyst was purged one more time in N<sub>2</sub> only, as stage 6. The state/form of stored S-species at this point was observed to be (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub>. Finally, the sample was heated to 830 °C (stage 7) using the same TPD conditions as described in the previous section.

## 4.2.4 Characterization of Cu<sub>x</sub>SO<sub>y</sub> and (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub>

As explained above, S was observed in two states/forms (1)  $Cu_xSO_y$ , or (2)  $(NH_4)_xCu_ySO_z$ , and different characterization experiments were performed to identify/compare these two forms of S. Note that each experiment containing sulfur was also conducted in the absence of  $SO_2$ , for comparison purposes. The samples treated without sulfur have "no S" as a suffix in their notation.

The sulfur content of Cu-SAPO-34 samples that contained  $Cu_xSO_y$  and  $(NH_4)_xCu_ySO_z$  were determined using two methods: (1) inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Galbraith Laboratories, Inc.) and (2) temperature programmed desorption (TPD) where the S release was measured (H<sub>2</sub>SO<sub>4</sub> and SO<sub>3</sub> were also monitored).

The effect of  $Cu_xSO_y$  and  $(NH_4)_xCu_ySO_z$  on  $NH_3$ -SCR performance was also investigated. These experiments involved (1)  $Cu_xSO_y$  or  $(NH_4)_xCu_ySO_z$  deposition, (2) stepwise desulfation at 430, 530, 630, 730, and 830 °C, with a 10 °C/min heat ramp in N<sub>2</sub>, (3) standard NH<sub>3</sub>-SCR performance evaluation at 210 °C, (4) TPD in N<sub>2</sub> from 210 to 830 °C at 10 °C/min and then holding the temperature at 830 °C for 10 min.

Diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS) was used to characterize  $Cu_xSO_y$  formation and any effect on NO adsorption on Cu sites. The fresh Cu-SAPO-34 powder was pressed into a ~60 mg pellet, which was placed in a high temperature Harrick Scientific Praying Mantis reaction chamber equipped with ZnSe windows. Before each run, the samples were pre-treated in 10% O<sub>2</sub> at 500 °C for 2 hr with a balance of He. NO adsorption spectra were collected using a Nicolet 6700 IR spectrometer. NO adsorption was examined on two samples that underwent the same protocol used to make  $Cu_xSO_y$ , one with and one without (no S) SO<sub>2</sub> as part of the procedure.

#### 4.3 Results and discussion

#### **4.3.1** SO<sub>2</sub> TPD after exposures to different feed gas mixtures

Figure 4.1 shows the amounts of  $SO_2$  released from the Cu-SAPO-34 sample during temperature programmed desorption (TPD) experiments after the sample had been exposed to different feed compositions at 210 °C. Despite having different amounts of released S, all TPD spectra showed similar features at temperatures higher than 600 °C.



**Figure 4.1** SO<sub>2</sub> TPD spectra after the catalyst was exposed to SO<sub>2</sub> + NH<sub>3</sub> + NO + O<sub>2</sub>, SO<sub>2</sub> + NH<sub>3</sub> + O<sub>2</sub>, or SO<sub>2</sub> + O<sub>2</sub> at 210 °C. Experimental conditions: 450 ppm NH<sub>3</sub> (if present), 55 ppm SO<sub>2</sub> (if present), 450 ppm NO (if present), 10% O<sub>2</sub> (if present) and a balance of N<sub>2</sub> at 210 °C, temperature ramp to 830 °C at 10 °C/min in N<sub>2</sub>.

More specifically, a desorption peak at 650 °C and in most cases one at 800 °C can be found in the TPD profiles. Previous studies have assigned these high temperature desorption peaks to sulfate species ( $SO_4^{2-}$ ) on different adsorption sites <sup>43,48</sup>, however, the nature of these adsorption sites is not clear. As shown in Fig. 4.1, having both NH<sub>3</sub> and

 $SO_2$  in the feed resulted in another desorption peak centered at 390 °C with a shoulder at around 500 °C. The peak at 390 °C was previously assigned to decomposition of ammonium sulfate <sup>43</sup>. It is also apparent that a significantly larger amount of S was released when SO<sub>2</sub> and NH<sub>3</sub> were both present in the feed. For better comparison, the S coverages at different exposure conditions were calculated based on moles of S released during the TPD per amount of Cu measured by ICP-OES, and are listed in Figure 4.1. Note that previous work has shown that adsorbed S species (i.e. ammonium sulfate and other S species) were only formed over Cu-containing samples, not on the bare zeolite material. More specifically, a series of Cu-SAPO-34 with different Cu loadings as well as H-SAPO-34 were exposed to NH<sub>3</sub> and SO<sub>2</sub> at ~200 °C. The amount of desorbed sulfur from H-SAPO-34 was negligible. Moreover, the amount of adsorbed S increased as a function of Cu loading <sup>77</sup>. In evaluating the sulfur coverages, with only SO<sub>2</sub> and O<sub>2</sub> in the feed, a small amount of S was released during the TPD. These data demonstrate that SO<sub>2</sub> itself does not adsorb significantly on the available Cu sites. With NH<sub>3</sub> added a much larger amount of S adsorbed, as the presence of NH<sub>3</sub> opens up the ammonium sulfate formation pathway. Note that H<sub>2</sub>O was not present during sulfation phase. However, adding water to SCR feed in the presence of SO<sub>2</sub> at 210 °C (data not shown here) was found not to affect S storage as well as nature of S species.

# 4.3.2 Cu<sub>x</sub>SO<sub>y</sub> versus (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub>

In an attempt to distinguish between the effects of ammonium sulfate and other possible S-containing species on NH<sub>3</sub>-SCR over Cu-SAPO-34, two sets of experiments

were performed as described in Table 4.1. The results are shown in Figures 4.2 and 4.3 and discussed in this section.

Figure 4.2 shows the inlet and outlet concentrations during the experiment targeting  $Cu_xSO_y$  only formation, which includes 5 stages as described in the left column of Table 4.1. Stage (1) adsorption: as shown in Fig. 4.2, the SO<sub>2</sub> signal reached its maximum at 55 ppm, which was the inlet value, within a short time after the onset of adsorption. After saturation, the SO<sub>2</sub> concentration remained unchanged until NH<sub>3</sub> was introduced. The SO<sub>2</sub> signal decreased and NH<sub>3</sub> was not immediately detected in the outlet. This is due to the formation of ammonium sulfate as well as NH3 adsorption. Simultaneously, water formation was also observed, which can be attributed to some small level of NH<sub>3</sub> oxidation over the oxidized surface. Note that we have previously shown that  $NH_3$  oxidation can occur over Cu-SAPO-34 at such a low temperature (i.e. ~210 °C)<sup>11</sup>. In comparing this result to that in the absence of sulfur exposure, less water is observed, confirming deactivation of Cu sites for NH<sub>3</sub> oxidation. The NH<sub>3</sub> and SO<sub>2</sub> concentrations ultimately returned to their inlet values upon saturation. Stage (2) purge: when the SO<sub>2</sub>, NH<sub>3</sub> and O<sub>2</sub> were switched off, both the NH<sub>3</sub> and SO<sub>2</sub> signals dropped to zero. Stage (3)  $NO + O_2$ : at the end of stage 2, the catalyst was saturated with ammonium sulfate and other S-containing species. The catalyst was exposed to NO +  $O_2$  at 210 °C to remove all of the previously adsorbed NH<sub>3</sub>, as is proven below. As NO and O<sub>2</sub> were introduced, the NO concentration quickly increased to ~390 ppm (less than its inlet



Figure 4.2 Outlet and inlet concentrations during the experiment where Cu<sub>x</sub>SO<sub>y</sub> was formed. Experimental conditions: (1) 55 ppm SO<sub>2</sub> (120 min), 425 ppm NH<sub>3</sub> (90 min) and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C, (2) purging with only N<sub>2</sub> flowing for 120 min, (3) 425 ppm NO and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 120 min, (4) purging in N<sub>2</sub> for 30 min and (5) TPD phase with a temperature ramp from 210 to 830 °C at 10 °C/min in N<sub>2</sub> and holding at 830 °C for 10 min.

value) and continued to increase but at a slower rate until it reached its steady-state concentration (i.e. ~425 ppm, equal to the inlet value). Besides, the NH<sub>3</sub>-SCR reaction was further confirmed by two observations. First, the H<sub>2</sub>O concentration increased as it is a product of SCR, and then decreased since surface NH<sub>3</sub> coverage decreased via consumption. Second, NO<sub>2</sub> was not observed until NO reached a steady state concentration

value, suggesting consumption of NO<sub>2</sub> via fast SCR occurred simultaneous with NH<sub>3</sub> consumption. The same test, but in the absence of SO<sub>2</sub>, was performed as a control experiment. To compare SCR reactivity on the control (without SO<sub>2</sub>) and sulfated samples, NO consumption during stage 3 of the experiments is plotted versus time in Figure A.1. NH<sub>3</sub>-SCR initially proceeded at a slower rate on the sulfur exposed sample relative to fresh Cu-SAPO-34. At about 500 seconds, the NO consumption on the non-sulfated sample dropped below that of the sulfated sample, which was simply due to the depletion of the NH<sub>3</sub> reactant. As a consequence, for the S-exposed sample, the NO concentration reached its steady state value much later due to the slower consumption of surface NH<sub>3</sub>. These results support our conclusion that the ammonium in the ammonium sulfate structure can be consumed as a reactant in the NH<sub>3</sub>-SCR reaction, but this is ultimately at a slower rate compared to "normal" SCR using  $NH_3$  via the nitrite or nitrate mechanism. In evaluating the amount of NO consumed over the fresh versus sulfated samples further proves that it is ammonium sulfate that is formed. Assuming NH<sub>3</sub> and NO react in 1:1 stoichiometric ratio, and using the data shown Fig. A.1, the amount of excess NO consumed over the sulfated sample is 167 mole gr<sup>-1</sup>. The amount of S stored on the catalyst, obtained from Figure 4.1, is 79 mole  $gr^{-1}$ . Therefore, the ratio of excess NO:stored S is ~ 2:1, strongly suggesting an ammonium sulfate species. Stages (4) and (5), purge followed by the TPD: these stages were used to examine the strength and amounts of the adsorbed S-containing species that remained after the first 3 stages. No NH<sub>3</sub> was observed during the TPD phase, demonstrating complete consumption of surface ammonia during stage 3. The TPD profile obtained during stage 4 was magnified and displayed in Figure 4.4. These profiles represent all the desorbing S-containing



**Figure 4.3** Outlet and inlet concentrations during the experiment where (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> was formed. Experimental conditions: (1) 55 ppm SO<sub>2</sub> (120 min), 450 ppm NH<sub>3</sub> (90 min) and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C, (2) purging with only N<sub>2</sub> flowing for 120 min, (3) 450 ppm NO and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 120 min, (4) purging in N<sub>2</sub> for 30 min, (5) 450 ppm NH<sub>3</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 90 min (6) purging in N<sub>2</sub> for 60 min and (7) TPD phase with a temperature ramp from 210 to 830 °C at 10 °C/min in N<sub>2</sub> and holding at 830 °C for 10 min.

species that remain after stage 3, i.e. after ammonium sulfate was removed. This can be concluded based on three observations: (1) no sulfur species (SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) were detected during stages 2 and 3, therefore the S stored during stage 1 remained on the sample, (2) all of the SO<sub>2</sub> desorption peaks observed during TPD experiments in Fig. 4.1

were again observed except the ammonium sulfate peak, and (3) NH<sub>3</sub> was absent during TPD. Furthermore, the TPD profile showed three desorption peaks, at 480, 650 and 800 °C, which are likely associated with Cu since similar features were not observed with H-SAPO-34<sup>77</sup>. The natures of these S species are not yet fully understood and here we tentatively assign these species as "Cu<sub>x</sub>SO<sub>y</sub>" to distinguish them from (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub>.

A separate experiment was performed in order to determine if ammonium sulfate can form if these  $Cu_x SO_y$  species are exposed to NH<sub>3</sub>, and the experimental procedure is described in the right column of Table 4.1. The inlet and outlet concentrations during this experiment are shown in Figure 4.3. The first 4 stages were the same as the experiment which was previously used to form  $Cu_xSO_y$ . The catalyst was then exposed to  $NH_3 + O_2$ after  $Cu_x SO_y$  formation (stage 5), followed by a purge in N<sub>2</sub> (stage 6) and TPD (stage 7). The TPD profile during stage 7 is again magnified, and plotted in Fig. 4.4. The SO<sub>2</sub> peak at 390 °C demonstrates ammonium sulfate formed with Cu<sub>x</sub>SO<sub>y</sub> exposed to NH<sub>3</sub> and O<sub>2</sub> at 210 °C. It is worth noting here that there was no loss of S during stage (2) and (3) in both experiments as confirmed by a mass balance analysis, data shown in Table 4.2. The S adsorbed during stage 1 (in both transient experiments) remained on the sample but can be transformed from Cu<sub>x</sub>SO<sub>y</sub> to (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> or vice versa. And it is apparent that a substantial amount of amount of the Cu<sub>x</sub>SO<sub>y</sub> can be transformed into ammonium sulfate, although some small amount of the other possible S species also exist (as shown in Fig. 4.4).

A key finding from these results is that the adsorbed sulfur species can interchangeably switch form from  $(NH_4)_x Cu_y SO_z$  to  $Cu_x SO_y$  or vice versa depending



**Figure 4.4** TPD profiles obtained after the experiments where Cu<sub>x</sub>SO<sub>y</sub> and (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> were formed. whether NH<sub>3</sub> is present or not. Even with no NH<sub>3</sub> in the sulfation procedure, ammonium sulfate can be made with a subsequent NH<sub>3</sub> exposure, as when SCR might be evaluated after a S exposure. Therefore, not co-feeding NH<sub>3</sub> and SO<sub>2</sub> does not exclude the effect of ammonium sulfate on NH<sub>3</sub>-SCR, suggesting that some conclusions in previous studies evaluating sulfur poisoning on NH<sub>3</sub>-SCR may need to be reconsidered. This also demonstrates that exposing S-containing species (Cu<sub>x</sub>SO<sub>y</sub>) to NH<sub>3</sub> at a relatively low temperature results in formation of less stable S species (i.e. ammonium sulfate) that can be removed at much lower temperatures (based on Fig. 4.4). In other words, ammonia can drive S-containing species from a seemingly more strongly adsorbed position/form to the less stable ammonium sulfate form. This unique phenomenon will be further discussed below, in terms of how desulfation might either be induced to occur at a relatively lower temperature, or is occurring during normal operation since NH<sub>3</sub> is always being fed.

Sample	S content (µmoleS·gr <sup>-1</sup> )	
	ICP-OES	TPD
Cu <sub>x</sub> SO <sub>y</sub> _Cu-SAPO-34	83.4	68.8
$(NH_4)_x Cu_y SO_z \_Cu-SAPO-34$	80.9	64.9

Table 4.2 Amount of stored sulfur in the samples with the two distributions of sulfur.

#### 4.3.3 Poisoning effect of S on low temperature NH<sub>3</sub>-SCR performance

In this section, steps 1-3 (described in Table 4.1) were first performed, followed by the addition of NH<sub>3</sub> to NO +  $O_2$  after step 3, in order to evaluate the NH<sub>3</sub>-SCR activity on the sample where Cu<sub>x</sub>SO<sub>y</sub> was formed. The NO<sub>x</sub> conversion after this treatment is shown in Figure 4.5(A). The more complete set of results from these experiments are shown in Figures A.2-4, and include two ancillary experiments; in one experiment, only SO<sub>2</sub> was added in step 1 (Figure A.2), and the other, SO<sub>2</sub> was also added during the NO + O<sub>2</sub> exposure in step 3 (Figure A.4).

According to the results shown in Figure 4.5(A), although SCR performance after  $SO_2$  exposure was not as severely inhibited as when  $SO_2$  was included in the feed, it is still obvious that there was a large loss in performance as compared to that of fresh sample ( $NO_x$  conversion dropped from 68 to 17%). In addition, some portion of the sulfate species became ammonium sulfate as soon as the sample was exposed to  $NH_3$ , which also impacted the SCR performance. As a result, this 75% loss in activity is due to both ammonium sulfate and other S species.



**Figure 4.5** (A) NO<sub>x</sub> reduction conversion at 210 °C with the fresh sample, in the presence of 50 ppm SO<sub>2</sub>, and with the sample that contains Cu<sub>x</sub>SO<sub>y</sub>, and regenerated Cu<sub>x</sub>SO<sub>y</sub> at 530, 730 and 830 °C. (B) Outlet concentrations during the experiment with a desulfation to 730 °C. Experimental conditions: (1) Cu<sub>x</sub>SO<sub>y</sub> deposition (see Table 4.1), (2) heating from 210 to 730 °C at 10 °C/min and holding the temperature at 730 °C for 15 min in N<sub>2</sub>, (3) exposure to 450 ppm NH<sub>3</sub>, 450 ppm NO, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C, (4) purging in N<sub>2</sub> followed by heating to 830 °C at 10 °C/min and holding there for 10 min. (C) SO<sub>2</sub> released from the sample with Cu<sub>x</sub>SO<sub>y</sub> during the ramp to 530, 730 and 830 °C. (D) SO<sub>2</sub> released from the

As noted above (Fig. 4.4), there were three desorption peaks (i.e. 480, 650 and 800 °C) in the TPD profile that were associated with Cu sulfate formation. Here, the impact of each of the Cu sulfate forms on SCR performance was studied. Three desulfation

experiments were performed at 530, 730, and 830  $^{\circ}$ C, respectively and the measured NO<sub>x</sub> reduction activities are also shown in Fig. 4.5(A). As an example, the

performance after desulfation at 730 °C is discussed here. The outlet concentrations are shown in Figure 4.5(B) and the corresponding inlet concentrations are plotted in Figure A.5 for reference. To begin with,  $Cu_xSO_y$  was formed by following steps 1-4 as described in Table 1. Next, the catalyst was heated to 730 °C at 10 °C/min to remove species associated with the desorption peaks at 480 and 650 °C. SO<sub>2</sub> evolution during desulfation (shown in Fig. 4.5(C)) followed the same pattern as that from the earlier experiment

shown in Fig. 4.4. Standard NH<sub>3</sub>-SCR performance was then evaluated at 210 °C, shown in Fig. 4.5(B). At this stage, the NO signal increased immediately giving rise to a sharp NO spike while at the same time there was no ammonia signal observed. As NO and NH<sub>3</sub> reached the catalyst, NH<sub>3</sub> started to adsorb resulting in the normal delay in the output NH<sub>3</sub> signal. This was expected due to the fact that all the NH<sub>3</sub> was consumed during the previous exposure to the NO + O<sub>2</sub>, and therefore the catalyst surface initially had zero NH<sub>3</sub> coverage. On the other hand, NO molecules, with no adsorbed NH<sub>3</sub> to react with, slipped through the catalyst, resulting in the sharp NO spike. Finally, at the end of stage 3, after the surface was saturated with NH<sub>3</sub> under these conditions, the NO and NH<sub>3</sub> concentrations reached steady-state values, well below their inlet values. It should be noted that NO<sub>x</sub> conversion was compared to that calculated from the experiment with no SO<sub>2</sub> added (e.g. Figure A.6 is the control experiment for Fig. 4.5 (B) that includes a TPD to 730 °C). After the SCR performance test, a TPD to 830 °C was performed (stage 4 in Fig. 4.5(B)) to determine what S-species remained and the results are shown in Fig. 4.5(D). In comparing NO<sub>x</sub> conversions after the stepwise desulfations at different temperatures, it is clear that a significant amount of the SCR activity was recovered after the TPD at 530 °C, as shown in Figure 4.5(A). NO<sub>x</sub> conversion increased from 17 to 53% after removal of the first Cu<sub>x</sub>SO<sub>y</sub> peak. This suggests that the species associated with the desorption peak at 480 °C may play a major role in poisoning the catalyst. However, this is not necessarily true, since as noted earlier, the poisoning effect may not be exclusively due to Cu<sub>x</sub>SO<sub>y</sub> - the sample was exposed to NH<sub>3</sub> as part of the SCR test and therefore ammonium sulfate could have formed. Thus it is actually a combination of ammonium sulfate, again, and/or copper sulfate species. This will be discussed in more detail in the following section. The second and third peaks showed a more straightforward pattern, the amount of catalyst regeneration was proportional to the amount of S desorbed.

Interestingly, and key in comparing results from different studies, in comparing the results shown in Fig. 4.5(C) with (D), it is apparent that the Cu<sub>x</sub>SO<sub>y</sub> species were "stabilized" after being heated to the higher temperatures during the TPD experiments. Reexposing these species to NH<sub>3</sub> at 210 °C did not result in formation of ammonium sulfate as occurred when the sample was not exposed to high temperature exposures. In other words, exposing adsorbed sulfur to NH<sub>3</sub> at the original SO<sub>2</sub> adsorption temperature led to formation of ammonium sulfate. However, when the sample was heated after being exposed to SO<sub>2</sub>, the sulfur species that formed became more stable when considering their reactivity towards NH<sub>3</sub> and ammonium sulfate formation. As reported by Hass et al.<sup>81</sup>, on Cu-exchanged ZSM-5 catalysts, stable copper sulfate complexes can form via different pathways. They concluded CuSO<sub>3</sub> or CuSO<sub>2</sub> can form upon SO<sub>2</sub> adsorption and can be further oxidized to CuSO<sub>4</sub> or Cu(SO<sub>4</sub>)Cu<sup>81</sup>, which are more stable sulfate complexes. Another possibility is the loss of the OH ligands on Cu, i.e. [CuOH]<sup>+</sup> decomposition, and this resulting Cu moiety might lead to formation of a more stable Cu sulfate species. Therefore, it can be argued that higher temperatures allow formation of more stable sulfate species, compared to those formed at the adsorption temperature (i.e. 210 °C). Higher temperature was required to decompose such sulfate species and re-exposing them to NH<sub>3</sub> did not result in ammonium sulfate formation as evidenced by the results shown in Fig. 4.5(D). Another observation is that, as shown in Fig. 4.5(D), after removal of the sulfur species associated with the first peak, the residual chemisorbed S redistributed as indicated by three evident peaks in the following TPD. Therefore, the Cu sulfate species at elevated temperature have an unstable nature and transform into more stable species at elevated temperature.

#### 4.3.4 Poisoning effect of ammonium sulfate versus Cu<sub>x</sub>SO<sub>y</sub> species

A set of experiments was used to compare the effect of  $(NH_4)_x Cu_y SO_z$  (ammonium sulfate) on SCR activity at 210 °C to that of  $Cu_x SO_y$ . Figure 4.6(A) shows a comparison between the poisoning effects of the two after stepwise desulfation. As an example, the experiment corresponding to SCR performance evaluation of the sample denoted  $(NH_4)_x Cu_y SO_z$  after its desulfation at 630 °C is examined here. The outlet concentrations during this experiment are shown in Figure 4.6(B).

The corresponding inlet concentrations and results from the experiment without S exposure are shown in Figures A.7 and A.8, respectively. After  $(NH_4)_x Cu_y SO_z$  deposition, a desulfation stage was performed with the temperature ramped to 630 °C, followed by NH<sub>3</sub>-SCR evaluation at 210 °C. During desulfation, SO<sub>2</sub> desorption followed the expected

pattern for  $(NH_4)_x Cu_y SO_z$  decomposition (shown in Fig. 4.6(C)). This was followed by stage 4 including a TPD to 830 °C. The SO<sub>2</sub> released during stages 2 and 4 are magnified and shown in Fig. 6(C) and (D), respectively.

As shown in Fig. 4.6(A), in the  $(NH_4)_xCu_ySO_z$  scenario, after TPD to a certain temperature, a greater amount of SCR activity was regenerated compared to the  $Cu_xSO_y$ scenario described above. For example, after TPD at 530 °C, the NO<sub>x</sub> conversion was 53% on the sample where  $Cu_xSO_y$  formed, whereas the NO<sub>x</sub> conversion was 60% when ammonium sulfate was deliberately formed prior to the SCR performance evaluation. Correspondingly, comparing the amount of SO<sub>2</sub> released during the desulfation step with  $Cu_xSO_y$  (Fig. 4.5(C)) and  $(NH_4)_xCu_ySO_z$  (Fig. 4.6(C)), a larger amount of S was removed at lower temperature from  $(NH_4)_xCu_ySO_z$  compared to  $Cu_xSO_y$ . This observation is in good agreement with the TPD data presented in Fig. 4.4 and as explained earlier, exposing  $Cu_xSO_y$  to ammonia resulted in formation of less stable ammonium sulfate that decompose at lower temperatures.

One question remaining from the last section concerns the significant increase in  $NO_x$  conversion after TPD to 530 °C on the  $Cu_xSO_y$  sample. Interestingly, the same  $NO_x$  conversion was recovered by increasing the temperature to 430 °C in the  $(NH_4)_xCu_ySO_z$  scenario. This suggests that ammonium sulfate is responsible for this NOx conversion recovery since by increasing the temperature to 430 °C, as shown in Fig. 4.6(C) and (D), the ammonium sulfate peak was removed. Therefore, by removing ammonia sulfate, 80% of the original SCR activity can be recovered. Ammonia sulfate species decompose at temperatures as low as 300-350 °C. Note that  $Cu_xSO_y$  species did not decompose at such low temperatures.



Figure 4.6 (A) SCR conversion at 210 °C with the fresh sample, in the presence of 50 ppm SO<sub>2</sub>, the sample where Cu<sub>x</sub>SO<sub>y</sub> was formed and then exposed to 430, 530, 630, 730 and 830 °C in N<sub>2</sub> or (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> was formed and exposed to 430, 530, 630, 730 and 830 °C in N<sub>2</sub>. (B) Outlet concentrations during the experiment where (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> was formed and then after its desulfation at 630 °C. Experimental conditions: (1) similar to the (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> deposition experiment (see Table 4.1), (2) heating from 210 to 630 °C at 10 °C/min and holding at 630 °C for 15 min in N<sub>2</sub>, (3) exposure to 450 ppm NH<sub>3</sub>, 450 ppm NO, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C, (4) purging in N<sub>2</sub> followed by heating to 830 °C at 10 °C/min. (C) SO<sub>2</sub> released during a desulfation from the sample where (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> was formed, where the temperature was ramped to 430, 530, 630, 730 and 830 °C. (D) SO<sub>2</sub> released during the final TPDs (step 4 described above) using the sample where (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> was formed.
# 4.3.5 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

# characterization

DRIFTS was used to characterize the interactions between S and Cu sites. IR spectroscopy of NO adsorption is a useful technique that can provide information about the nature of active cationic sites available in the CHA framework <sup>63,82</sup>. Characterizing NO adsorption on Cu-CHA with IR spectroscopy was found to be sensitive to both pretreatment conditions and also the position of Cu<sup>2+</sup> ions <sup>73,83</sup>. Kwak et al. <sup>74</sup> observed two distinct IR peaks at 1948 and 1914 cm<sup>-1</sup> upon NO adsorption on Cu-SSZ-13 and assigned them to Cu<sup>2+</sup> in the 6MR (i.e. 6-membered ring or d6r) and 8MR (i.e. 8-membered ring or CHA) cages. Giordanino et al.<sup>83</sup> also performed NO adsorption on Cu-SSZ-13 that had been pretreated in an  $O_2$ -containing environment and found that  $Cu^{2+}(NO)$  adducts gave rise to multiple IR adsorption features in the 1970-1850 cm<sup>-1</sup> region. These peaks were assigned to different cationic positions available for  $Cu^{2+}$ . Importantly, this study revealed the presence of [Cu-OH]<sup>+</sup>, identified by an IR band at 1890 cm<sup>-1</sup>. Zhang et al. <sup>73</sup>, combining DRIFTS and density functional theory (DFT) analysis, studied NO chemisorption on Cu-SSZ-13 with various Cu/Al and Si/Al ratios. They assigned an IR peak at 1948 cm<sup>-1</sup> to NO adsorbed on  $Cu^{2+}$  sites in the faces of the 6MR. This assignment was in line with the earlier assignment proposed by Kwak et al.<sup>25</sup>. Based on this study, the band at 1932 cm<sup>-1</sup> was also attributed to NO-Cu<sup>2+</sup> in the 6MR face, but for a different Al distribution than that associated with the 1948 cm<sup>-1</sup> feature. Overall, there is consensus that the bands at 1948 and 1932 represent NO adsorbed on  $Cu^{2+}$  located inside a 6-membered ring <sup>23,25,26</sup>. The bands at 1870 to 1915 cm<sup>-1</sup> have been assigned to [Cu<sup>II</sup>(OH)]<sup>+</sup>-NO in the 8MR. However, there is some debate about the nature of these sites. Very recently <sup>27</sup>, a tri-coordinated [CuOH]<sup>+</sup> species was

found to be the most dominant structural component after O<sub>2</sub> pretreatment, which further confirms the peak assignment by Zhang et al.<sup>23</sup> at wavenumbers between 1815-1915 cm<sup>-</sup> <sup>1</sup>. For the purposes of our study, peaks at 1945  $\text{cm}^{-1}$  were assigned to NO-Cu<sup>2+</sup> inside the 6MR and we tentatively assigned peaks at 1891-1917 cm<sup>-1</sup> to [CuOH]<sup>+</sup> bound to only one Al site close to 8MR.



Figure 4.7 IR spectra of NO adsorption (500 ppm NO balanced with He) at 50 °C after (1) exposing the sample to NH<sub>3</sub> and SO<sub>2</sub> (or no SO<sub>2</sub> – upper spectrum) at 210 °C, (2) a purging phase in N<sub>2</sub> while keeping the temperature constant, and (3) a NO +  $O_2$  exposure at 210 °C.

Figure 4.7 shows the NO adsorption DRIFTS results from steps 1-3 (described in Table 4.1) with and without the presence of S. During NO adsorption with no S present, the peaks mentioned above (i.e. 1945 and 1891-1917 cm<sup>-1</sup>) were observed, which confirmed that  $Cu^{2+}$  and  $[CuOH]^+$  were available for NO adsorption in the absence of SO<sub>2</sub>. On the other hand, NO adsorption on the sample after S exposure showed only one sharp 76

peak at 1909 cm<sup>-1</sup>. The absence of an IR peak at 1945 cm<sup>-1</sup>, which was previously assigned to the Cu<sup>2+</sup> inside the six-membered ring, indicates that this particular Cu site was no longer accessible for NO adsorption after SO<sub>2</sub> poisoning. The presence of the 1909 cm<sup>-1</sup> feature, which corresponds to Cu sites close to 8MR revealed that NO could still adsorb on this type of Cu site. And based on this being a sharper feature, S affected [CuOH]<sup>+</sup> such that adsorbed NO on Cu is perturbed relative to that by -OH, and now seemingly has a more uniform local environment (leading to the less broad shape).

The IR data overall show that the Cu at the 6-membered ring position was fully poisoned by sulfur with exposure to  $SO_2$  at low temperature and the Cu close to the 8-membered ring was perturbed by the sulfur exposure. The IR data suggests that the response of [CuOH]<sup>+</sup> to sulfur poisoning is different fromm that of Cu<sup>++</sup>, and comparing these data to the conversion data in Figure 4.5(A), it can be arguably proposed that the 17% conversion obtained over the Cu<sub>x</sub>SO<sub>y</sub> sample corresponded to reaction with [CuOH]<sup>+</sup>.

## 4.3.6 Low temperature SO<sub>2</sub> poisoning mechanism

Based on the reaction and DRIFTS data, our proposed low temperature SCR over Cu-SAPO-34 deactivation/regeneration mechanism is as follows. SO<sub>2</sub> and NH<sub>3</sub> adsorption results in formation of ammonium sulfate in a complex with Cu. This Cu-associated ammonium sulfate can participate in NH<sub>3</sub>-SCR, making it different from bulky ammonium sulfate. The DRIFTS data suggest that these species mainly form on Cu<sup>2+</sup> located at the 6MR and are this is the main low temperature deactivation mechanism. With an increase in temperature two scenarios are possible. In scenario 1, the ammonia in the ammonium sulfate structure is consumed by NO at its deposition temperature, as might be a case where too little NH<sub>3</sub> is available. In that case, the ammonium sulfate reacts to form more stable Cu sulfate species. This can lead to higher required temperatures for NO<sub>x</sub> activity regeneration (i.e.  $Cu_xSO_y$  species, Fig. 4.5). In scenario 2 the ammonium sulfate remains unchanged after its formation, i.e. there is sufficient NH<sub>3</sub> supply for reaction with incoming NO. In this case, with an increase in temperature, decomposes at temperatures as low as  $350 \ C ((NH_4)_xCu_ySO_z, Fig. 4.6)$ , resulting in lower temperature regeneration.

## 4.3.7 Desulfation cycles at 350 °C

Based on previous studies<sup>43,48,51,78</sup>, catalyst regeneration using thermal desulfation (deSOx) processes can be used to recover some or all SCR performance after S poisoning. These deSO<sub>x</sub> processes, in almost all cases, included treating the catalyst at temperatures higher than 550 °C and in the presence of oxygen <sup>43,48,49</sup>. Based on the results shown in Fig. 4.4, two scenarios seem possible: (1) Cu<sub>x</sub>SO<sub>y</sub> species exist, where there is no ammonium sulfate and higher temperature is required for catalyst regeneration, and (2) (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> exists, in which SO<sub>2</sub> starts to desorb at temperatures as low as 300 °C, if there had not been an intermediate high temperature exposure leading to the stable sulfate species discussed earlier. Here, although we describe it as a deSOx process, this is likely naturally occurring during normal operation since NH<sub>3</sub> is always present. Detailed experimental results for this experiment are shown in Figure A.9.

		DeSO <sub>x</sub> Cycle			
(NH4) <sub>x</sub> Cu <sub>y</sub> SO <sub>x</sub> DeSO <sub>x</sub>	Sulfation Step: Cu <sub>x</sub> SO <sub>y</sub> deposition (described in Table 1)	SCR 500 ppm NG 500 ppm NH 10% O <sub>2</sub> in balance with at T=210 °C	$\begin{array}{c} \mathbf{D}\\ \mathbf{D}\\ \mathbf{I}_3\\ \mathbf{I}_3\\ \mathbf{N}_2\\ \mathbf{D}\\ \mathbf{N}_2\\ \mathbf{D}\\ D$	DeSOx at 350 °C heating up from 210 to 350 at 10 °C/min in N <sub>2</sub> with holding temperature at T=350 °C for 15 min	
Cu <sub>x</sub> SO <sub>y</sub> deSO <sub>x</sub>	Sulfation Step: Cu <sub>x</sub> SO <sub>y</sub> deposition (described in <b>Table 1</b> )	SCR 500 ppm NO 500 ppm NH <sub>3</sub> 10% O <sub>2</sub> in balance with N <sub>2</sub> at T=210 °C	Ammonium- Sulfate removal 500 ppm NO 10% O <sub>2</sub> for 120 min at T=210 °C	DeSOx at 350 °C heating up from 210 to 350 at 10 °C/min in N <sub>2</sub> with holding temperature at T=350 °C for 15 min	



**Figure 4.8** NH<sub>3</sub>-SCR conversions at 210 °C with the fresh, sample with Cu<sub>x</sub>SO<sub>y</sub>, and after regeneration of the samples with (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> and Cu<sub>x</sub>SO<sub>y</sub> at 350 °C. The header table describes the steps used.

Firstly, prior to the deSO<sub>x</sub> cycles: fresh SCR activity of the catalyst was measured at 210 °C, and Cu<sub>x</sub>SO<sub>y</sub> species were formed according to steps 1-3 described in Table 4.1. Then, these Cu<sub>x</sub>SO<sub>y</sub> species were exposed to NH<sub>3</sub> (as part of the NH<sub>3</sub>-SCR test) while keeping the temperature constant. This was followed by a TPD in N<sub>2</sub> to 350 °C, subsequently the temperature was again returned to 210 °C for another SCR activity measurement. The basic idea was to induce the S-containing species into their less stable state (i.e.  $(NH_4)_xCu_ySO_z$ ) by exposing them to NH<sub>3</sub>. Therefore, the main stage of the deSO<sub>x</sub> protocol was a cycle consisting of three steps: (1) exposing Cu<sub>x</sub>SO<sub>y</sub> species to NH<sub>3</sub>

(by running standard-SCR) at low temperature, (2) a TPD to 350 °C to decompose any ammonium sulfate formed, and (3) cooling to 210 °C. Repeating this cycle 4 times, as shown on Fig. 4.8, led to 80% SCR activity recovery. Note that leaving the sulfur as  $Cu_xSO_y$ , as shown in Fig. 4.8 (detailed experimental results and procedures for this case are shown in Figure A.10), and increasing the temperature to 350 °C led to only a 5-7% increase in NO<sub>x</sub> conversion.

#### 4.3.8 Concluding remarks

The poisoning mechanism of  $SO_2$  on Cu-SAPO-34 was studied. The key findings are as follows:

- 1- NH<sub>3</sub> facilitated SO<sub>2</sub> adsorption on Cu-SAPO-34 at 210 °C and more importantly, a significantly larger amount of S was stored as a result of SO<sub>2</sub> and NH<sub>3</sub> co-adsorption compared to other feed compositions. This co-adsorption of SO<sub>2</sub> and NH<sub>3</sub> resulted in formation of ammonium sulfate.
- 2- The ammonium component of this ammonium sulfate can be consumed by NO to produce  $N_2$  in a SCR reaction.
- 3- Two different distributions of S-containing species were found to form on Cu-SAPO-34 when using different experimental protocols: (1) ammonium sulfate

and Cu sulfate species when  $NH_3$  and  $SO_2$  were present, and (2) Cu sulfate when only  $SO_2$  was present. Cu sulfate species, with three different states were identified, as evidenced by  $SO_2$  desorption peaks during TPD experiments at 480, 650 and 800 °C.

- 4- DRIFTS data obtained during NO adsorption were used to evaluate the interaction between S species and Cu cations, in the absence of NH<sub>3</sub>. The results showed that Cu at the 6-membered ring site was completely poisoned by S species. The Cu at the 8-membered ring site was not completely poisoned, but the environment around the Cu site was perturbed according to the DRIFTS results.
- 5- Desulfation when S was in the form of ammonium sulfate resulted in more extensive catalyst regeneration compared to just the Cu sulfate form. In other words, ammonia can drive sulfur from a more thermodynamically favorable position/form to less stable ammonium sulfate. This observation can be used to more efficiently regenerate the SO<sub>2</sub> poisoned Cu-SAPO-34 catalyst, such that 80% of the original activity was regained after exposure to temperatures of 350 °C.

# Chapter 5 On the nature of Cu active centers in Cu-SSZ-13 and their responses to SO<sub>2</sub> exposure

Note: The material presented in this chapter has been published (Jangjou et al., ACS Catalysis, 2018, 8 (2), 6612-6622). The introduction and experimental methods material have been summarized to avoid redundancy with Chapters 1 and 2. Reference and figure numbers also changed for dissertation consistency.

## 5.1 . Introduction

It has now been almost a decade since the introduction of commercial Cu-exchange small pore zeolites (Cu-SSZ-13) for the selective reduction of NO<sub>x</sub> (NO and NO<sub>2</sub>) from lean-burn engines<sup>26,27,63,32</sup>. This SCR catalyst formulation is active over a wide temperature range and is resistant to high temperature dealumination, both a significant part of their introduction being a success<sup>26,85,86</sup>.

Having a well-defined chabazite (CHA) framework, Cu-SSZ-13 contains catalytically active Cu sites for ammonia selective catalytic reduction (SCR) of NO<sub>x</sub> in the presence of excess oxygen<sup>25</sup>. For the past several years, numerous studies have used both experimental and theoretical methods to unravel the complexity of the active sites. In an early study on this subject, Fickel et al.<sup>87</sup> defined copper locations and occupancies of Cu-SSZ-13. They showed that the Cu seemed to be mainly in the form of Cu<sup>2+</sup> located in six-membered ring cages coordinated to three oxygen atoms<sup>87</sup>. Kwak et al.<sup>74</sup> performed temperature programmed reduction (TPR) and Fourier transform infrared spectroscopy (FTIR) over a variety of Cu-SSZ-13 samples with different ion-exchange levels. They observed an additional IR or TPR feature from samples with ion exchange levels higher

than 20%, relative to those with lower loadings, and these features increased with increasing Cu loading. They concluded that  $Cu^{2+}$  ions primarily occupy two cationic positions within the Cu-SSZ-13 structure: (A) inside, within or close to the face of 6membered rings and (B) inside the 8-membered rings<sup>74</sup>. More recent studies have shown that Cu speciation and positioning not only depend on the copper ion exchange levels but also on Si:Al ratio<sup>39,84,88,89</sup>. In terms of Cu speciation, in addition to naked Cu<sup>2+</sup>, Giordanino et al.<sup>89</sup> reported formation of [Cu-OH]<sup>+</sup> species in an O<sub>2</sub> activated Cu-SSZ-13 sample (Si:Al = 13.1 and Cu:Al = 0.444) via IR spectroscopy using  $N_2$ , CO and NO as probes. In partial contrast with the study reported by Bates et al.<sup>90</sup>, Giordanino et al.<sup>89</sup> excluded the formation of copper dimers [Cu-O-Cu]<sup>2+</sup> on/in Cu-SSZ-13. Most Cu speciation and positioning, based on recent findings, can be summarized as: (1) copper is predominantly present in the form of  $Cu^{2+}$  and  $[CuOH]^+$ , (2) at low Si:Al ratios, the majority of copper ions occupy 2Al T-sites in the vicinity of the 6-membered ring - as the Si:Al ratio increases, the possibility of finding two neighboring Al atoms becomes less possible resulting in formation of [CuOH]<sup>+</sup> near 1Al T-sites<sup>39,88</sup>. Not only are those two sites regularly mentioned, recently, Gao et al.<sup>38</sup> and Paolucci et al.<sup>40</sup> reported formation of [(NH<sub>3</sub>)<sub>2</sub>Cu<sup>II</sup>-O<sub>2</sub>-Cu<sup>II</sup>(NH<sub>3</sub>)<sub>2</sub>] from mobile ammonia-solvated Cu species i.e. Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>, providing yet another possible active type species under reaction conditions. Deka et al. <sup>91</sup> also reported possible conformational change in the local geometry of the copper (from a planar form toward a distorted tetrahedron) as a result of its interaction with NH<sub>3</sub>.

Despite these characterization achievements, there are still questions regarding possible changes in Cu-SSZ-13 active sites under real-world conditions. Specifically, sulfur poisoning and hydrothermal aging influence activity and stability of Cu-SSZ-13 catalysts<sup>25,43–45,48,49,63,66,67,77–79,84,87,92,93</sup>, and are likely related to changes in Cu active sites. Recent studies suggest unique responses of Cu<sup>2+</sup> and CuOH<sup>+</sup> towards hydrothermal aging. For example, [CuOH]<sup>+</sup> in the CHA cage was reported to be more susceptible to agglomeration than Cu<sup>2+</sup> in 6-membered ring positions<sup>45</sup>. Moreover, using NH<sub>3</sub>-TPD to quantify the population of different Cu sites, Luo et al.<sup>94</sup> reported that hydrothermal aging changes the site density of ZCuOH and Z2Cu.

In terms of sulfur poisoning, it is clear that  $SO_x$  (x = 2 and 3) inhibits lowtemperature SCR activity<sup>42,43,48,49,66,67,78,79,93</sup>. In principle, this low-temperature regime is rather important due to the increased challenge in reducing NO<sub>x</sub> during cold start or lowload conditions<sup>27</sup>.

Interestingly, sulfur poisoning over Cu-CHA seems to be reversible in nature<sup>43,49,51,93</sup>; i.e. SCR activity can be recovered by treatment at high temperatures and under lean conditions (commonly notated as de-sulfation or deSO<sub>x</sub>). But, temperatures needed for de-sulfation were found to be highly dependent on sulfation procedures, which ultimately change the nature of sulfur intermediates formed on the surface<sup>51,93</sup>. Specifically, two different S-containing species form upon sulfur exposure: (1) ammonium sulfate together with Cu sulfate species when NH<sub>3</sub> and SO<sub>2</sub> both were present and (2) Cu sulfate with only SO<sub>2</sub> in the feed. In the case of ammonium sulfate, poisoned samples can be regenerated at temperatures as low as 350 °C (i.e. ammonium sulfate decomposition temperature), whereas in the latter case, temperatures higher than 550 °C were needed<sup>93</sup>.

Research has also focused on the effect of sulfur on active Cu sites and the nature of the sulfur intermediates. For example Cheng et al.<sup>48</sup> observed formation of highly

dispersed Z-CuSO<sub>4</sub> by comparing XANES spectra of CuSO<sub>4</sub> with that of a SO<sub>3</sub>-treated sample. They proposed formation of  $SO_4^{2-}$  species on Cu sites as the main poisoning mechanism of Cu-CHA catalysts under the conditions they used. With the addition of NH<sub>3</sub> to the S-containing poisoning mixture, formation of ammonium sulfate-like species was observed. Evidence also demonstrates that ammonium sulfate did not form on Brønsted sites, and requires Cu ions<sup>77</sup>. Furthermore, IR spectroscopy results show that [CuOH]<sup>+</sup> and Cu<sup>2+</sup> respond to SO<sub>2</sub> poisoning differently. Luo et al.<sup>42</sup> used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with NH<sub>3</sub> adsorption as a probe to study fresh and sulfated Cu-SSZ-13 samples. They found that NH<sub>3</sub> adsorption on both Cu sites decreases with sulfur exposure (SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>) and with a high temperature (550 °C) desulfation treatment, NH<sub>3</sub> adsorption on [CuOH]<sup>+</sup> remained lost, suggesting a strong interaction of that site with sulfur.

Even with the breadth of research focused on Cu-SSZ-13 sulfur poisoning, how Z2Cu and ZCuOH respond to sulfur poisoning, the nature of the S-Cu complexes, and a detailed poisoning mechanism are yet to be agreed upon. In this paper, we aimed to experimentally and theoretically study/distinguish effect(s) of sulfur on Z2Cu and ZCuOH sites and unravel the nature of sulfur complexes formed during sulfur interaction with Cu-SSZ-13 at low temperatures (< 250 °C). To accomplish this goal, we evaluated the possible S poisoning routes with respect to the two main Cu active centers i.e. Z2Cu and ZCuOH. By varying the Si:Al ratio, two model Cu-SSZ-13 catalysts with different distributions of Z2Cu and ZCuOH were prepared. The possible forms of S complexes, fresh versus poisoned SCR activity, de-sulfation and S storage capacity of these two model catalysts were evaluated. Borfecchia et al.<sup>84</sup>, Paolucci et al.<sup>39</sup>, and Giordanino et al.<sup>89</sup> utilized

different techniques such as FTIR, X-ray absorption (XAS) and emission (XES) spectroscopies, NH<sub>3</sub> titrations and density functional theory (DFT) to characterize CuOH<sup>+</sup> and  $Cu^{2+}$  sites in the vicinity of 1Al and 2Al. In line with these techniques, Gao et al.<sup>88</sup>. Kwak et al.<sup>74</sup> and Wang et al.<sup>44</sup> utilized H<sub>2</sub>-TPR and DRIFTS to identify and quantify copper active sites present in Cu-SSZ-13. Based on the literature, a variety of techniques can be implemented to study Z2Cu and ZCuOH sites<sup>39,44,74,84,88,89,95</sup>. Here, combining temperature programed desorption (TPD), in-situ DRIFTS and H<sub>2</sub> temperature programmed reduction ( $H_2$ -TPR) and density functional theory (DFT) calculations, we demonstrate that depending on the Cu site, sulfur can either be present as ammonium sulfate or copper bisulfite, and two different sulfur poising mechanisms exist on Z2Cu versus ZCuOH. More importantly, compared to Z2Cu, ZCuOH more readily interacts with SO<sub>2</sub> and that interaction leads to formation of highly stable S species. Note that DFT calculations were done in collaboration with Grabow research group at University of Houston. In this thesis, DFT calculation methods together with results are presented in Appendix B.

# 5.2 Experimental methods

# 5.2.1 Sample preparation and characterization

Two Na-SSZ-13 samples with Si:Al = 6 and 30 (notated as Cu-SSZ-13\_SAR\_6 and Cu-SSZ-13\_SAR\_30) were synthesized using a recipe reported by Gao et al.<sup>88</sup> and Fickel et al.<sup>87</sup>. Briefly, N,N,N-trimethyl-1-adamantanamine iodide (TMAAI-25 wt.%) (Sachem Inc., ZeoGen<sup>TM</sup> SDA 2825) as the structure directing agent (SDA) was dissolved in DI water with the sequential addition of NaOH, Al(OH)<sub>3</sub> and fumed silica (all purchased from

Sigma-Aldrich) under vigorous stirring for 2 h until the solution was homogenous. Different Si:Al ratios were obtained by tuning the precursor Al(OH)<sub>3</sub>:SiO<sub>2</sub> ratio. The solution was then transferred into a 125 ml Teflon-lined stainless steel autoclave (Parr Instruments) and kept at 160 °C for 5 days while being stirred. The catalyst powder was then separated using centrifugation and washed 3 times with DI water. The product was dried at 120 °C under a flow of N<sub>2</sub> overnight. This was followed by calcination at 550 °C for 8 h in air, forming Na-SSZ-13. The Na-SSZ-13 was dissolved in 0.1 M NH<sub>4</sub>NO<sub>3</sub> solution at 80 °C for 8 h while stirring, producing NH<sub>4</sub>-SSZ-13. This step was repeated 3 times. Finally, Cu-SSZ-13 was obtained by ion exchanging NH<sub>4</sub>-SSZ-13 in 0.1 M CuSO<sub>4</sub> solution at 80 °C followed by vacuum filtration steps and a calcination at 550 °C for 8 h. Cu, Al and Si contents were quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES) at Galbraith Laboratories, Inc. (Knoxville, TN, USA).

A Micromeritics AutoChem II analyzer was used to perform  $H_2$  temperature programmed reduction (TPR). In each TPR run, ~20 mg of sample was used, in a flow of 5%  $H_2$ /Ar (30 sccm total flow rate). The temperature ramp was 10 °C/min, up to 650 °C.  $H_2$ -TPR was performed with the hydrated samples; there was no pre-treatment prior to the measurement. Since  $H_2O$  was present in our base feed (similar to the real-world exhaust condition), this case would be closer and more relevant to the state of the Cu in our experiments. Moreover, even with pre-treatment at high temperature, residual  $H_2O$  can still adsorb while cooling down the system. Ex-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), with a focus on the T-O-T bond region, was used to characterize Cu species present in the prepared samples. A Nicolet 6700 FT-IR spectrometer equipped with a Harrick Scientific Praying Mantis DRIFTS cell with ZnSe windows was used. In each measurement, ~50 mg of the prepared Cu-SSZ-13 powders were pressed into a pellet, which was then placed into the sample cup. Before each run, the samples were treated in a flow of 10%  $O_2$  using He as the carrier at 500 °C for 2 h. An IR spectrum was then collected at 50 °C using H form zeolite spectra as the background. The background spectrum was collected under similar conditions from the corresponding H form zeolite.

#### **5.2.2 In-situ DRIFTS experiments**

For the in-situ measurements, the same DRIFTS setup described above was used. Two sets of experiments were designed to study/distinguish effect of SO<sub>2</sub> on ZCuOH and Z2Cu, denoted as experiment #1 (without S) and experiment #2 (with S). Before each experiment, the catalyst sample was treated in 10% O<sub>2</sub>/He at 500 °C for 2 h then cooled down to 200 °C. During the first set of the experiments (experiment #1), the catalyst sample was exposed to 500 ppm NH<sub>3</sub> in the base feed (i.e.  $10\%O_2$ /He) with a constant 50 sccm total flow rate. This was followed by a purging step in only He, and a subsequent NO (500 ppm) exposure step in the base feed. Using Nicolet OMNIC software to convert the absorbance data into Kubelka-Munk (KM) units, the DRIFTS spectra were collected from 4000 to 650 cm<sup>-1</sup>. The second set of the experiments (experiment #2) was repeated similarly but with addition of 50 ppm SO<sub>2</sub> during the NH<sub>3</sub> adsorption step.

## **5.2.3 TPD experiments**

All of the temperature programmed desorption (TPD) experiments were carried out in a microreactor setup (described elsewhere<sup>77</sup>) equipped with a MKS MultiGas 2030 FTIR with in-house calibrations for SO<sub>2</sub>, SO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub><sup>96</sup>. The base feed composition was kept

similar for all reaction tests and consisted of 5%  $H_2O$  and 10%  $O_2$  with a balance of  $N_2$ , and a total gas flow rate of 400 sccm, for a gas hourly space velocity (GHSV) of 400,000 h<sup>-1</sup>. The pretreatment condition for each test was 10% O<sub>2</sub> balanced with N<sub>2</sub> at 550 °C for 4 h. As mentioned above, hydrothermal aging and sulfur poisoning can both affect Cu sites. Here, the focus is studying S poisoning, not thermal degradation, thus we did not age our samples at higher temperatures (> 550 °C). For SO<sub>2</sub> and SO<sub>2</sub> + NH<sub>3</sub> TPD experiments, samples were exposed to 50 ppm SO<sub>2</sub>, 500 ppm NH<sub>3</sub> (if used) in the base feed at 150 °C until saturation. This was followed by a purge phase in only N2 for 2 h, and then the temperature was increased from 150 to 800 °C at a rate of 10 °C/min. Note that the sulfation step was done at 150 °C in the presence of  $H_2O$  which differs from the protocol used during in-situ DRIFTS experiments. However, as shown in Figure B.3, H<sub>2</sub>O and temperature do not influence the nature of S species formed upon  $SO_2 + NH_3$  exposure at temperatures lower than 300 °C. Moreover, 200 °C was used for sulfation during in-situ DRIFTS experiments because subsequent steps ( $NH_3 + O_2$  and  $NO + O_2$  adsorptions) were also done at 200 °C. Therefore, to avoid changing temperature during transient in-situ DRIFTS experiments, sulfation was done at 200 °C.

Ex-situ DRIFTS using NH<sub>3</sub> as a probe was also carried out on the fresh, and desulfated samples at 450, 500 and 550 °C. The same DRIFTS set-up described above was used. Both Cu-SSZ-13 samples, with silicon to aluminum ratios (SAR) of 6 and 30, were pretreated in  $10\%O_2$ /He at 500 °C for 2 h before cooling down to 150 °C. Samples were then exposed to 500 ppm NH<sub>3</sub> with 10% O<sub>2</sub> balanced with He until saturation. To evaluate de-sulfated samples, after pretreatment, samples were exposed to 500 ppm NH<sub>3</sub> + 50 ppm SO<sub>2</sub> in 10% O<sub>2</sub> balanced with He, followed by a purging phase in He and subsequent temperature ramp in 10% O<sub>2</sub>/He to 450, 500 or 550 °C at 10 °C/min. That temperature was held for 4 h before cooling down to 150 °C. Similar NH<sub>3</sub> adsorption experiments were repeated for these de-sulfated samples.

## 5.2.4 SCR activity and regeneration experiments

All of the reaction tests over fresh and sulfated samples were carried out in a bench flow reactor microreactor described above. Accurate calibrations for SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> measurement in the presence of water were used, as described previously<sup>96</sup>. Before each test, the samples underwent a pretreatment procedure consisting of exposure to 10% O<sub>2</sub> balanced with N<sub>2</sub> at 550 °C for 4 h. To evaluate the fresh activity, simulated exhaust gases consist of 550 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub>, which were fed to the reactor at ~400,000 h<sup>-1</sup> gas hour space velocity (GHSV). Low-temperature SCR activity was measured at multiple temperature points within the 110-210 °C range. Note that no ammonium nitrate was observed during these SCR activity experiments. To study the effects of sulfur, the sample was exposed to 50 ppm SO<sub>2</sub>, 550 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub> at 150 °C until saturation, followed by subsequent purging in N<sub>2</sub>. De-sulfation procedures consisted of treating samples at 450, 500 or 550 °C for 4 h in 10% O<sub>2</sub>/N<sub>2</sub>. NO<sub>x</sub> conversion was calculated based on the following equation:

$$NO_{x} \ conversion \ (\%) = \frac{(NO+NO_{2})_{inlet} - (NO+NO_{2}+N_{2}O)_{outlet}}{(NO+NO_{2})_{inlet}} \times 100$$
(5-1)

Assuming a first-order reaction<sup>36</sup>, turnover frequencies (TOF) for the standard SCR reaction over the fresh, poisoned and de-sulfated samples were calculated (mol NO·mol  $Cu^{-1} \cdot s^{-1}$ ). Activity recovery of de-sulfated versus fresh samples were calculated based on:

Regeneration (%) = 
$$\frac{k_{desulfated}}{k_{fresh}} \times 100$$
 (5-2)

where  $k = \frac{\frac{F}{W}(-\ln(1-x))}{[NO]_0}$ , F is the total NO flow rate (mol NO·s<sup>-1</sup>), W the mass of the catalyst

(g) and x the  $NO_x$  conversion.

# 5.3 . Results and discussion

#### 5.3.1 Z2Cu versus ZCuOH site populations in Cu-SSZ-13 with different Si:Al ratios

Cu contents, Si:Al ratios as well as Cu:Al ratios for both model catalysts, Cu-SSZ-13\_SAR\_6 and Cu-SSZ-13\_SAR\_30, are listed in Table 5.1.

Table 5.1 Elemental analysis of model catalysts used in this study. Results are obtained from ICP-OES.

Sample	Si:Al Ratio	Cu content (wt.%)	Cu:Al (molar %)
Cu-SSZ-13_SAR_6	5.75	3.58	30
Cu-SSZ-13_SAR_30	30.17	1.20	43

Note, we did not list the ion exchange level values, because often they are calculated based on the assumption that each Cu exchanges at 2Al sites, which is not the case for Cu in the ZCuOH form. Therefore, the lower bound would be the Cu:2Al ratio, but is actually higher since ZCuOH is present. In an early Cu-SSZ-13 Cu speciation study, Kwak et al.<sup>74</sup> used H<sub>2</sub>-TPR to differentiate between two different Cu active centers. Since then, H<sub>2</sub>-TPR has been widely used to characterize/quantify Cu species present in Cu-SSZ-13 zeolites<sup>63</sup>. Recently, Gao et al.<sup>88,97</sup> reported that only temperatures lower than 600 °C are needed to reduce all of the Cu species with a 2+ oxidation state. Figure 5.1(A) displays H<sub>2</sub>-TPR results for the two model catalysts. The Cu-SSZ-13 with Si:Al = 30 showed only two reduction peaks, centered at ~210 and 340 °C, whereas for the sample with a Si:Al = 6, an extra reduction peak was observed at ~480 °C.



Figure 5.1 Catalyst characterization: (A)  $H_2$ -TPR, (B) ex-situ DRIFTS spectra of T-O-T vibration region over Cu-SSZ-13\_SAR = 6 and 30.

Previous studies revealed that the stability of  $Cu^{2+}$  in different positions and conditions plays an important role in interpreting TPR data<sup>88,94,97</sup>. For example, having hydrated versus 'naked'  $Cu^{2+}$  results in distinct TPR features.  $Cu^{2+}$  in the form of Z2Cu located near the openings of a 6-memebered ring neighboring 2 framework Al was found, both theoretically and experimentally, to be the most stable Cu species in samples with a low Si:Al ratio <sup>39,74,84</sup>. Therefore,  $Cu^{2+}$  in the form of Z2Cu is expected to show a higher temperature reduction peak compared to that of ZCuOH. Based on this, the first reduction peak (at ~210 °C) is assigned to reduction of  $Cu^{2+}$  in the form of Z2CuH, and the higher temperature peak (~ 310-380 °C) is assigned to reduction of  $Cu^{2+}$  in Z2Cu<sup>88,94,97</sup>. The reduction peak at ~480 °C in the TPR profile of Cu-SSZ\_13\_SAR\_6 could be either from the partial dehydration of  $Cu^{2+}$  in the form of Z2Cu or reduction of  $CuAl_2O_4$  species<sup>98</sup>. The latter is associated with the dealumination process, which is less probable here, since Cu-SSZ-13 samples were tested in their fresh form. "Naked" Cu<sup>2+</sup> species located in their most

sable position (i.e. Z2Cu) require higher reduction temperatures compared to their hydrated form<sup>97</sup>. The Cu-SSZ-13 sample with Si/Al = 6 contains a higher amount of Cu in the form of Z2Cu (i.e. 3.58 wt.%, Cu/Al = 0.3) and some of  $Cu^{2+}$  can be partially dehydrated during the temperature ramp resulting in the higher temperature reduction peak. Note that S uptake was found to be almost zero over a physical mixture of CuO and Cu-CHA after exposure to NH<sub>3</sub> + SO<sub>2</sub>, as shown in Figure B.4, suggesting that S effects observed in this study are mainly related to Cu ions i.e. Z2Cu or ZCuOH sites. Assuming the effect of autoreduction on the ratio of ZCuOH:Z2Cu is negligible, peak deconvolution can be used to quantify Z2Cu and ZCuOH sites based on their relative area under the TPR curve as shown in Figure 5.1(A). Results of such quantification, together with that obtained from ex-situ DRIFTS experiments (discussed later), are listed in Table 5.2. Based on H<sub>2</sub>-TPR, of all the Cu species present in the sample with Si:Al = 6, 69% (389  $\mu$ mol·gr<sup>-1</sup>) were in the form of Z2Cu and 31% (175 µmol·gr<sup>-1</sup>) were ZCuOH. An opposite distribution of Cu species was found for the sample with Si:Al = 30, i.e.  $Z2Cu:Cu_{tot} = 36\%$  (68 µmol·gr<sup>-1</sup>) and ZCuOH:Cu<sub>tot</sub> = 64% (121  $\mu$ mol·gr<sup>-1</sup>). These results are in a good agreement with the data reported by Paolucci et al.<sup>39</sup> for Cu-SSZ-13 samples with different Si:Al ratios. For Cu-SSZ-13\_SAR\_6, the ~480 °C TPR peak was assumed to contribute to the amount of Z2Cu sites. Even without such an assumption, the Z2Cu:Cu<sub>tot</sub> would be 56% and ZCuOH:Cu<sub>tot</sub> = 35%demonstrating that the sample with lower Si:Al ratio has more Z2Cu compared to ZCuOH. Note that even though ZCuOH:Cu<sub>tot</sub> is higher in the case of Si:Al = 30, the moles of ZCuOH available in Cu-SSZ-13\_SAR\_6 are 1.44 times higher than those available in Cu-SSZ-13\_SAR\_30.

Ex-situ DRIFTS was also carried out to further confirm Cu quantification obtained from the H<sub>2</sub>-TPR method. The asymmetric T-O-T vibration of the framework oxygen has been reported to be IR sensitive to interactions with exchanged cations<sup>99</sup>. In the case of SSZ-13, IR features at 900 and 950 cm<sup>-1</sup> have been attributed to asymmetric T-O-T vibrations perturbed by Cu<sup>2+</sup> in the form of Z2Cu and ZCuOH, respectively<sup>42,74,100</sup>. Note that these positive peaks do not exist in the H form SSZ-13. In this study, in an attempt to validate such assignments, IR spectra of the T-O-T region from several Cu-SSZ-13 samples with different Cu contents were compared and are shown in Figure B.5. Ex-situ DRIFTS spectra in the T-O-T vibration region from Cu-SSZ-13\_SAR\_6 and Cu-SSZ-13\_SAR\_30 are shown in Figure 5.1(B). While both IR bands (900 and 950 cm<sup>-1</sup>) were present for both samples, their corresponding intensities/areas varied suggesting different populations of Z2Cu and ZCuOH in these two model catalysts. From the Cu-SSZ-13\_SAR\_30 spectra, the ZCuOH peak (i.e. 950 cm<sup>-1</sup>) appeared to be asymmetric. Cu<sup>2+</sup> species located inside large cavities may become partially hydrated via some residual H<sub>2</sub>O while cooling down the DRIFTS cell, resulting in weakening the T-O-T perturbation induced by Cu species. The fully dehydrated Cu<sup>2+</sup> species inside the large CHA rings were reported to result in a peak at 940 cm<sup>-1</sup> and shift to higher wavenumbers (945-954 cm<sup>-1</sup>) as a result of interaction with water<sup>100</sup>. To better quantify ZCuOH species, we did not fix the 950 cm<sup>-1</sup> peak location during fitting process. Calculated area ratios of Z2Cu and ZCuOH per total amount of Cu based on ex-situ DRIFTS data are tabulated in Table 5.2. In agreement with H<sub>2</sub>-TPR, exsitu DRIFTS data reveals an opposite ratio of ZCuOH:Cutot and Z2Cu:Cutot in the model catalysts. These results demonstrate that these two samples were good candidates for the current study.

Sample		H <sub>2</sub> -TPR	Ex- situ DRIFTS
Cu-SSZ-13_SAR_6	Z2Cu : Cu tot	0.69	0.80
	ZCuOH :Cu tot	0.31	0.20
Cu-SSZ-13_SAR_30	Z2Cu : Cu tot	0.36	0.34
	ZCuOH:Cu tot	0.64	0.66

Table 5.2 Z2Cu and ZCuOH populations for two model catalysts used in this study quantified using  $H_2$ -TPR and ex-situ DRIFTS.

## **5.3.2 In-situ DRIFTS experiments**

In an attempt to determine whether sulfur interactions with Z2Cu and ZCuOH are similar or different, in-situ DRIFTS was used to capture T-O-T vibration changes during experiments with and without sulfur. As mentioned above, the SSZ-13 framework internal asymmetric T-O-T vibrations can be used to distinguish Z2Cu and ZCuOH, and can differentiate between effects of sulfur on these two sites since any interaction with Cu can weaken or intensify T-O-T perturbations<sup>42</sup>. In-situ DRIFTS experiments results are shown in Figure 5.2. Figure. 5.2 (A) presents IR spectra within the T-O-T region collected from Cu-SSZ-13\_SAR\_30 during a NH<sub>3</sub> +  $O_2$  exposure experiment at 200 °C. During NH<sub>3</sub> adsorption, NH<sub>3</sub> bonds to both  $Cu^{2+}$  and  $[CuOH]^+$  sites as reported by Giordanino et al. <sup>95</sup>. Negative IR features at 900 and 950 cm<sup>-1</sup> were found to gradually increase in intensity versus time suggesting solvation of Z2Cu and ZCuOH by NH<sub>3</sub> as a result of NH<sub>3</sub> adsorption. Specifically,  $Cu^{2+}$  ions in both forms perturb the oxygen rings less, resulting in the increasing in size negative T-O-T perturbation peaks<sup>94</sup>. This adsorption step was followed by a He purge and then a  $NO + O_2$  adsorption step, with spectra collected during the exposure shown in Figure 5.2 (B). During this phase, the 900 and 950 cm<sup>-1</sup> IR features return to the baseline, zero, suggesting consumption of adsorbed NH<sub>3</sub> via the SCR reaction. Through this step, the catalytic cycle is being completed and Cu ions return to their initial

states. This experiment was repeated but with 50 ppm  $SO_2$  included during the first step (i.e. experiment #2 as described above).



Figure 5.2 In-situ DRIFTS spectra of T-O-T vibrations of Cu-SSZ-13\_SAR\_30 during experiments with/without sulfur; (A) NH<sub>3</sub> + O<sub>2</sub> adsorption followed by a purging phase in He and (B) NO + O<sub>2</sub> adsorption at 200 °C, (C) NH<sub>3</sub> + O<sub>2</sub> + SO<sub>2</sub> adsorption at 200 °C followed by a purging phase in He and (D) NO + O<sub>2</sub> adsorption at 200 °C.

Results are shown in Fig. 5.2(C) and Fig. 5.2(D). During  $SO_2 + NH_3 + O_2$  exposure, as shown in Fig. 5.2 (C), the two features both increase in intensity toward more negative values. In comparing Fig. 5.2(A) and Fig. 5.2(C), having  $SO_2$  in the feed changes the

intensity ratio of two perturbed asymmetric IR features. Note that we are comparing the ratio of 900 and 950 cm<sup>-1</sup> peaks not the actual intensities. Specifically, the intensity ratio of the feature at 900 cm<sup>-1</sup> to that of 950 cm<sup>-1</sup> was higher when SO<sub>2</sub> was present. This could be due to either: (1) severe poisoning of ZCuOH resulting in lower NH<sub>3</sub> adsorption coverage on this site, which would lower the IR intensity at 950 cm<sup>-1</sup>, or (2) a stronger interaction of NH<sub>3</sub>with Z2Cu because of an increase in ammonium formation (as in ammonium sulfate), which would increase the intensity at 900 cm<sup>-1</sup> compared to that of 950 cm<sup>-1</sup>.

Note that negative peak at 900 or 950 cm<sup>-1</sup> are not assigned to NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup> adsorption but to changes in T-O-T perturbations induced by Cu<sup>2+</sup> or CuOH<sub>+</sub>, respectively. Utilizing DRIFTS, Zhang et al.<sup>43</sup> and Luo at al.<sup>42</sup> have both reported an increase of NH<sub>4</sub><sup>+</sup> formation as a result of SO<sub>2</sub> interaction with NH<sub>3</sub> over Cu-CHA. Having a constant population of Brønsted sites for both fresh and sulfated samples, extra NH<sub>4</sub><sup>+</sup> adsorption should primarily come from formation of ammonium sulfate species associated with Cu sites. This explains different intensity ratios of the two perturbed IR features observed when comparing Fig. 5.2 (A) and Fig. 5.2(C). The spectra shown in Fig. 5.2 (D) were taken during NO +  $O_2$  exposure after the sample had been exposed to  $SO_2$  and NH<sub>3</sub>. Analogues to Fig. 5.2 (B), both IR peaks started to go back to their initial states, however, this occurred at a slower rate with the sulfated sample. This observation is in good agreement with our recent study where we showed that ammonium in the form of ammonium sulfate can participate in the SCR reaction but at slower rate<sup>93</sup>. Interestingly, a new positive IR band at 920 cm<sup>-1</sup> is observed in Fig. 5.2 (D), which was not during the experiment with no SO<sub>2</sub>, Fig. 5.2 (B). This peak is due to the perturbation of T-O-T vibrations induced by sulfur complexes associated with ZCuOH, discussed in more detail later. In comparing Fig. 5.2 (B) and Fig. 5.2(D), the time scales over which IR features evolve differ between fresh versus sulfated samples.



**Figure 5.3** Evolution of area of 900 and 950 cm<sup>-1</sup> peaks versus time during last step of in-situ DRIFTS experiment on fresh versus sulfated Cu-SSZ-13\_SAR\_30. These areas were calculated/normalized based on data shown in Fig. 5.2 (B) and (D).

To better distinguish these responses of Z2Cu and ZCuOH to sulfur exposure, IR feature peak areas in Fig. 5.2 (B) and Fig. 5.2(D) were calculated. These areas were then normalized and plotted versus time in Figure 5.3. In the case of fresh sample, the peak areas associated with both Z2Cu and ZCuOH were found to grow similarly suggesting identical SCR rates over these two sites, as suggested by previous studies<sup>39,88</sup>. In the case of the sulfated sample, however, the changes were different, which clearly suggests distinct responses of Z2Cu and ZCuOH to sulfur poisoning, possibly via formation of unique sulfur

complexes. These experiments were also repeated using Cu-SSZ-13\_SAR\_6 and the corresponding data are provided in Fig. B.6 and B.7.

## 5.3.3 SO<sub>2</sub> + NH<sub>3</sub> interactions with Cu-SSZ-13

A remaining question from the last section is why do ZCuOH and Z2Cu respond differently to sulfur poisoning? In the following sections, an attempt was made to address this question and understand the nature of sulfur intermediates formed with SO<sub>2</sub> exposure.

## 5.3.3.1 $SO_2 + NH_3 TPD$

Figure 5.4 describes SO<sub>2</sub> release from Cu-SSZ-13\_SAR\_6 and Cu-SSZ-13\_SAR\_30 after being exposed to NH<sub>3</sub> and SO<sub>2</sub> at 150 °C. Both samples resulted in two distinct desorption features; a low temperature peak centered at ~380 °C followed by a high temperature peak at ~580 °C. As mentioned above, several studies have reported an increase in sulfur and ammonia release as a result of NH<sub>3</sub> and SO<sub>2</sub> co-adsorption which would appear as an extra low temperature TPD feature<sup>42,43,77,93</sup>. By obtaining 2:1 ratio of the increase in released amount of NH<sub>3</sub> to the amount of additional SO<sub>2</sub>, Zhang et al.<sup>43</sup> concluded the additional NH<sub>3</sub> and SO<sub>2</sub> adsorption was via the formation of ammonium sulfate over Cu-SAPO-34. Formation of ammonium sulfate has been further confirmed by IR characterization of NH<sup>4</sup> formation on Cu<sup>42,43</sup>.

Taking into account these findings, the first TPD peak is due to the decomposition of ammonium sulfate. The peak at ~580 °C is, however, less straightforward and yet to be addressed. Based on previous studies, in almost all cases, low-temperature  $SO_2$  adsorption would result in formation of stable sulfur complexes identified by their high temperature

TPD peaks (higher than 550 °C)<sup>42,43,48,49,77,93</sup>. Utilizing XPS, Cheng at al.<sup>48</sup> assigned high temperature peaks to formation of  $SO_4^{2-}$ , which formed during  $SO_3$  exposure, but in the case of SO<sub>2</sub>, the amount of  $SO_4^{2-}$  was not measurable. Based on Fig. 5.4, interestingly, by changing the Si:Al ratio, the intensity of the high temperature peak increased with respect to the low temperature peak. Since the sample with Si:Al = 30 has a larger amount of  $ZCuOH:C_{tot}$  compared to that of Si:Al = 6, this clearly suggests that the TPD peaks might be site related. Peak deconvolution was used to quantify the amount of S associated with each TPD peak and correlate them to the total amount of S being released. Peak deconvolution is shown in Figure B.8 and the calculated amounts are tabulated in Table 5.3. Note that the total amount of S released was a 1:1 molar ratio with the amount of Cu in each sample. Specifically, the total amount of S being stored on Cu-SZZ-13\_SAR\_6 and Cu-SZZ-13\_SAR\_30, integrated based on data shown in Fig. 5.4, were 569 and 204 µmol·gr<sup>-1</sup>, respectively. Interestingly, the relative amounts of released sulfur associated with each of TPD peak agrees with those quantified using H<sub>2</sub>-TPR and ex-situ DRIFTS (i.e. Table 5.1). For both samples, the ratio of sulfur released at 350 and 580 °C to the total amount of stored sulfur were almost identical to the ratio of Z2Cu:Cutot and ZCuOH:Cutot , respectively, measured via TPR. The moles of sulfur released at 580 °C from Cu-SSZ-13\_SAR\_6 to that of Cu-SSZ-13\_SAR\_30 was 1.50, agreeing the ratio of ZCuOH moles available in these samples as obtained from H<sub>2</sub>-TPR results. This suggests that the type of sulfur species formed depends on the active site (i.e. Z2Cu or ZCuOH), S can either decompose as ammonium sulfate or copper sulfate/sulfite species from these two forms of Cu.



Figure 5.4 SO<sub>2</sub> TPD spectra of Cu-SSZ-13 with SAR = 6 and 30 after exposure to SO<sub>2</sub> + NH<sub>3</sub>. Experimental conditions: 500 ppm NH<sub>3</sub>, 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub> at 150 °C, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>.

**Table 5.3** Quantification of  $SO_2 + NH_3$  TPD on Cu-SZZ-13 SAR=6 and 30 based on TPD data presented in<br/>Fig. 5.4.

Sample	Ratio of integrated SO <sub>2</sub> TPD areas	
Cu-SSZ-13_SAR_6	Low temperature peak:Total TPD yield	0.61
	High temperature peak:Total TPD yield	0.39
Cu-SSZ-13_SAR_30	Low temperature peak:Total TPD yield	0.37
	High temperature peak:Total TPD yield	0.63

# 5.3.3.2 Ex-situ DRIFTS

 $NH_3$  adsorption as a probe during DRIFTS experiments was used to characterize Z2Cu or ZCuOH sites on fresh samples and after stepwise de-sulfations at 450, 500 and 550 °C. The results are shown in Figure 5.5. For the fresh samples, both sites were available for  $NH_3$  adsorption as evident by two negative IR features at 900 and 950 cm<sup>-1</sup>. After SO<sub>2</sub>

exposure and then with de-sulfation at 450 °C, the IR feature at 950 cm<sup>-1</sup> is absent in both cases suggesting ZCuOH is not available for  $NH_3$  adsorption. Taking the  $SO_2 + NH_3$  TPD data (i.e. Fig. 5.4) into account, de-sulfation at 450 °C should recover the Z2Cu site, which is in total agreement with the ex-situ DRIFTS data shown in Fig. 5.5.



**Figure 5.5** *Ex-situ* DRIFTS spectra of perturbed T-O-T bond region after  $NH_3$  adsorption at 150 °C on fresh and desulfated (deSO<sub>x</sub> at 450, 500 and 550 °C) Cu-SSZ-13\_SAR\_6 (A) and Cu-SSZ-13\_SAR\_30 (B).

A similar observation was also reported by Luo et al.<sup>42</sup> regarding the recovery of the 900 but disappearance of the 950 cm<sup>-1</sup> IR band, with their reported data after de-sulfation at 550 °C. Further de-sulfation at 500 and 550 °C did result in partial recovery of 950 cm<sup>-1</sup> peak and also appearance of a shoulder at 920 cm<sup>-1</sup>. Similar to that in Fig. 5.2 (D), the new feature at 920 cm<sup>-1</sup> suggests formation of stable sulfur complexes on the ZCuOH site. The nature of such sulfur complexes will be addressed in the following sections.

 $NH_3 + SO_2$  TPD and ex-situ DRIFTS data taken together suggest and resolve that sulfur adsorbs on Z2Cu via formation of ammonium sulfate whereas more stable sulfur complexes can be formed on ZCuOH.

#### 5.3.4 SO<sub>2</sub> interaction with Cu-SSZ-13

As discussed above, the key distinguishing factor between Z2Cu and ZCuOH is an interaction with SO<sub>2</sub> with formation of S intermediates of different stabilities. Specifically, having a higher ZCuOH:Cu<sub>tot</sub> ratio (i.e. higher Si:Al) resulted in formation of a higher amount of more stable sulfur species. However, the nature of such sulfur species is not yet clear. To determine this, density functional theory, SO<sub>2</sub>-TPD and in-situ DRIFTS were used to study SO<sub>2</sub> interactions with Cu-SSZ-13 in the absence of NH<sub>3</sub>.

## 5.3.4.1 SO<sub>2</sub> TPD and in-situ DRIFTS experiments of SO<sub>2</sub> adsorption

To understand SO<sub>2</sub> interactions with Cu sites in the absence of NH<sub>3</sub>, TPD experiments were performed over Cu-SSZ-13\_SAR\_30 after exposing it to SO<sub>2</sub> at different temperatures (i.e. 100, 150, 250 °C). Results are shown in Figure 5.6. Note that the SO<sub>2</sub> profile during SO<sub>2</sub> + NH<sub>3</sub> adsorption on the same catalyst (taken from Fig. 5.4) is also replotted here to better illustrate/distinguish NH<sub>3</sub> + SO<sub>2</sub> and SO<sub>2</sub> trends. Interestingly, unlike NH<sub>3</sub> + SO<sub>2</sub>, SO<sub>2</sub> adsorption resulted in only one desorption feature observed at ~580 °C. Taking our assignments from previous sections into account, this suggests formation of sulfur complexes on ZCuOH even in the absence of NH<sub>3</sub> in the feed. However, the TPD feature at 380 °C, i.e. ammonium sulfate decomposition from Z<sub>2</sub>Cu, was not observed, as would be expected in the absence of NH<sub>3</sub>.



**Figure 5.6** SO<sub>2</sub> TPD spectra of Cu-SSZ-13 with SAR = 30 after exposure to SO<sub>2</sub> at 100, 150 and 250 °C or SO<sub>2</sub> + NH<sub>3</sub> at 150 °C. Experimental conditions: 500 ppm NH<sub>3</sub> (if needed), 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>.

Moreover, the S on ZCuOH site still decomposes at ~580 °C showing that having NH<sub>3</sub> in the feed doesn't change the S desorption chemistry on ZCuOH sites. However, looking at figure 5.6 and comparing S uptake form ZCuOH site in the presence and absence of NH<sub>3</sub> at the same temperature, it is clear that NH<sub>3</sub> can facilitate formation of high temperature S species. This could be due to either (1) CuOH<sup>+</sup> cation structures/location in the presence and absence of NH<sub>3</sub>; i.e. NH<sub>3</sub> can change the coordination geometry of Cu<sup>12,17</sup>, or (2) formation of ammonium sulfate as an intermediate.

Another interesting finding from Fig. 5.6 is that sulfur coverage increased as a function of temperature. This observation clearly suggests SO<sub>2</sub> adsorption on ZCuOH via an activated adsorption process.



**Figure 5.7** In-Situ DRIFTS spectra of T-O-T vibrations of Cu-SSZ-13\_SAR\_30 during a SO<sub>2</sub> adsorption at 150 °C.

To further confirm the identification and also to understand the nature of IR feature at 920 cm<sup>-1</sup>, in-situ DRIFTS during SO<sub>2</sub> adsorption at 150 °C was performed with the Cu-SSZ-13\_SAR\_30 sample and results are presented in Figure 5.7. With SO<sub>2</sub> adsorption, the 950 cm<sup>-1</sup> band decreased with a concomitant increase in the band at 920 cm<sup>-1</sup>. This clearly shows S affecting ZCuOH, perturbing the T-O-T band, in this case more strongly as evident by the lowered IR wavenumber at 920 cm<sup>-1</sup>. Compared to monovalent cations (Cu<sup>+</sup>), divalent cations (Cu<sup>2+</sup>) were reported to exert much stronger perturbation due to either a stronger electrostatic interaction or a more significant extent of covalent bonding<sup>99</sup>. This means that transformation  $Cu^{2+}$  to  $Cu^{1+}$  would result in a shift to higher wavenumbers, which is not the case for the data presented in Fig. 5.7. Therefore, adsorption of SO<sub>2</sub> seems not to change the oxidation state of the Cu, but stabilizes ZCuOH by formation of sulfur complexes incorporated with Cu. Note that the 900 cm<sup>-1</sup> feature, assigned to Z2Cu, remained absent during SO<sub>2</sub> adsorption, coinciding with the TPD data discussed above.

## 5.3.5 SCR activity, regeneration and S storage of the NH<sub>3</sub> + SO<sub>2</sub> poisoned catalysts

There have been numerous studies focused on low-temperature (< 200 °C) SCR kinetics due to its importance in NO<sub>x</sub> reduction especially during cold-start conditions<sup>27</sup>. These studies agree in general that NH<sub>3</sub>-SCR is being catalyzed on isolated Cu ions but not oxides, and the TOF should be calculated based on such active sites<sup>27,36,38,88</sup>. Recently, Gao et al.<sup>38</sup> reported that a low-temperature SCR redox cycle cannot be completed on a single Cu site, and a pair of mobile  $[Cu^{I}(NH_{3})_{2}]^{+}$  sites are required to the catalyze oxidation halfcycle. Paolucci et al. also confirmed the possibility of formation of [(NH<sub>3</sub>)<sub>2</sub>Cu<sup>II</sup>-O<sub>2</sub>-Cu<sup>II</sup>(NH<sub>3</sub>)<sub>2</sub>] complex which can react with two NO molecules to regenerate mobile Cu species i.e.  $[Cu^{l}(NH_{3})_{2}]^{+}$ . These studies, however, focused on the activity of fresh Cu-SSZ-13 and not on the sulfated/de-sulfated samples. Here, to study the impact of sulfur on lowtemperature (110-210 °C) SCR functionality of Cu-SSZ-13 with different Si:Al ratios, standard SCR activity was evaluated on fresh, sulfated, and de-sulfated samples with results shown in Figure B.9. The corresponding Arrhenius plots and apparent activation energies ( $E_a$ ) are shown in Figure 5.8. In the case of fresh samples,  $E_a$  values for Si:Al = 6 and 30 appear to differ. Specifically, a lower value of E<sub>a</sub> (67 kJ·mol<sup>-1</sup>) was observed for the sample with a higher Si:Al compared to that with a Si:Al = 6 ( $E_a = 88 \text{ kJ} \cdot \text{mol}^{-1}$ ).



Figure 5.8 Arrhenius plots for standard SCR over fresh, sulfated, de-sulfated (at 450, 500 and 550 °C) Cu-SSZ-13 (A) Si:Al = 6 and (B) Si:Al = 30. Experimental conditions: 550 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub>, GHSV of 400,000 hr<sup>-1</sup>.

It should be noted that a similar observation was reported by Gao et al.<sup>88</sup> on the SCR activity over fresh Cu-SSZ-13 with different Si:Al ratios. This could be due to either distinct (low-temperature) catalytic centers (ZCuOH versus  $Z_2Cu$ ) or rate-limiting steps over the two model catalysts. In the case of sulfated samples, sulfur poisoning was found to severely influence SCR rates on both catalysts as evident by a significant decrease in  $E_a$  values. SO<sub>2</sub> + NH<sub>3</sub> TPD findings (Fig. 5.4) support this observation. Upon SO<sub>2</sub> + NH<sub>3</sub> exposure at 150 °C, isolated Cu ions, both Z2Cu and ZCuOH, store sulfur with a 1:1 SO<sub>2</sub>:Cu molar ratio. Thus, all of SCR active sites are poisoned under the exposure conditions used and no longer available, thus the loss in activity observed in Fig. 5.8. A key distinguishing feature between the two model catalysts is in their responses to regeneration experiments. With de-sulfation at 450 °C, Cu-SSZ-13 with a Si:Al = 6 noticeably recovered activity. Cu-SSZ-13 with a Si:Al = 30, in contrast, remained poisoned

and higher temperatures (i.e. 550 °C) were needed to regain SCR functionality. To better demonstrate these results, activity regeneration is compared based on the TOF for fresh and de-sulfated samples. These data are plotted in Figure 5.9 (A). It should be noted that different temperatures were chosen for the two catalysts such that the TOF values were obtained in the differential regime and comparable to each other (i.e. TOF<sub>143°C</sub> of Cu-SSZ-13\_SAR\_6 = TOF\_{184°C}^{fresh} of Cu-SSZ-13\_SAR\_30 \approx 1 \times 10^{-3} \text{ mol NO-mol Cu}^{-1} \cdot \text{s}^{-1}). Per the data shown in Figure 5.9 (A), it is clear that the sample with the higher Si:Al ratio and thus the higher ratio of ZCuOH:Cutot to Z2Cu:Cutot, is more severely poisoned and higher temperatures (> 550 °C) are needed to regain the activity. SO<sub>2</sub> release during de-sulfation experiments was also measured and shown in Figure B.10. Note that the second TPD peaks in figure B.10 are not superimposed. During the deSO<sub>X</sub> processes, the temperature was ramped up and then held at temperatures lower than the 580 °C (i.e. where the second TPD feature peaks in figure 5.4). This results in a shift in where the feature peaks - it peaks at the highest temperature of the TPD. Comparing activity regeneration (Fig. 5.9(A)) with the amount of S being released during de-sulfation experiments (Fig. 5.9(B)), it is clear that severe poisoning of the sample with Si:Al = 30 is due to its higher capacity of formation of more stable copper bisulfite species, which remain on the catalyst even at temperatures as high as 500 °C. Note that none of samples should be fully regenerated since all samples have some ZCuOH sites that lead to formation of the more stable S species. These S species are released at higher temperature as evident in TPD spectra (Fig. B.11) taken after desulfation experiments. Analogous to our previous study<sup>93</sup>, more stable copper sulfate species form with exposure to sulfur at higher temperatures. Note that formation of such species cannot happen at low temperatures as evident from Fig. 5.4, where no such high temperature peaks were observed.



Figure 5.9 (A) NH<sub>3</sub>-SCR activity regeneration after stepwise desulfation at different temperatures based on rate constant measured at T = 143 °C for Cu-SSZ-13 Si:Al = 6 and T = 184 °C for Cu-SSZ-13 Si:Al = 30. (B) S released per total amount of S stored after stepwise desulfation at different temperatures over Cu-SSZ-13 with Si:Al = 6 and 30.

# 5.3.6 Low-temperature SO<sub>2</sub> poisoning mechanism on Z<sub>2</sub>Cu versus ZCuOH

With the above findings, a straightforward SO<sub>2</sub> poisoning mechanism can be proposed. Depending on the nature of the Cu site, i.e. Z2Cu or ZCuOH, two reaction routes exist: (1) SO<sub>2</sub> poisoning of Z2Cu: Cu<sup>2+</sup> in the form of Z2Cu did not to adsorb sulfur with exposure to SO<sub>2</sub> at low temperatures (< 250 °C). DFT calculations (presented in Appendix B) and in-situ DRIFTS during adsorption of SO<sub>2</sub> (Figure 5.7) lead to the same conclusion. In contrast, NH<sub>3</sub> + SO<sub>2</sub> exposure resulted in sulfur deposition via formation of ammonium sulfate with its fingerprint TPD peak at 380 °C (Fig. 5.4). Results discussed above together with previous studies suggest that such species are in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (NH<sub>3</sub>:SO<sub>2</sub> is 2:1) over Cu<sup>2+</sup> coordinated with H<sub>2</sub>O molecules and it decomposes to SO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O at 380 °C. Comparing SCR activity, regeneration and S storage on/over the NH<sub>3</sub> + SO<sub>2</sub> 109

poisoned Cu-SSZ-13 samples with different Si:Al ratios, the Z2Cu SCR activity significantly recovered after ammonium sulfate decomposition. Therefore, on Z2Cu, lowtemperature SCR is inhibited by formation of ammonium sulfate and it can be fully recovered by treating the catalyst at temperatures as low as 380 °C. (2) SO<sub>2</sub> poisoning of ZCuOH: unlike Z2Cu, ZCuOH adsorbed sulfur directly during low-temperature  $SO_2$ adsorption. DFT calculations (see Appendix B), SO<sub>2</sub>-TPD and in-situ DRIFTS experiments all favor this argument that, in the absence of SO<sub>2</sub> oxidation, SO<sub>2</sub> adsorbs on ZCuOH via formation of copper bisulfite with its desorption feature at 580 °C. However, increasing the temperature in the presence of O<sub>2</sub> can result in oxidation of CuHSO<sub>3</sub> to form CuHSO<sub>4</sub> requiring even higher temperatures (~750 °C) for decomposition, as suggested by DFT and shown in figure A2.10. As a result, formation of more stable bisulfite/sulfate species makes S poisoning of ZCuOH more severe compared to that of Z2Cu. This was confirmed by SCR activity and regeneration data presented in Fig. 5.9 together with the TPD data shown in Figure S10. Note that, as evident in figures 5.4 and 5.6, CuHSO<sub>4</sub> did not form as a result of SO<sub>2</sub> or SO<sub>2</sub> + NH<sub>3</sub> adsorption (i.e. no 750 °C peak was observed). This suggests that formation of such species could be hindered by the presence of a reductant like NH<sub>3</sub>.

## **5.4 Conclusions**

In this study, the two Cu active sites in Cu-SSZ-13 i.e. Z2Cu and ZCuOH, were found to have different responses towards sulfur poisoning. On Z2Cu, SO<sub>2</sub> only adsorbed when it was co-fed with ammonia, suggesting formation/decomposition of ammonium sulfate as the main poisoning/de-sulfation route on this site. In contrast, SO<sub>2</sub> interacted more readily with ZCuOH, resulting in formation of copper bisulfite species. With
increasing temperature, and in the presence of O<sub>2</sub>, copper bisulfite can be oxidized to form copper bisulfate species. In terms of low-temperature SCR activity, SO<sub>2</sub> severely inhibited both Cu-SSZ-13 samples. However, Cu-SSZ-13 with a higher relative amount of ZCuOH sites, compared to Z2Cu, required higher de-sulfation temperatures (> 550 °C). ZCuOH sites led to formation of highly stable bisulfite/bisulfate species resulting in higher de-sulfation temperatures needed for deNO<sub>x</sub> recovery.

# Chapter 6 Mechanism-based kinetic modeling of Cu-SSZ-13 sulfation and desulfation for NH<sub>3</sub>-SCR applications

## **6.1 Introduction**

Selective catalytic reduction of NO<sub>x</sub> by ammonia over small pore Cu-exchanged molecular sieves with a chabazite (CHA) structure, i.e. Cu-SSZ-13 and Cu-SAPO-34, has been extensively studied as a promising technology for emission control in diesel exhaust aftertreatment systems<sup>27,63</sup>. Depending on the NO<sub>2</sub>:NO ratio, NH<sub>3</sub>-SCR can proceed via three main reactions; the most basic reaction, commonly known as standard NH<sub>3</sub>-SCR is as follows:

$$4NO + 4NH_3 + O_2 \to 4N_2 + 6H_2O \tag{6-1}$$

The SCR reaction can proceed at a faster rate when  $NO_2$  and NO are present in a 1:1 ratio. This reaction, referred to as fast SCR, occurs as follows:

$$2NO_2 + 2NO + 4NH_3 + O_2 \to 4N_2 + 6H_2O \tag{6-2}$$

Pure NO<sub>2</sub>, in the absence of NO, can participate in SCR when the NO<sub>2</sub>:NO is larger than 1. Having the lowest rate compared to the other two SCR reactions, NO<sub>2</sub>-SCR takes place based on the reaction below:

$$6NO_2 + 8NH_3 \to 7N_2 + 12H_2O$$
 (6-3)

These SCR reactions can be accompanied with undesirable  $NH_3$  oxidation reactions as follows<sup>27,101</sup>:

$$4NH_3 + 5O_2 \to 4NO + 6H_2O \tag{6-4}$$

$$4NH_3 + 3O_2 \to 2N_2 + 6H_2O \tag{6-5}$$

These non-selective NH<sub>3</sub> oxidation reactions over small pore Cu-CHA catalysts only occur at high temperatures (>  $350 \ ^{\circ}C)^{26}$ .

With regard to catalytic active centers, monomeric Cu exchanged at 1Al or 2Al sites (i.e. ZCuOH and Z2Cu, respectively) are agreed to be the most active sites for NH<sub>3</sub>-SCR<sup>38,39,84</sup>. Varying Cu:Al and Si:Al ratios, during the Cu-SSZ-13 preparation process, can result in different populations of Cu ions in six-membered 2Al sites and in eight-membered 1Al sites<sup>39,88</sup>.

Many catalytic mechanisms have been proposed to describe SCR reactions over Cu-exchanged zeolite catalysts<sup>27,38,40,41</sup>. Most recent mechanistic studies revealed that the SCR reaction follows Cu<sup>I</sup>  $\leftrightarrow$  Cu<sup>II</sup> redox cycles<sup>27,38,40</sup>. According to Paolucci et al.<sup>39</sup>, the reduction half-cycle starts with a NO molecule attacking a NH<sub>3</sub>-solvated Cu site, during which, Cu accepts an electron and a proton is transferred to either Cu-OH or framework oxygen (O<sub>f</sub>). This results in H<sub>2</sub>NNO formation as an intermediate, which can be easily decomposed to N<sub>2</sub> and H<sub>2</sub>O<sup>39</sup>. The oxidation half-cycle, however, requires participation of two Cu sites. Very recently, Paolucci et al.<sup>40</sup> and Gao et al.<sup>38</sup> reported that two [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> intermediates can migrate to the vicinity of each other catalyzing NO oxidation and consequently oxidizing Cu<sup>I</sup> to Cu<sup>II</sup>.

Despite having high SCR activity in a wide temperature window (200-450 °C) and thermal stability, Cu-SSZ-13 and Cu-SAPO-34, under practical conditions, are prone to sulfur poisoning and to some extent hydrothermal  $aging^{43,44}$ . Therefore, a large body of research has focused on the understanding the effect(s) of sulfur on Cu-exchanged catalyst and finding possible regeneration strategies<sup>43,45,48,49,66,67,69,86,93,102</sup>. These studies revealed that SO<sub>x</sub> (SO<sub>2</sub> and SO<sub>3</sub>) can significantly inhibit low-temperature (< 350 °C) SCR activity<sup>43,48,49,66,67,69,93,102</sup>. In an early study on this subject, using X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES), Cheng et al.<sup>48</sup> reported formation of highly dispersed CuSO<sub>4</sub> species as the main poisoning mechanism. Utilizing temperature programmed desorption (TPD) of NH<sub>3</sub> during NH<sub>3</sub> and NH<sub>3</sub> + SO<sub>2</sub> adsorption, Zhang et al.<sup>43</sup> suggested formation of ammonium sulfate as a result of NH<sub>3</sub> and SO<sub>2</sub> co-adsorption. Studying sulfur poisoning over Cu-SSZ-13 samples with different Si:Al ratios, we found that the two Cu active sites i.e., Z2Cu and ZCuOH respond differently to SO<sub>2</sub> exposure<sup>102</sup>. On ZCuOH, low-temperature SO<sub>2</sub> adsorption resulted in formation of copper bisulfite species, which can be further oxidized to form copper bisulfate species in the presence of O<sub>2</sub> and increasing temperature. On Z2Cu, however, SO<sub>2</sub> can be stored only when it is co-fed with ammonia via formation of ammonium sulfate<sup>102</sup>. In terms of regeneration, also known as deSO<sub>x</sub>, higher temperatures (> 550 °C) were required for ZCuOH sites compared to Z2Cu which was recovered at temperatures as low as 350 °C<sup>102</sup>.

Capable of describing the catalytic performance as a function of operating parameters, kinetic models of exhaust aftertreatment systems can benefit system design and development<sup>25,103</sup>. Therefore, a large body of research has also been devoted to developing kinetic models for the diesel oxidation catalyst (DOC), lean NO<sub>x</sub> trap (LNT) and NH<sub>3</sub>-SCR catalysts. Details of these models together with reactor modeling in the diesel exhaust aftertreatment systems are comprehensively reviewed by Guthenke et al.<sup>103</sup>. Many kinetic models have been developed for NH<sub>3</sub>-SCR on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> <sup>104,105</sup> and different metal exchanged zeolites such as H-ZSM-5<sup>52,53</sup>, Cu-<sup>57</sup> and Fe-ZSM-5<sup>54,55</sup>, and Cu-faujasite<sup>56</sup>. Metkar et al.<sup>106</sup> developed a global kinetic model for NH<sub>3</sub>-SCR over a

commercial Cu-CHA assuming a single active site. The steady state NO<sub>x</sub> conversions during NH<sub>3</sub> oxidation, NO oxidation, standard SCR, fast SCR and NO<sub>2</sub> SCR were successfully predicted using this model<sup>106</sup>. Olsson et al.<sup>107</sup> implemented a three-site model describing the NH<sub>3</sub> TPD as well as NO<sub>x</sub> conversion over Cu-SSZ-13. In this model, Cu sites located in six-membered rings, Cu<sub>x</sub>O<sub>y</sub> located in CHA cages and Brønsted sites were assumed as the three sites participating in SCR (only Cu sites) and NH<sub>3</sub> adsorption-desorption reaction schemes<sup>107</sup>.

Very recently, Olsson et al.<sup>60</sup> developed a kinetic model for sulfur poisoning and regeneration of NH<sub>3</sub>-SCR on Cu-SSZ-13. However, formation/decomposition of S intermediates i.e. copper sulfate and ammonium sulfate, the effect of S on different active sites and S adsorption/desorption were not included in this model.

In this study, an attempt was made to develop a mechanism-based kinetic model capable of describing NH<sub>3</sub>-SCR activity over fresh, sulfated and regenerated (desulfated or deSO<sub>x</sub>) Cu-SSZ-13. In our previous study, we experimentally and theoretically evaluated the possible sulfur intermediates and its interactions with Cu active centers<sup>102</sup>. Based on our experimental evidence, a low temperature Cu-CHA deactivation/regeneration mechanism was proposed. This mechanism is being used as the basis for the kinetic model development.

### **6.2 Experimental methodology**

Three catalyst samples with different Si:Al and Cu:Al were used. These samples are notated as Cu-SSZ-13\_SAR\_6, Cu-SSZ-13\_SAR\_30 and commercial Cu-SSZ-13. The first two samples were prepared using a preparation method described and well-

characterized elsewhere<sup>102</sup>. The last sample was a commercial NH<sub>3</sub>-SCR catalyst. Inductively coupled plasma optical emission spectroscopy (ICP-OES) at Galbraith Laboratories, Inc. (Knoxville, TN, USA) was used to quantify Cu, Al and Si contents. To get the ZCuOH:Cu<sub>tot</sub> and Z2Cu:Cu<sub>tot</sub> ratios, H<sub>2</sub> temperature programmed reduction (TPR) was performed over hydrated samples. H<sub>2</sub>-TPR was done using a Micromeritics AutoChem II analyzer. In each TPR run, ~20 mg of sample was placed in the sample holder under a flow of 5% H<sub>2</sub>/Ar with a total flow rate of 30 sccm. The temperature ramp was 10 °C/min, up to 650 °C. Cu:Al, Si:Al, ZCuOH:Cu<sub>tot</sub> and Z2Cu:Cu<sub>tot</sub> values for three model catalyst samples are given in figure 6.1. ICP-OES and H<sub>2</sub>-TPR were used to obtain these values.



Figure 6.1 Z<sub>2</sub>Cu and ZCuOH populations together with elemental analysis of model catalysts used in this study. Quantified utilizing H<sub>2</sub>-TPR and ICP-OES.

Based on our previous study<sup>102</sup>, using peak deconvolution, Z2Cu:Cu<sub>tot</sub> and ZCuOH:Cu<sub>tot</sub> can be obtained using H<sub>2</sub>-TPR or SO<sub>2</sub> + NH<sub>3</sub> TPD results. Here, as an example, in figure 6.2, H<sub>2</sub>-TPR together with the SO<sub>2</sub> signal in SO<sub>2</sub> + NH<sub>3</sub> TPD experiments for the

commercial Cu-SSZ-13 sample are shown. The ratio Z2Cu:Cu<sub>tot</sub> and ZCuOH:Cu<sub>tot</sub> ratios were calculated using area under the curve of  $H_2$ -TPR and validated using SO<sub>2</sub> + NH<sub>3</sub> TPD experiments.



**Figure 6.2** (A) H<sub>2</sub>-TPR and (B) SO<sub>2</sub> in SO<sub>2</sub> + NH<sub>3</sub> TPD for commercial Cu-SSZ-13. These data were used to obtain Z2Cu and ZCuOH population values presented in the figure 6.1.

A microreactor setup (described elsewhere<sup>77</sup>) equipped with a MKS MultiGas 2030 FTIR was used to perform TPD experiments and SCR activity and regeneration experiments. Before each test, the samples were pre-treated under the flow of 10% O<sub>2</sub> balanced with N<sub>2</sub> at 550 °C for 4 h. For SO<sub>2</sub>, NH<sub>3</sub> and SO<sub>2</sub> + NH<sub>3</sub> TPD experiments, samples were exposed to 45-60 ppm SO<sub>2</sub> (if used), 475 or 550 ppm NH<sub>3</sub> (if used) in the presence of 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub> at 100, 150, or 250 °C until saturation. Subsequently, a N<sub>2</sub> purge phase was performed by flowing only N<sub>2</sub>, and then the temperature was increased from 150 to 750-850 °C at a rate of 5, 10 or 50 °C/min. For fresh SCR, sulfated and regenerated activity, catalyst samples were exposed to 550 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub>. The gas hour space velocity (GHSV) was estimated to be ~400,000 h<sup>-1</sup>. Multiple temperature points within the 110-210

°C range was used to measure the fresh low-temperature SCR activity. Sulfation was done by exposing samples to 50 ppm SO<sub>2</sub>, 550 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub> at 150 °C. DeSO<sub>x</sub> was done by treating samples at 550 °C for 4 h in 10% O<sub>2</sub>/N<sub>2</sub>. The following equation was used to calculate the NO<sub>x</sub> conversion:

$$NO_{x} \ conversion \ (\%) = \frac{(NO+NO_{2})_{inlet} - (NO+NO_{2}+N_{2}O)_{outlet}}{(NO+NO_{2})_{inlet}} \times 100$$
(6-6)

#### 6.3 Modeling

### 6.3.1 Reactor Model

GT-ISE v2017 was used to define the reaction scheme and solve the governing equations for gas-phase and surface concentrations and temperatures. The optimization process was performed using Matlab's constrained optimizer, i.e. the fmincon function. A quasi-steady state approximation was assumed, meaning that the gas in the reactor has a short residence time compared to other time scales present in the system. In other words, the temporal changes in most aftertreatment systems are much smaller than spatial ones. Therefore, 1-D governing equations can be simplified becoming less time-consuming to solve.<sup>108</sup> This approximation can be applied for most aftertreatment applications. A 1-D heterogeneous packed-bed reactor model was used. Catalyst input data used in the model is listed in Table 6.1. The solid- and gas-phase energy balances were solved along the reactor, and an adiabatic condition was assumed. Heat generation by reactions was neglected, with this assumption demonstrated allowable per Metkar et al.<sup>59</sup>. The reaction rates were defined based on the surface concentrations on the surface.

The governing equations are as follows:

Solid phase energy:

$$\psi_s \frac{\partial T_s}{\partial t} = \frac{\partial}{\partial z} \left( f_{sb} \lambda_{sb} \frac{\partial T_s}{\partial z} \right) + hS \left( T_g - T_s \right) - \sum_{j=1}^{nrct} a_j \Delta H_j r_j + h_x S_x (T_x - T_s)$$
(6-7)

Gas phase energy:

$$\varepsilon \rho_g \nu C_{pg} \frac{\partial T_g}{\partial z} = h S(T_s - T_g) \tag{6-8}$$

Reaction rates:

$$r_j = r_j(\overrightarrow{C_s}, T_s, \vec{\theta}) \tag{6-9}$$

$$\sum_k \theta_k = 1 \tag{6-10}$$

$$\frac{d\theta_k}{dt} = \sum_j s_{ij} r_j \tag{6-11}$$

Trace species conservation:

$$\varepsilon \rho_g v \frac{\partial \omega_g}{\partial z} = k_{m,i} S(\omega_{s,i} - \omega_{g,i}) = \sum_j s_{ij} r_j$$
(6-12)

Fully developed laminar flow was assumed in order to calculate the heat and mass transfer coefficients based on a single Nusselt number as follows:

$$Nu = \frac{D_p}{1 - \varepsilon} \frac{h}{\lambda_g}$$
(6-13)

$$Sh_i = \frac{D_p}{1-\varepsilon} \frac{k_{m,i}}{\rho \, D_{i,m}} \tag{6-14}$$

The binary diffusion,  $D_{i,m}$ , values were calculated using the Fuller correlation. D<sub>p</sub> is defined as follows:

$$D_p = \frac{6(1-\varepsilon)}{S} \tag{6-15}$$

## 6.3.2 Kinetic model

A multisite kinetic model was assumed to include: Lewis acid sites, including site 1 (notated as Z1) and 2 (notated Z2) representing Z2Cu and ZCuOH active centers, respectively, and the Brønsted acid site notated as site B. The Brønsted acid site was assumed to mainly participate in  $NH_3$  adsorption/desorption and not in SCR. The Advanced Direct Optimizer toolbox in GT-ISE v2017 was used to fit parameters. The objective function is defined as below:

$$Objective_{Function} = \left(y_{predicted} - y_{measured}\right)^2 \tag{6-16}$$

Catalyst Input Data		
Packed-bed geometry		
Total frontal area	12.5 mm <sup>2</sup>	
Length of catalyst	4 mm	
Specific Area	5.32 1/mm	
Void fraction	0.7	
Thermal Input Data		
Initial Wall Temperature	150 °C	
Convection Coefficient	Catalyst was assumed fully insulated and it was assumed that external heat transfer from catalyst is negligible.	

**Table 6.1** Catalyst bed input data used in the model.

## 6.4 Results and discussion

## 6.4.1 Transient kinetics of SO<sub>2</sub> adsorption-desorption

Using SO<sub>2</sub> TPD experiments over Cu-SSZ-13 samples with different Si:Al ratios, we showed that SO<sub>2</sub>, in the presence of O<sub>2</sub> and H<sub>2</sub>O, can be adsorbed over ZCuOH sites via a bisulfite formation route<sup>102</sup>. These results also revealed that S surface coverage, in



SO<sub>2</sub> TPD on Cu-SSZ-13\_SAR\_30 with adsorption at 100, 150 and 250 °C

**Figure 6.3.** Experimental result (green line) and model prediction (blue dashed line) of SO<sub>2</sub> TPD over Cu-SSZ-13\_SAR\_30 with adsorption at (A) 100, (B) 150 and (C) 250 °C. Experimental conditions: 60 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>. the case of SO<sub>2</sub> adsorption, increases as a function of temperature<sup>102</sup>. Here, the results for SO<sub>2</sub>-TPD experiments and simulations for a Cu-SSZ-13\_SAR\_30 with adsorption at 150, 200 and 250 °C are shown in Figure 6.3 (A), (B) and (C), respectively. A typical SO<sub>2</sub> TPD over Cu-SSZ-13 includes three stages: (1) adsorption, during which the catalyst is exposed to SO<sub>2</sub> and the SO<sub>2</sub> adsorbs, and with breakthrough its concentration increases with time until the saturation, (2) purging in N<sub>2</sub>; upon SO<sub>2</sub> shutoff, the outlet concentration immediately decreases showing an insignificant amount of physisorbed sulfur is present, and (3) TPD; with increasing temperature the rate of S desorption increases and strongly adsorbed S starts to desorb. To simulate the transient kinetics of SO<sub>2</sub> desorption, a simple

Langmuir approach was assumed with a constant value for the desorption activation energy. The sulfur adsorption-desorption mechanism was assumed based on the experimental results and corresponding reactions and rate expressions and estimated kinetic values are listed in Table 6.2 and 6.3, respectively.

As mentioned earlier, in our previous study, we have shown that ZCuOH sites are required for SO<sub>2</sub> adsorption in the absence of  $NH_3^{102}$ . Paolucci et al.<sup>39</sup> reported  $Z[Cu^{II}(OH)(H_2O)_3](H_2O)_3$  as the most stable complex at 1Al sites in the presence of 2%  $H_2O$ , 20%  $O_2$  and at ambient temperature. Utilizing X-ray absorption spectroscopy (XAS) and FTIR experiments, Borfecchia et al.<sup>84</sup> revealed that with increasing temperature, Cu cations undergo dehydration. Upon completion of dehydration, at around 250 °C, the majority of Cu cations in the vicinity of 1Al sites are in the form of ZCuOH. Here, we propose that Cu dehydration process is the reason behind the temperature dependent S adsorption. Therefore, to capture this behavior, an inhibition function was added to the SO<sub>2</sub> adsorption rate expression.

To fit the experimental data, pre-exponential factors and the desorption activation energy were tuned. Assuming first order kinetics, using a Redhead analysis<sup>109</sup> provides a desorption energy of  $103\pm10$  kJ/mol. This was used as the initial guess and limits for the desorption activation energy optimization in the model. In other words, only values between 93 and 113 were allowed during the optimization process. To check if the preexponential factors were reasonable, statistical thermodynamics was used to calculate the entropy change for SO<sub>2</sub> adsorption. More specifically, two extreme cases were assumed, (1) localized adsorption in which an adsorbed species does not move on the surface

Table 6.2. Reaction and rate expressions for SO<sub>2</sub> adsorption and desorption model.

Reaction	Rate expression	Eq. number	
$SO_2+Z2\to Z2_{SO_2}$	$r_1 = a_{Z2}k_1 C_{so_2}\theta_{Z2} = a_{Z2}f(T)A_1C_{so_2}\theta_{Z2}$	6-18	
$Z2_{SO_2} \rightarrow SO_2 + Z2$	$r_{2} = a_{Z2}k_{2}\theta_{Z2_{SO_{2}}} = a_{Z2}A_{2}exp(\frac{E_{a,2}}{RT_{s}})\theta_{Z2_{SO_{2}}}$	6-19	
* $f(T) = (1 - \frac{1.3 \times 10^{10}}{T^4})$ inhibition function			

Table 6.3. Estimated kinetic parameters for SO<sub>2</sub> adsorption and desorption model.

Rate	Rate Constants	Pre-exponential factor	Activation energy (kJ/mole)
$SO_2$ adsorption (r <sub>1</sub> )	$k_1$	3.16 [m <sup>3</sup> /mole-site s]	0
SO <sub>2</sub> desorption (r <sub>2</sub> )	$k_2$	1.5×10 <sup>6</sup> [mole/mole-site s]	104

(notated as  $\Delta S_{loc}$ ), and (2) two dimensional (2D) gas adsorption in which adsorbed species are completely free to move on the surface (notated as  $\Delta S_{2D}$ ).

 $\Delta S_{model}$  was calculated based on the equation below<sup>110</sup>

$$\Delta S_{model} = R \ln \frac{A_{ads}}{A_{des}} \tag{6-17}$$

Pre-exponential factors were optimized such that  $\Delta S_{model}$  lies between  $\Delta S_{2D}$  and  $\Delta S_{loc}$ .

Knox et al.<sup>111</sup> calculated/reported  $\Delta S_{loc} = -242 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$  and  $\Delta S_{2D} = -100 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ 

for SO<sub>2</sub> at 636 K.  $\Delta S_{model}$ , based on our predicted pre-exponential factors, was estimated to be -191 J<sup>•</sup>mol<sup>-1</sup> K<sup>-1</sup>. More specifically, the predicted  $A_{ads}$  and  $A_{des}$  were optimized within the entropy limits (i.e.  $\Delta S_{loc} = -242$  J<sup>•</sup>mol<sup>-1</sup> K<sup>-1</sup> and  $\Delta S_{2D} = -100$  J<sup>•</sup>mol<sup>-1</sup> K<sup>-1</sup>). As shown in Fig. 6.3, SO<sub>2</sub> concentrations during adsorption and desorption phases are predicted by the model.



**Figure 6.4** Experimental result (green line) and model prediction (blue dashed line) of SO<sub>2</sub> TPD over (A) Cu-SSZ-13\_SAR\_6 with adsorption at 150 °C, commercial Cu-SSZ-13 with adsorption at (B) 150 and (C) 250 °C. Experimental conditions: 45-50 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>.

To validate the fitted kinetic parameters, the model predictions were tested against separate experimental data, i.e. data not used to fit or tune the kinetic parameters. These data along with the model predictions are plotted in figure 6.4. It is clear that the fitted parameters are able to predict SO<sub>2</sub> adsorption and desorption for different samples. Note that the only changed parameter in predicting the separate experimental data was the active site density i.e.  $a_{Z2}$  obtained using H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) experiments. Sulfur storage values obtained using experimental data (i.e. area under the TPD curves) and model predictions are also plotted in figure 6.5.



Figure 6.5 Experimental data and model predictions for sulfur storage over catalyst samples used in this study.

## 6.4.2 Transient kinetics of NH<sub>3</sub> adsorption-desorption

One of the most important steps in modeling the transient kinetics of NH<sub>3</sub>-SCR over Cu-CHA is NH<sub>3</sub> adsorption and desorption, since it determines the NH<sub>3</sub> storage capacity of the catalyst<sup>112</sup>. As mentioned above, many studies have already developed kinetic models for fresh SCR. Here, to capture NH<sub>3</sub> adsorption-desorption kinetics, a dual site model was assumed based on the mechanism reported by Metkar et al.<sup>59</sup>. Here, the two sites are Lewis and Brønsted acid sites, notated as Z and B, respectively. Note that since Cu sites are similar in terms of NH<sub>3</sub> storage and release, they are lumped together into one site (i.e. Z = Z1 + Z2). A non-activated NH<sub>3</sub> adsorption with a Langmuir- and Temkin-type desorption kinetics were assumed for Lewis and Brønsted acid sites, respectively. The NH<sub>3</sub> TPD experimental data together with the model predictions are plotted in figure 6.6. The adsorption and desorption reactions and rate expressions, and the estimated kinetic parameters are listed in Tables 6.4 and 6.5, respectively. As shown in Fig. 6.6, estimated

parameters were able to satisfactorily predict the transient kinetics of NH<sub>3</sub> adsorptiondesorption. Two distinct desorption activation energies were estimated for two acid sites showing different acid strengths. In line with previous studies, the higher desorption activation energy values observed for Brønsted acid sites showed that NH<sub>3</sub> is attached more strongly on these sites compared to Lewis acid sites.



**Figure 6.6** Experimental result (green line) and model prediction (blue dashed line) of NH<sub>3</sub> TPD over Cu-SSZ-13\_SAR\_6 with adsorption at 150 °C. Experimental conditions: 550 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>.

Rate	Rate Constants	Pre-exponential factor	Activation energy (kJ/mol)
$NH_3$ adsorption-site Z ( $r_3$ )	$k_3$	2.4 [m <sup>3</sup> /mole-site s]	0
$NH_3$ desorption-site Z ( $r_4$ )	$k_4$	8.0×10 <sup>8</sup> [mole/mole-site s]	82
NH <sub>3</sub> adsorption-site B (r <sub>5</sub> )	$k_5$	0.1 [m <sup>3</sup> /mole-site s]	0
NH <sub>3</sub> desorption-site B (r <sub>6</sub> )	$k_6$	2.8×10 <sup>7</sup> [mole/mole-site s]	106
$\alpha_1 = 0.15$			

Table 6.4 Reaction and rate expressions for NH<sub>3</sub> adsorption and desorption model.

Table 6.5. Estimated kinetic parameters for NH<sub>3</sub> adsorption and desorption model.

Reaction	Rate expression	Eq. number
$NH_3 + Z \rightarrow Z_{NH_3}$	$r_3 = a_Z k_3 C_{NH_3} \theta_Z$	6-20
$Z_{NH_3} \to NH_3 + Z$	$r_4 = a_Z k_4 \theta_{Z_{NH_3}} = a_Z A_4 exp(-\frac{E_{a,4}}{RT_s}) \theta_{Z_{NH_3}}$	6-21
$NH_3 + B \to B_{NH_3}$	$r_5 = a_B k_5 C_{NH_3} \theta_B$	6-22
$B_{NH_3} \rightarrow NH_3 + B$	$r_{6} = a_{B}k_{6}\theta_{B_{NH_{3}}} = a_{B}A_{6}exp(-\frac{E_{a,6}(1-\alpha_{1}\theta_{B_{NH_{3}}})}{RT_{s}})\theta_{B_{NH_{3}}}$	6-23

## 6.4.3 Transient kinetics of ammonium sulfate formation-decomposition

Comparing NH<sub>3</sub> uptake during NH<sub>3</sub> and NH<sub>3</sub> + SO<sub>2</sub> TPD experiments, Zhang et al.<sup>43</sup> reported an increase in NH<sub>3</sub> storage with a 2:1 molar ratio with respect to SO<sub>2</sub>. Based on this, formation of (NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>) was suggested as the key poisoning mechanism for low-temperature SCR (< 300 °C). Ammonium sulfate can form/decompose based on the reactions below:

$$(NH_4)_2 SO_4 \leftrightarrow NH_4 HSO_4 + NH_3 \tag{6-24}$$

127

$$NH_4HSO_4 \leftrightarrow NH_3 + SO_2 + \frac{1}{2}O_2 + H_2O$$



(6-25)

**Figure 6.7** (A) Inlet concentrations and (B) experimental result (green line) and model prediction (blue dashed line) of SO<sub>2</sub> + NH<sub>3</sub> TPD over Cu-SSZ-13\_SAR\_6 with adsorption at 150 °C. Experimental conditions: 475 ppm NH<sub>3</sub>, 75 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>.

Today, it is generally accepted that ammonium sulfate forms over Cu-SSZ-13 during  $NH_3$  and  $SO_2$  co-exposure<sup>42,93,113</sup>. Very recently, utilizing in-situ DRIFTS and TPD, we have shown that ammonium sulfate formation/decomposition is the key low temperature S

storage mechanism over the Z2Cu site<sup>102</sup>. Here, we assumed site 2 (i.e. Z2) is responsible for such a reaction. Based on this assumption, adsorbed NH<sub>3</sub> (i.e.  $Z1_{NH_3}$ ) reacts with SO<sub>2</sub> (g) and NH<sub>3</sub>(g) in the presence of H<sub>2</sub>O and O<sub>2</sub> to form  $(NH_4)_2SO_4$  on the surface, which is notated as  $AS = Z1_{NH_3SO_2NH_3}$ .



**Figure 6.8** Experimental result of SO<sub>2</sub> + NH<sub>3</sub> TPD over Cu-SSZ-13\_SAR\_6 with adsorption at 150, 200, 250 and 300 °C. Experimental conditions: 475 ppm NH<sub>3</sub>, 75 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub> and TPD rate of 10 °C/min.

Note that  $H_2O$  and  $O_2$  are present in excess and governing equations are therefore not solved for these species. The formation and decomposition reactions and rate expressions, and the estimated kinetic parameters are listed in Tables 6.6 and 6.7, respectively. The ammonium sulfate formation/decomposition experimental data together with model output are shown in figure 6.7. The NH<sub>3</sub> and SO<sub>2</sub> inlet concentrations are shown in Fig. 6.7 (A). Initially, at t = 0s, the catalyst sample was only exposed to SO<sub>2</sub> in order to get a stable signal before NH<sub>3</sub> injection. Upon the NH<sub>3</sub> step feed, at t = 3600s, the SO<sub>2</sub> signal dropped immediately suggesting consumption of SO<sub>2</sub> in the ammonium sulfate formation reaction. This stepwise injection of SO<sub>2</sub> and NH<sub>3</sub> allowed us to capture ammonium sulfate formation. Ammonium sulfate formation was assumed to proceed based on the reaction below:

$$2NH_3 + SO_2 + \frac{1}{2}O_2 + H_2O \iff (NH_4)_2SO_4$$
(6-26)

Table 6.6 Reaction and rate expressions for ammonium sulfate formation and decomposition model.

Reaction	Rate expression	Eq. number	
$Z1_{NH_3} + SO_2 + NH_3 \rightarrow AS$	$r_7 = a_{Z1}k_7 C_{NH_3}C_{SO_2}\theta_{NH_3}$	6-21	
$AS \rightarrow ABS + NH_3$	$r_8 = a_{Z1}k_8\theta_{AS} = a_{Z1}A_8\exp\left(\frac{-E_{a,8}(1-\alpha_2\theta_{AS})}{RT}\right)\theta_{AS}$	6-22	
$ABS \rightarrow Z1 + NH_3 + SO_2$	$r_9 = a_{Z1}k_9 \theta_{ABS}^2 = a_{Z1}A_9 \exp\left(\frac{-E_{a,9}}{RT}\right)\theta_{ABS}^2$	6-23	
AS = 71 and $ABS = 7$	1		
$AS = Z I_{NH_3SO_2NH_3}$ and $ADS = Z$	ISO <sub>2</sub> NH <sub>3</sub>		
Coverage balance for site 1 i.e. Z1: $\theta_{AS} + \theta_{ABS} + \theta_{NH_3} + \theta_{Z1} = 1$			
$\alpha_2 = 0.1$			

Table 6.7 Estimated kinetic parameters for ammonium sulfate formation and decomposition model

Rate	Rate Constants	Pre-exponential factor	Activation energy (kJ/mol)
Ammonium sulfate formation	<i>k</i> <sub>7</sub>	$6.3 \times 10^3$ [m <sup>6</sup> /mole mole-site	0
Ammonium sulfate decomposition to ammonium bisulfate	$k_8$	1.5×10 <sup>9</sup> [mole/mole-site s]	104
Ammonium bisulfate decomposition	<i>k</i> 9	1.9×10 <sup>12</sup> [mole/mole-site s]	150



**Figure 6.9** Experimental result (green line) and model prediction (blue dashed line) of SO<sub>2</sub> + NH<sub>3</sub> TPD over Cu-SSZ-13\_SAR\_6 with adsorption at 150 °C and TPD rate of (A) 5 and (B) 50 °C/min. Experimental conditions: 475 ppm NH<sub>3</sub>, 75 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub>.

Combining experimental and DFT studies, we have shown that  $SO_2$  does not interact with Z2Cu in the absence of  $NH_3^{102}$ . Therefore, we assumed  $NH_3$  adsorption is a prerequisite step for ammonium sulfate formation on Z2Cu sites. Furthermore, based on the area under the  $SO_2 + NH_3$  TPD curve during the ramping phase, the  $SO_2$ :Cu molar ratio was found to be 1:1 showing that each ammonium sulfate molecule occupies only one Cu site. Therefore,

we assumed a first-order dependence on  $\theta_{NH_3}$ . This adsorbed NH<sub>3</sub> was assumed to react with NH<sub>3</sub> (g) and SO<sub>2</sub> (g) to form  $(NH_4)_2SO_4$ . O<sub>2</sub> and H<sub>2</sub>O both were

present in excess and were not included in the reaction rate. Using  $NH_3 + SO_2$  TPD with adsorption at different temperatures, as shown in figure 6.8, it was found that the probability of desorption is greater at higher coverage. The second-order kinetics was found to be the best fit to model the reaction steps associated with the ammonium sulfate decomposition/desorption resulting in better prediction of the experimental behavior. As shown in Figure 6.7, the model was able to predict both formation of ammonium sulfate and its decomposition (i.e. TPD ramp). In order to validate the model, two different sets of experiments were performed using different ramp rates, 5 and 50 °C/min and the results are shown in figure 6.9.

### 6.4.4 Sulfur storage on different samples

The above SO<sub>2</sub> and SO<sub>2</sub> + NH<sub>3</sub> kinetic models were validated by simulating sulfur storage over samples with different Si:Al ratios. As mentioned above, in our model, ZCuOH (site Z2) and Z2Cu (site Z1) were assumed to be responsible for SO<sub>2</sub> adsorptiondesorption and ammonium sulfate formation-decomposition reactions, respectively. Experimentally, a typical SO<sub>2</sub> + NH<sub>3</sub> TPD shows two desorption peaks; a peak at around 380 °C assigned to ammonium sulfate decomposition on the Z2Cu site, and a peak at around 580 °C related to copper bisulfite decomposition on the ZCuOH site. By changing the Si:Al ratio, one would expect different ratios of high versus low temperature TPD peaks coinciding the different ZCuOH and Z2Cu ratios.



**Figure 6.10** SO<sub>2</sub> + NH<sub>3</sub> TPD experimental data together with model predictions for three catalyst samples used in this study. Experimental conditions: 475-500 ppm NH<sub>3</sub>, 50-75 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub> and a TPD rate of 10 °C/min.

The catalyst samples used in this study are Cu-SSZ-13\_SAR\_6 (Si:Al = 6), Cu-SSZ-13\_SAR\_30 (Si:Al = 30) and a commercial Cu-SSZ-13 (Si:Al = 17). Figure 6.10 shows SO<sub>2</sub> + NH<sub>3</sub> TPD experimental data together with model output for the three catalyst samples. The kinetic parameters were fitted using data obtained from Cu-SSZ-13\_SAR\_6. The SO<sub>2</sub> concentrations for Cu-SSZ-13\_SAR\_30 and commercial Cu-SSZ-13 were predicted by the model without tuning kinetic parameters. The only change was the values for  $a_{Z1}$  and  $a_{Z2}$  obtained utilizing H<sub>2</sub>-TPR experiments. The model was found, as shown in figure 6.10, to satisfactorily predict sulfur storage behavior over the different Cu-SSZ-13 samples.

### 6.5 NH<sub>3</sub>-SCR kinetic model

Many kinetic models have been developed to predict the performance of Cu-CHA for the standard SCR reaction. Metkar et al.<sup>106</sup> developed a global single site model for commercial Cu-SSZ-13 capable of predicting the steady state conversions for ammonia oxidation, NO oxidation, standard, fast and NO<sub>2</sub> SCR reactions. In their model, the standard SCR reaction was described using an Eley-Rideal mechanism. This suggests that NO adsorption-desorption was not considered in the reaction schemes and SCR was assumed to occur between adsorbed NH<sub>3</sub> and gas phase NO and O<sub>2</sub>. Olsson et al.<sup>107</sup> developed a multi-site kinetic model for NH<sub>3</sub>-SCR over Cu-SSZ-13. Two sites were assumed to be participating in standard SCR; site 1, associated with Cu in six-membered rings, was assumed as the main and most active site, site 2, correlated to the Cu in eightmembered rings and  $Cu_xO_y$  species, was assumed to be responsible for some high temperature SCR activity. Using this approach, they were able to describe NO<sub>x</sub> conversion during SCR in a broad temperature window (100-600 °C). We took a similar approach, using an Eley-Rideal mechanism to describe standard SCR over two Cu sites, namely Z2Cu and ZCuOH, notated as Z1 and Z2, respectively. More specifically, a dual-site kinetic model was developed capable of describing standard SCR over Z2Cu and ZCuOH. Note that the Brønsted site, i.e. B, was assumed to not participate in SCR but provide NH<sub>3</sub> to Cu sites via a fast spillover reaction. Experimentally, we measured NO<sub>x</sub> conversion on the three Cu-SSZ-13 samples with different Cu:Al and Si:Al ratios in the temperature range of 120-220 °C and the data are shown in figure 6.11. Note that low-temperature SCR was the region of interest since sulfur poisoning significantly affects SCR performance in this temperature range. The Cu-CHA catalyst with the lowest Si:Al



**Figure 6.11** Experimental results and model predictions of SCR over three catalyst samples with different Si:Al and Cu:Al ratios. Experimental conditions: 550 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub>.

(higher Z2Cu:Cu<sub>tot</sub> ratio) was found to be the most active standard SCR catalyst. Experimental data together with model predictions for steady state NO<sub>x</sub> conversion for NH<sub>3</sub>-SCR over the three Cu-SSZ-13 samples are shown in figure 6.11. The standard SCR reactions and rate expressions, and the estimated kinetic parameters are listed in Table 6.8 and 6.9, respectively. Note that the only data used for parameter fitting was the SCR data from Cu-SSZ-13\_SAR\_6. The SCR performance for the other two samples was predicted by just tuning active site densities  $a_{Z1}$ ,  $a_{Z2}$  and  $a_B$  obtained using H<sub>2</sub>-TPR and ICP-OES data.

Reaction	Rate expression	Eq. number
$4Z1_{NH_3} + 4NO + O_2 \rightarrow 4N_2 + 6H_2O + 4Z1$	$r_{10} = a_{Z1} k_{10} C_{NO} \theta_{Z1_{NH_3}}$	6-24
$4Z2_{NH_3} + 4NO + O_2 \rightarrow 4N_2 + 6H_2O + 4Z2$	$r_{11} = a_{Z2} k_{11} C_{NO} \theta_{Z2_{NH_3}}$	6-25
Brønsted sites act as the NH <sub>3</sub> source for the Lewis sites, i.e. $B_{NH_3} \rightarrow Z_{NH_3}$		

**Table 6.8** Reaction and rate expressions for SCR kinetic model.

 Table 6.9 Estimated kinetic parameters for SCR kinetic model.

Rate	Rate Constants	Pre-exponential factor	Activation Energy (kJ/mole)
Standard SCR - site 1 (r <sub>10</sub> )	<i>k</i> <sub>10</sub>	$3.8 \times 10^8$ [m <sup>3</sup> /mole-site s]	88
Standard SCR - site 2 (r <sub>11</sub> )	<i>k</i> <sub>11</sub>	$1.9 \times 10^6  [\text{m}^3/\text{mole-site s}]$	70

## 6.5.1 NH<sub>3</sub>-SCR kinetic model for sulfated/regenerated Cu-SSZ-13

To capture the steady state NO<sub>x</sub> conversion over sulfated and regenerated Cu-SSZ-13, the SO<sub>2</sub> adsorption-desorption and ammonium sulfate formation-decomposition reactions were added to the fresh SCR model reaction schemes. More specifically, taking ammonium sulfate formation-decomposition into account for site 1, i.e. Z2Cu, the coverage balance  $\theta_{NH_3} + \theta_{Z1} = 1$  was replaced with  $\theta_{AS} + \theta_{ABS} + \theta_{NH_3} + \theta_{Z1} = 1$ . Similarly, on site 2, i.e. ZCuOH,  $\theta_{NH_3} + \theta_{Z2} = 1$  was replaced with  $\theta_{SO_2} + \theta_{NH_3} + \theta_{Z2} = 1$  by including SO<sub>2</sub> adsorption-desorption into the model.



**Figure 6.12** Experimental results and model predictions for the steady state NO<sub>x</sub> conversion over fresh, sulfated and regenerated Cu-SSZ-13\_SAR\_6. Experimental conditions: 550 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub>. Sulfation: 50 ppm SO<sub>2</sub>, 550 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub> at 150 °C. DeSO<sub>x</sub> was done at 550 °C for 4 h in 10% O<sub>2</sub>/N<sub>2</sub>.

Figure 6.12 compares experimental results and model predictions for steady state NO<sub>x</sub> conversion over fresh, sulfated and regenerated Cu-SSZ-13\_SAR\_6. Note there was no parameter tuning done at this stage. To further validate the estimated kinetic parameters, the model was used to predict steady state NO<sub>x</sub> conversion for three catalyst samples after a deSO<sub>x</sub> treatment at 550 °C. These data are shown in figure 6.13. The model was able to accurately predict the regenerated SCR performance over the three samples.



**Figure 6.13** Experimental results and model predictions for the steady state NO<sub>x</sub> conversion over regenerated Cu-SSZ-13\_SAR\_6, Cu-SSZ-13\_SAR\_30 and commercial Cu-SSZ-13. Experimental conditions: 550 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub>. Sulfation: 50 ppm SO<sub>2</sub>, 550 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub> at 150 °C. DeSO<sub>x</sub> was done at 550 °C for 4 h in 10% O<sub>2</sub>/N<sub>2</sub>.

#### 6.6 Conclusions

A mechanism-based kinetic model was developed to predict Cu-SSZ-13 sulfation and desulfation for NH<sub>3</sub>-SCR. Our previous work showed that low-temperature sulfur poisoning of a SCR catalyst is site-dependent. Based on this, a multi-site kinetic model was developed describing different S intermediates formed over Z2Cu and ZCuOH sites. SO<sub>2</sub> and SO<sub>2</sub> + NH<sub>3</sub> TPD were used to simulate transient kinetics of copper sulfite and ammonium sulfate formation-decomposition over ZCuOH and Z2Cu, respectively. The model was found to accurately predict sulfur concentrations during sulfur storage and release over three Cu-SSZ-13 samples with different Si:Al and Cu:Al ratios. The model also accounted for steady state NO<sub>x</sub> conversion over fresh, sulfated and regenerated (at 550 °C) Cu-SSZ-13 samples. The model was found to be capable of describing fresh, sulfated and regenerated SCR performance for commercial and lab-prepared samples without tuning any kinetic parameters, but by only changing ZCuOH and ZCu site densities.

#### **Chapter 7 Conclusions and Recommendations**

The main objective of this work was to study the chemistry of Cu-CHA sulfur poisoning with the focus on understanding and development of a low-temperature SCR deactivation/regeneration mechanism. This thesis has presented a comprehensive experimental and kinetic modeling study of sulfation and desulfation of Cu-SSZ-13 and Cu-SAPO-34 for NH<sub>3</sub>-SCR applications. The results of this work show that SO<sub>2</sub> significantly inhibits low-temperature SCR and oxidation functionality of Cu-exchanged catalysts. In-situ DRIFTS and transient kinetics studies revealed that depending on Cu active sites, SO<sub>2</sub> interaction with Cu-CHA results in either formation of highly stable sulfite/sulfate species or ammonium sulfate depending on whether NH<sub>3</sub> is present or not. Based on these findings, a low-temperature sulfur poisoning mechanism was proposed and used to develop a mechanism-based kinetic model capable of describing S adsorption/desorption behavior and SCR activity on fresh, sulfated and regenerated catalyst. The following are the main findings of the present study.

### 7.1 Conclusions

## 7.1.1 Effect of SO<sub>2</sub> on NH<sub>3</sub> oxidation over a Cu-SAPO-34 SCR catalyst

The impact of SO<sub>2</sub> on NH<sub>3</sub> oxidation, an undesired side reaction that can occur during NH<sub>3</sub>-SCR, was studied using Cu-SAPO-34. Based on kinetic analysis, monomeric Cu<sup>++</sup> was active toward NH<sub>3</sub> oxidation. In terms of the SO<sub>2</sub> effect, significant loss in NH<sub>3</sub> oxidation activity was observed at temperatures below 350 °C. However, at higher temperatures, SO<sub>2</sub> had no significant effect on NH<sub>3</sub> oxidation. NH<sub>3</sub> + SO<sub>2</sub> TPD data obtained after NH<sub>3</sub> and SO<sub>2</sub> exposures demonstrate that SO<sub>2</sub> inhibited monomeric copper NH<sub>3</sub> oxidation activity through formation of ammonium sulfate, whose formation was catalyzed by the Cu. The monomeric copper regained NH<sub>3</sub> oxidation activity after ammonium sulfate decomposed.

## 7.1.2 SO<sub>2</sub> poisoning of the NH<sub>3</sub>-SCR reaction over Cu-SAPO-34: Impact of ammonium sulfate versus other S-containing species

SO<sub>2</sub> poisoning of NH<sub>3</sub>-SCR over Cu-SAPO-34 was studied, specifically to evaluate the forms/states of stored S and the effect of such species on low temperature  $NO_x$ reduction activity. Two primary sulfur species types were observed, and were found to be interchangeable depending on whether NH<sub>3</sub> was available or not. In one case both ammonium sulfate and Cu sulfate species could be present and in the other only Cu sulfate species. Cu sulfate, in the absence of ammonia, was found in three different states/forms identified by three desorption features during TPD experiments. DRIFTS of NO adsorption was used to investigate the nature and accessibility of the Cu species before and after sulfate formation, without the interference of ammonium sulfate; these data revealed that the  $Cu^{2+}$  inside the 6-membered rings was completely blocked by sulfur and that the nature of the [CuOH]<sup>+</sup> close to the 8-membered ring changed. In comparing the effect of different forms of S on low temperature  $NO_x$  reduction activity, ammonium sulfate had the largest impact on performance loss. Interestingly, results also show that ammonium sulfate can actually play a role as a SCR reactant, likely analogous to the mechanism involving ammonium nitrate. Ammonium sulfate decomposes at temperatures as low as ~300-350 °C, whereas higher temperatures (> 480 °C) were needed to desorb other S-containing species. This appears favorable, as NH<sub>3</sub> can react with pre-adsorbed sulfur on the catalyst to form ammonium sulfate, which decomposes at lower temperatures than the other sulfate forms.

## 7.1.3 On the nature of Cu active centers in Cu-SSZ-13 and their responses to SO<sub>2</sub> exposure

The effect(s) of  $SO_2$  on the two types of active sites on Cu-SSZ-13 NH<sub>3</sub>-SCR catalysts, Z2Cu and ZCuOH, were investigated. Two Cu-SSZ-13 catalysts with Si:Al ratios 6 and 30 were synthesized, and provide very different distributions of these two active sites. ICP-OES, H<sub>2</sub>-TPR and DRIFTS were utilized to characterize catalyst samples and quantify the amounts of total Cu, Z2Cu and ZCuOH. In-situ DRIFTS results show that Z2Cu and ZCuOH responses to low-temperature (< 200 °C) SO<sub>2</sub> poisoning were site dependent. Results of SO<sub>2</sub> and SO<sub>2</sub> + NH<sub>3</sub> temperature programmed desorption (TPD) and DRIFTS experiments, supplemented with DFT calculations (presented in Appendix B), revealed that the different observed responses correspond to different sulfur intermediates that form. On Z2Cu sites, SO<sub>2</sub> only adsorbs when it is co-fed with NH<sub>3</sub> via formation of ammonium sulfate, with its fingerprint TPD feature at 380 °C. However, low-temperature interaction between SO<sub>2</sub> and ZCuOH leads to copper bisulfite species formation, which can be further oxidized to form copper bisulfate with increasing temperature. In terms of low-temperature SCR functionality, the activity of both Cu-SSZ-13 samples were found to be significantly inhibited by SO<sub>2</sub>. However, in terms of regeneration (i.e. de-sulfation) behavior, Cu-SSZ-13 with a Si:Al = 30 (higher ZCuOH compared to Z2Cu) seemed to require higher de-sulfation temperatures (> 550 °C). Therefore, compared to Z2Cu,

ZCuOH sites are more susceptible to severe low-temperature SO<sub>2</sub> poisoning because of the formation of highly stable bisulfite and ultimately bisulfate species.

# 7.1.4 Mechanism-based kinetic modeling of Cu-SSZ-13 sulfation and desulfation for NH<sub>3</sub>-SCR applications

A multi-site kinetic model was developed to predict the effect of sulfur dioxide on Cu-SSZ-13 for the NH<sub>3</sub>-SCR of NO<sub>x</sub>. To develop a mechanism-based kinetic model, two different Cu sites were assumed describing the formation-decomposition of S intermediates i.e. copper bisulfite on Z2Cu (site 1) and ammonium sulfate (site 2). Transient kinetics of SO<sub>2</sub> interactions with Cu-SSZ-13 were simulated, exploiting SO<sub>2</sub> and SO<sub>2</sub> + NH<sub>3</sub> temperature programmed desorption (TPD) experiments. Besides S1 and S2, a 3<sup>rd</sup> site was assumed to account for the Brøsnted acid site, NH<sub>3</sub> adsorption. The model also accounts for NH<sub>3</sub>-SCR activity over fresh, sulfated and regenerated (at 550 °C) Cu-SSZ-13 samples with different Si:Al and Cu:Al ratios. Finally, the model was capable of well describing fresh SCR for commercial and prepared samples without tuning any kinetic parameters but only varying ZCuOH and ZCu site densities obtained utilizing H<sub>2</sub>-TPR and ICP-OES.

#### 7.2 Recommendations for future work

Based on the insights gained in this study, the following recommendations are proposed for future work:

1.  $SO_2$  was used in this study as the main sulfur component in the raw diesel exhaust. However,  $SO_2$  oxidation to  $SO_3$  can happen over an upstream diesel oxidation catalyst. In the presence of H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub> is also likely to form. Furthermore, similar to the model developed for  $SO_2$ , kinetic models can be developed to predict the  $SO_3$  and  $H_2SO_4$  effects on Cu-CHA,

- 2. According to the present study, using DRIFTS and TPD, Z2Cu and ZCuOH were found to have different responses to sulfur poisoning. X-ray absorption spectroscopy (XAS), under similar conditions to those employed for DRIFTS and TPD, can be used to study the oxidation state and local coordination environment of Cu ions in the presence of SO<sub>2</sub>.
- As shown/discussed in chapter 4, ammonium sulfate can actually play a role as a SCR reactant. A detailed kinetic study could be conducted to understand the chemistry and measure the reactivity of such specie.
- 4. According to the results presented in chapter 5, SO<sub>2</sub> adsorbs on ZCuOH via formation of copper bisulfite. However, increasing the temperature in the presence of O<sub>2</sub> can result in oxidation of CuHSO<sub>3</sub> to form CuHSO<sub>4</sub>. Detailed kinetics would help understand the oxidation functionality of Cu species present in Cu-CHA catalysts. The transformation of CuHSO<sub>3</sub> to CuHSO<sub>4</sub> can be added to the developed kinetic model.
- 5. Recent SCR mechanistic studies<sup>38,40</sup> pointed out the importance of Cu cation mobility for catalyzing the low-temperature oxidation half-cycle. Therefore, impact of sulfur on formation and mobility of  $[Cu^{I}(NH_{3})_{2}]^{+}-O_{2}-[Cu^{I}(NH_{3})_{2}]^{+}$  intermediate could be investigated in detail.
- 6. Sulfur interaction with ammonia-solvated Cu sites and  $NH_3 + SO_2$  interaction with Z2Cu and ZCuOH sites can be investigated in detail using DFT calculations.

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Appendix A. Supporting information for chapter 4: SO<sub>2</sub> poisoning of the NH<sub>3</sub>-SCR reaction over Cu-SAPO-34: Impact of ammonium sulfate versus other S-containing species



Figure A.1 Comparison between NO consumption rates during Cu<sub>x</sub>SO<sub>y</sub> and Cu<sub>x</sub>SO<sub>y</sub> \_no S transient experiments.



Figure A.2 Outlet and inlet concentration during NO<sub>x</sub> conversion on Fresh sample experiment.
Experimental conditions: (1) 425 ppm NH<sub>3</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 90 min, (2)
Purging with only N<sub>2</sub> flowing for 120 min, (3) 425 ppm NO and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 120 min, and (4) 425 ppm NH<sub>3</sub>, 425 ppm NO, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 35 min.



**Figure A.3** Outlet and inlet concentration during NO<sub>x</sub> conversion on Cu<sub>x</sub>SO<sub>y</sub> Cu-SAPO-34. Experimental conditions: (1) 425 ppm NH<sub>3</sub>, 55 ppm SO<sub>2</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 120 min, (2)

Purging with only N<sub>2</sub> flowing for 120 min, (3) 425 ppm NO and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 120 min, and (4) 425 ppm NH<sub>3</sub>, 425 ppm NO, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 35 min.



**Figure A.4** Outlet and inlet concentration during  $NO_x$  conversion in presence of 55 ppm  $SO_2$  transient experiment. Experimental conditions: (1) 425 ppm  $NH_3$ , 55 ppm  $SO_2$  and 10%  $O_2$  with a balance of  $N_2$  at

# 210 °C for 120 min, (2) Purging with only $N_2$ flowing for 120 min, (3) 425 ppm NO, 55 ppm SO<sub>2</sub> and 10% O<sub>2</sub> with a balance of $N_2$ for 120 min, and (4) 425 ppm NH<sub>3</sub>, 425 ppm NO, 55pm SO<sub>2</sub>, and 10% O<sub>2</sub> with a balance of $N_2$ at 210 °C for 35 min.



**Figure A.5** Inlet concentration during NO<sub>x</sub> activity measurement of Cu<sub>x</sub>SO<sub>y</sub>\_Cu-SAPO-34 after its desulfation at 730 °C. Experimental conditions: (1): (a) 425 ppm NH<sub>3</sub>, 55 ppm SO<sub>2</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 120 min, (b) Purging with only N<sub>2</sub> flowing for 120 min, (c) 425 ppm NO and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 120 min, and (d) Purging with only N<sub>2</sub> flowing for 30 min, (2) deSO<sub>x</sub>: TPD from 210 to 730 °C at 10 °C/min in N<sub>2</sub>, (3) SCR: 425 ppm NH<sub>3</sub>, 425 ppm NO, and 10%O<sub>2</sub> with a

## balance of N<sub>2</sub> at 210 °C for 35 min, (4) Purging with N<sub>2</sub> for 60 min, followed by a TPD from 210 to 830 °C at 10 °C/min with holding temperature at 830 °C for 10 min.



**Figure A.6** Inlet and outlet concentration during NO<sub>x</sub> activity measurement of Cu<sub>x</sub>SO<sub>y</sub>\_Cu-SAPO-34\_Bkg after TPD at 730 °C (Background experiment). Experimental conditions: (1) 450 ppm NH<sub>3</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 120 min, (2) Purging with only N<sub>2</sub> flowing for 120 min, (3) 450 ppm NO and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 120 min, and (4) Purging with only N<sub>2</sub> flowing for 30 min, (5) TPD from 210 to 730 °C at 10 °C/min in N<sub>2</sub>, (6) 450 ppm NH<sub>3</sub>, 450 ppm NO, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 35 min, (7) Purging with N<sub>2</sub> for 60 min, and (8) TPD from 210 to 830 °C at 10 °C/min with holding temperature at 830 °C for 10 min.



Figure A.7 Inlet concentration during NO<sub>x</sub> activity measurement of (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> \_Cu-SAPO-34 after its desulfation at 630 °C. Experimental conditions: (1) 425 ppm NH<sub>3</sub>, 55 ppm SO<sub>2</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 120 min, (2) Purging with only N<sub>2</sub> flowing for 120 min, (3) 425 ppm NO and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 120 min, and (4) Purging with only N<sub>2</sub> flowing for 30 min, (5) 425 ppm NH<sub>3</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 90 min, (6) Purging in N<sub>2</sub> for 60 min followed by a TPD from 210 to 630 °C at 10 °C/min in N<sub>2</sub> with holding temperature at 630 °C for 15 min, (7) 425 ppm NH<sub>3</sub>, 425 ppm NO, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 35 min, (8) Purging with N<sub>2</sub> for 60 min followed by a TPD from 210 to 830 °C at 10 °C/min with holding temperature at 830 °C for 10 min.



Figure A.8 Inlet and outlet concentration during NO<sub>x</sub> activity measurement of (NH<sub>4</sub>)<sub>x</sub>Cu<sub>y</sub>SO<sub>z</sub> \_Cu-SAPO-34\_no S after TPD at 630 °C (background experiment). Experimental conditions: (1) 450 ppm NH<sub>3</sub>, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 900 min, (2) Purging with only N<sub>2</sub> flowing for 120 min, (3) 450 ppm NO and 10% O<sub>2</sub> with a balance of N<sub>2</sub> for 120 min, and (4) Purging with only N<sub>2</sub> flowing for 30 min, (5) 425 ppm NH<sub>3</sub> and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 90 min, (6) Purging in N<sub>2</sub> for 60 min followed by a TPD from 210 to 630 °C at 10 °C/min in N<sub>2</sub> with holding temperature at 630 °C for 15 min, (7) 425 ppm NH<sub>3</sub>, 425 ppm NO, and 10% O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C for 35 min.

Stage 1	Stage 2		Sta	ige 4	Stage 5	Stage 6			
NOx reduction activity on Fresh sample	Pre-treatment at 550 °C in 10%	a	b	с	d	a	b	Repeating stage 4 for 4 times	TPD phase by heating up the
flowing 500 ppm NO, 500 ppm NH <sub>3</sub> and 10% O <sub>2</sub> in balance with N <sub>2</sub> at 210 °C	$O_2$ balanced with $N_2$ for 2 hr	Co-adsorption of NH <sub>3</sub> and SO <sub>2</sub> : 55 ppm SO <sub>2</sub> (120 min), 500 ppm NH <sub>3</sub> (90 min), 10% O <sub>2</sub> , T=210 °C	Purging in N <sub>2</sub> for 120 min, T=210 °C	Ammonium- Sulfate removal: 500 ppm NO and 10% O <sub>2</sub> for 120 min, T=210 °C	Purging in N <sub>2</sub> for 30 min, T=210 °C	flowing 500 ppm NO, 500 ppm NH <sub>3</sub> and 10% O <sub>2</sub> in balance with N <sub>2</sub> at 210 °C	heating up from 210 to 350 at 10 °C/min in N <sub>2</sub> with holding temperature at 350 °C for 15 min		catalyst from 210 to 830 °C at 10 °C/min and holding temperature at 830 for 10 min.



**Figure A.9** Inlet and outlet concentrations during  $(NH_4)_x Cu_y SO_z$  deSO<sub>x</sub> cycles at 350 °C. Experimental conditions: (1) measuring NO<sub>x</sub> reduction activity on Fresh sample, flowing 500 ppm NO, 500 ppm NH<sub>3</sub> and 10% O<sub>2</sub> in balance with N<sub>2</sub> at 210 °C, (2) pre-treatment at 550 °C in 10% O<sub>2</sub> balanced with N<sub>2</sub> for 2 hr, (3) Cu<sub>x</sub>SO<sub>y</sub> depositions (see table 4.1), (4) Purging in N<sub>2</sub> for 30 min followed by flowing 500 ppm NO, 500 ppm NH<sub>3</sub> and 10% O<sub>2</sub> in balance with N<sub>2</sub> at 210 °C, finally heating up from 210 to 350 at 10 °C/min in N<sub>2</sub> with holding temperature at 350 °C for 15 min, (5) repeating stage 4 for 4 times, (6) TPD phase by heating up the catalyst from 210 to 830 °C at 10 °C/min and holding temperature at 830 for 10 min.

Stage 1	Stage 2	Stage 3			Stage 4	Stage 5	Stage 6	Stage 7	Stage 8	
NOx reduction activity on Fresh sample	Pre-treatment at 550 °C in 10%	a	b	с	d	heating up from 210 to 350 at 10 °C/min	flowing 500 ppm NO, 500	Purging in N <sub>2</sub> followed by flowing	repeating stage 4,5, and 6	TPD phase by heating up the
flowing 500 ppm NO, 500 ppm NH <sub>3</sub> and 10% O <sub>2</sub> in balance with N <sub>2</sub> at 210 °C	O2 balanced with N2 for 2 hr	Co-adsorption of NH <sub>3</sub> and SO <sub>2</sub> : 55 ppm SO <sub>2</sub> (120 min), 500 ppm NH <sub>3</sub> (90 min), 10% O <sub>2</sub> , T=210 °C	Purging in N <sub>2</sub> for 120 min, T=210 °C	Ammonium- Sulfate removal: 500 ppm NO and 10% O <sub>2</sub> for 120 min, T=210 °C	Purging in N <sub>2</sub> for 30 min, T=210 °C	in N <sub>2</sub> with holding temperature at 350 °C for 15 min	ppm NH <sub>3</sub> and 10% O <sub>2</sub> in balance with N <sub>2</sub> at 210 °C	of 500 ppm NO + 10% O <sub>2</sub> with a balance of N <sub>2</sub> at 210 $^{\circ}C$		catalyst from 210 to 830 °C at 10 °C/min and holding temperature at 830 for 10 min.



**Figure A.10** Inlet and outlet concentration during  $Cu_xSO_y$  deSO<sub>x</sub> cycles at 350 °C. Experimental conditions: (1) measuring NO<sub>x</sub> activity on Fresh sample, flowing 500 ppm NO, 500 ppm NH<sub>3</sub> and 10% O<sub>2</sub> in balance with N<sub>2</sub> at 210 °C, (2) pre-treatment at 550 °C in 10% O<sub>2</sub> balanced with N<sub>2</sub> for 2 hr, (3)  $Cu_xSO_y$  depositions (see table 4.1), (4) Purging in N<sub>2</sub> for 30 min followed by heating up from 210 to 350 at 10 °C/min in N<sub>2</sub> with holding temperature at 350 °C for 15 min, (5) flowing 500 ppm NO, 500 ppm NH<sub>3</sub> and 10% O<sub>2</sub> in balance with N<sub>2</sub> at 210 °C, (6) flowing 500 ppm NO + 10 % O<sub>2</sub> with a balance of N<sub>2</sub> at 210 °C, (7) repeating stage 4,5, and 6, (8) TPD phase by heating up the catalyst from 210 to 830 °C at 10 °C/min and holding temperature at 830 °C for 10 min.

### Appendix B. Supporting information for chapter 5: nature of Cu active centers in Cu-SSZ-13 and their responses to SO<sub>2</sub> exposure

#### **B.1** Computational methods

The periodic density functional theory (DFT) calculations were performed using the Vienna ab initio Simulation Package (VASP)<sup>114–117</sup> in the Atomic Simulation Environment (ASE)<sup>118</sup>. The projector augmented wave (PAW) method<sup>119</sup> was used in conjunction with the Bayesian error estimation functional with van der Waals correction (BEEF-vdW)<sup>120</sup> using an energy cutoff of 540 eV for the plane wave expansion; the BEEFvdW functional has been shown to accurately describe and model the van der Waals interactions within zeolites.<sup>121</sup> In all calculations, the Brillouin zone was sampled at the  $\Gamma$ point and Gaussian smearing<sup>122</sup> was used with a Fermi temperature of  $k_bT = 0.1 \text{ eV}$ ; electronic energies are subsequently extrapolated to  $k_bT = 0$  eV. All geometries were optimized until the residual forces on each atom were less than the convergence criterion of 0.02 eV/Å. Transition states were found using the climbing image nudged elastic band (CI-NEB) method<sup>123</sup> and were confirmed to be true saddle points using a vibrational analysis with a Cartesian displacement of 0.01 Å, which showed one imaginary frequency along the reaction pathway. SSZ-13 was modeled in its rhombohedral unit cell.<sup>92</sup> Taking into consideration the reaction conditions (200 °C, 10% O<sub>2</sub>, and 10% H<sub>2</sub>O) and using the H<sub>2</sub>O pressure phase diagrams from Paolucci et al.<sup>39</sup>, the copper-exchanged, high SAR SSZ-13 was modeled with the ZCuOH configuration, while the low SAR zeolite was modeled as Z2Cu(H<sub>2</sub>O). The ZCuOH configuration contained one Si $\rightarrow$ Al substitution and the  $Z_2Cu(H_2O)$  configuration contained two. The location of the copper ions, the hydroxide ion, and the water molecule were selected based on the work of Paolucci et al.<sup>39</sup> The unit cells, their lengths, and their angles were free to relax, resulting in triclinic unit cells that were nearly rhombohedral; the lattice constants a, b, and c and lattice angles  $\alpha$ ,  $\beta$ , and  $\gamma$ were within 2% of each other and are shown in Table B.1. The calculated volumes of the triclinic unit cells for ZCuOH and Z2Cu(H<sub>2</sub>O) were 848.6 Å<sup>3</sup> and 869.9 Å<sup>3</sup>, respectively. The locations of the copper ions are shown in Figure B.1.

A series of sulfur-related reactions were studied on both models. The reaction energies are reported with reference to gas-phase SO<sub>2</sub> and O<sub>2</sub>, centered in a  $20 \times 20 \times 20$ Å<sup>3</sup> box and calculated using the same settings as the ones used in the zeolite calculations, but with  $k_bT = 0.01$  eV and a dipole correction along all three Cartesian directions. Due to the known difficulties in calculating the O<sub>2</sub> gas-phase energy due to its triplet state, its energy value was derived from the gas-phase energies of H<sub>2</sub> and H<sub>2</sub>O through the watersplitting reaction. Unless otherwise noted, all reported energies are electronic energies, with the zero point energy, entropy, and enthalpy corrections omitted.

Parameter	Value for ZCuOH	Value for Z <sub>2</sub> Cu(H <sub>2</sub> O)
а	9.35 Å	9.57 Å
b	9.37 Å	9.46 Å
с	9.39 Å	9.34 Å
α	94.41°	93.86°
β	94.06°	94.86°
γ	94.28°	94.01°

Table B.1 The lattice constants and lattice angles of the ZCuOH and Z2Cu(H<sub>2</sub>O) models.

DFT was used to calculate/compare the thermodynamics and kinetics of the reactions of the ZCuOH and Z2Cu models with SO<sub>2</sub>. Based on DFT results, on both of the ZCuOH and hydrated Z2Cu models, SO<sub>2</sub> fails to directly bind to the copper site and sits within the pore of the zeolite. Thus, the reaction of both models with SO<sub>2</sub> would require

the formation of something more complex. Without the involvement of a SO<sub>2</sub> oxidation reaction (light off temperature is at ~300  $^{\circ}C^{43}$ ), the two possible and stable reactions are:

$$ZCuOH + SO_2 \rightarrow ZCuHSO_3 \tag{B-1}$$

and

$$Z_2Cu(H_2O) + SO_2 \rightarrow ZCuHSO_3 + ZH$$
(B-2)

In both reactions, the primary product is a copper bisulfite complex. The calculated activation and reaction energies are listed in Table B.2. The reaction with  $SO_2$  is more exothermic on the ZCuOH model (Eq. B-1) than on the hydrated Z2Cu model (Eq. B-2) while having a lower activation energy barrier. Under the assumption that SO<sub>2</sub> oxidation does not occur, ZCuOH should then bind more SO<sub>2</sub> and form more bisulfite than the Z2Cu. The greater uptake of  $SO_2$  on the ZCuOH compared to the Z2Cu is corroborated by the experimental evidence discussed in the previous section. Specifically, consumption of the 950 cm<sup>-1</sup> IR spectral band but not the 900 cm<sup>-1</sup> band during the SO<sub>2</sub> adsorption in-situ DRIFTS experiment clearly agrees with the DFT results suggesting possible SO<sub>2</sub> interaction with ZCuOH, but not Z2Cu, resulting in formation of copper bisulfite. Note that in the DFT model, Z2Cu was assumed to have 1 water molecule. This may not resemble the case for a Z2Cu site during in-situ DRIFTS experiments (i.e. figure 5.7), but in the absence of this water molecule, bisulfite formation is not possible on this site, such that molecular adsorption/desorption is the most plausible mechanism for poisoning. The main conclusion here is that SO<sub>2</sub> reacts to a bisulfite on the ZCuOH site, but it does not form the bisulfite species on Z2Cu(H<sub>2</sub>O). The optimized configurations of CuHSO<sub>3</sub> after the SO<sub>2</sub> interaction with ZCuOH and Z2Cu are shown in Figure B.1. SSZ-13 is within the chabazite topological group and contains 4-, 6-, and 8-member rings (MR).



Figure B.1 The locations of the copper ions i.e. ZCuOH and Z2Cu(H<sub>2</sub>O) in Cu-CHA framework.



**Figure B.2** The optimized configurations of CuHSO<sub>3</sub> after the SO<sub>2</sub> reaction with (A) ZCuOH and (B) Z2Cu (below) The locations of the respective CuHSO<sub>3</sub> locations and the extra hydrogen (H) from the reaction with Z2Cu in a standard chabazite cage.

The CuHSO<sub>3</sub> group formed from ZCuOH sits above the 8MR. Meanwhile, the CuHSO<sub>3</sub> group formed from  $Z_2Cu(H_2O)$  sits above the 6MR and the extra hydrogen is coordinated to a framework oxygen in the 4MR. The location of the extra hydrogen atom allows for a weak hydrogen bond to form between it and an oxygen atom coordinated to the sulfur atom. The positions of the CuHSO<sub>3</sub> groups on both models are consistent with the respective locations of the Cu ions in the original ZCuOH and  $Z_2Cu(H_2O)$  models<sup>39</sup>.

As reported in previous studies<sup>43,49</sup>, SO<sub>2</sub> directly oxidized to SO<sub>3</sub> over Cu-CHA at very low conversions under 300 °C. Therefore, if the sulfur-species is oxidized at all, it is

much more likely that it must first form CuHSO<sub>3</sub> before becoming oxidized. On ZCuOH, three partial oxidation reactions are possible:

$$ZCuHSO_3 + \frac{1}{2}O_2 \rightarrow ZCuHSO_4 \tag{B-3}$$

$$ZCuHSO_3 + \frac{1}{2}O_2 \rightarrow ZH + CuSO_4 \tag{B-4}$$

and

$$ZCuHSO_3 + \frac{1}{2}O_2 \rightarrow ZCuOH + SO_3 \tag{B-5}$$

In Eq. B5-3, the copper bisulfite is oxidized to form a copper bisulfate. In Eq. B-4, copper sulfate forms and the hydrogen atom provides the charge compensation. In Eq. B-7, the original ZCuOH site is recovered and sulfur trioxide is released. The reaction energies for these three reactions are given in Table B.3, and indicate that the formation of the bisulfate species is most favorable.

 $\label{eq:constraint} \begin{array}{l} \textbf{Table B.2} \mbox{ The thermodynamics and kinetics of the reactions of the ZCuOH and Z_2Cu models with SO_2 in the absence of SO_2 oxidation reaction.} \end{array}$ 

Eq.	Reaction	Reaction Energy (kJ/mol)	Activation Energy Barrier (kJ/mol)	SO <sub>2</sub> Desorption Barrier (kJ/mol)
B-1	$ZCuOH + SO_2 \rightarrow ZCuHSO_3$	-70	65	135
B-2	$Z_2Cu(H_2O) + SO_2 \rightarrow ZCuHSO_3 + ZH$	-42	92	134

Table B.3	The reaction	energies for	the partia	l oxidation o	f the copper	bisulfite spe	ecies on ZCuOH.

Eq.	Reaction	Reaction Energy (kJ/mol)
B-3	$ZCuHSO_3 + \frac{1}{2}O_2 \rightarrow ZCuHSO_4$	-204
B-4	$ZCuHSO_3 + \frac{1}{2}O_2 \rightarrow ZH + CuSO_4$	-181
B-5	$ZCuHSO_3 + \frac{1}{2}O_2 \rightarrow ZCuOH + SO_3$	-117

#### **B.2.** Computational Details

The settings for the INCAR of a standard geometry optimization calculation are

given below. If unlisted, the VASP setting is assumed to be set at the default value.

```
GGA = BF
LREAL = Auto
SIGMA = 0.1
ENCUT = 540
EDIFFG = -2.00e-02
PREC = Accurate
ALGO = Fast
NSW = 1000
IBRION = 2
ISIF = 2
LUSE VDW = .TRUE.
ZAB VDW = -1.886700
```

Two CONTCAR files are also attached in the Supporting Information.

These are the CONTCAR files used for the clean ZCuOH and Z<sub>2</sub>Cu(H<sub>2</sub>O) zeolite models.

#### **Other Oxidation Reactions**

The oxidation of ZCuHSO<sub>4</sub> was studied on the ZCuOH catalyst. The oxidation reactions and their respective reaction energies are given in Table B.4.

Eq.	Reaction	Reaction Energy (kJ/mol)
B-6	$ZCuHSO_4 + \frac{1}{2}O_2 \rightarrow ZCuOH-SO_4$	+69
B-7	$ZCuHSO_4 + \frac{1}{2}O_2 \rightarrow ZCuO-OSO_3H$	+79
B-8	$ZCuHSO_4 + \frac{1}{2}O_2 \rightarrow ZCuOH + SO_4$	+170

Table B.4 The oxidation reactions of ZCuHSO<sub>4</sub> on ZCuOH.

Equation B-6 describes the formation of a complex with one –OH ligand and one –SO<sub>4</sub> ligand, while Equation B-7 describes a complex that contains a peroxide group that bridges the Cu atom and an HSO<sub>3</sub> group.

Meanwhile, on Z<sub>2</sub>Cu(H<sub>2</sub>O), the oxidation of ZCuHSO<sub>3</sub> was also studied.

These reactions and their respective reaction energies are given in Table B.5. The highly

endothermic reaction energies indicate that these reactions are very unlikely to occur.

Eq.	Reaction	Reaction Energy (kJ/mol)
B-14	$ZCuHSO_3 + ZH + \frac{1}{2}O_2 \rightarrow ZCuHSO_4 + ZH$	+227
B-15	$ZCuHSO_3 + ZH + \frac{1}{2}O_2 \rightarrow Z_2Cu + H_2SO_4$	+295
B-16	$ZCuHSO_3 + ZH + \frac{1}{2}O_2 \rightarrow Z_2Cu + SO_3 + H_2O$	+318

**Table B.5** The oxidation reactions of ZCuHSO<sub>3</sub> on Z<sub>2</sub>Cu(H<sub>2</sub>O).



Figure B.3 (A) SO<sub>2</sub> TPD spectra of Cu-SSZ-13 with SAR = 6 after exposure to SO<sub>2</sub> + NH<sub>3</sub> at 150, 200, 250 and 300 °C. Experimental conditions: 500 ppm NH<sub>3</sub>, 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>. (B) SO<sub>2</sub> TPD spectra of Cu-SSZ-13 with SAR = 6 after exposure to SO<sub>2</sub> + NH<sub>3</sub> at 150 °C in the presence or absence of H<sub>2</sub>O. Experimental conditions: 500 ppm NH<sub>3</sub>, 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O and a balance of N<sub>2</sub>, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>.



**Figure B.4** SO<sub>2</sub> and NH<sub>3</sub> signals during NH<sub>3</sub> + SO<sub>2</sub> TPD experiment over a physical mixture of CuO + H/CHA catalyst. Experimental conditions: 500 ppm NH<sub>3</sub>, 50 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, and a balance of N<sub>2</sub>, purged by N<sub>2</sub>, then TPD with a heating rate of 10 °C/min in N<sub>2</sub>.



**Figure B.5** Ex-situ DRIFTS spectra of T-O-T vibration region taken from Cu-SSZ-13 Si:Al = 6 with various Cu % (pretreated in 10% O<sub>2</sub> at 500 °C for 30 min) at 50 °C in He/10% O<sub>2</sub>, KBr was used as the background spectra.



**Figure B.6** In-situ DRIFTS spectra of T-O-T vibrations of Cu-SSZ-13\_SAR\_6 during experiments without (A and B)/with (C and D) sulfur; (A)  $NH_3 + O_2$  adsorption followed by a purging phase in He and (B) NO


+  $O_2$  adsorption at 200 °C, (C)  $NH_3 + O_2 + SO_2$  adsorption at 200 °C followed by a purging phase in He and (D)  $NO + O_2$  adsorption at 200 °C.

**Figure B.7** Evolution of area of 900 and 950 cm<sup>-1</sup> peaks versus time during last step of in-situ DRIFTS experiment on fresh versus sulfated Cu-SSZ-13\_SAR\_6 (i.e. Fig. B.6).



Figure B.8 Peak deconvolution analysis for  $SO_2 + NH_3$  TPD experiments over Cu-SSZ-13 (A) Si:Al = 6 and (B) 30.



**Figure B.9** NO<sub>x</sub> conversion data for standard SCR over fresh, sulfated, de-sulfated (at 450, 500 and 550 °C) Cu-SSZ-13 (A) Si:Al = 6 and (B) Si:Al = 30. Experimental conditions: 550 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O balanced with N<sub>2</sub>, GHSV of 400,000 h<sup>-1</sup>.



**Figure B.10** SO<sub>2</sub> release during de-sulfation experiments over (A) Cu-SS-13\_SAR\_6 and (B) Cu-SSZ-13\_SAR\_30. Experimental conditions: treatment of sulfated samples by increasing temperature (with a heating rate of 10 °C/min) up to 450, 500 and 550 °C in the presence of 10% O<sub>2</sub> balances with N<sub>2</sub> and holding temperature for 4 h.



Figure B.11 SO<sub>2</sub> release after de-sulfation experiments. Experimental conditions: TPD to 800 °C with a heating rate of 10 °C/min in N<sub>2</sub>.