SO$_2$ poisoning impact on the NH$_3$-SCR reaction over a commercial Cu-SAPO-34 SCR catalyst

Li Zhang[a], Di Wang[a], Yong Liu[a], Krishna Kamasamudram[b], Junhui Li[b], William Epling[a,*]

[a] *University of Houston, Department of Chemical and Biomolecular Engineering, 4800 Calhoun Rd., Houston, TX 77204-4004, United States*
[b] *Cummins Inc, 1900 McKinley Ave, Columbus, IN 47201, United States*

ARTICLE INFO

ABSTRACT

Sulfur poisoning is a durability issue for Cu/SAPO-34 selective catalytic reduction (SCR) catalysts. In this study, the impact of SO$_2$ on the SCR performance, and the sulfur poisoning mechanism itself, was investigated. SO$_2$ inhibited SCR activity at low temperature (<300 °C), while at higher temperatures no evident effect was observed. Temperature programmed desorption data show significant SO$_2$ desorption starting at 300 °C, thus the lack of impact noted at high temperature. Low temperature deactivation is primarily caused by the formation of ammonium sulfate species, with some contribution from competitive adsorption between SO$_2$ and NO$_x$, which is considered a key step in the standard SCR reaction, possibly through the formation of metal sulfate species. However, the surface sulfur species decomposed under high temperature thermal treatment in an O$_2$/N$_2$ mixture, such that activity was reattained.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Selective catalytic reduction (SCR) of NO$_x$ by NH$_3$ is commonly used in diesel engine exhaust after treatment systems. Transition metal exchanged zeolite materials, with the zeolites including ZSM-5, BEA, and SAPO-34 have been studied [1–9]. Recently, chabazite materials have gained significant interest, due to the broad temperature range in which high conversions can be achieved, as well as their improved hydrothermal stability [10–17]. However, Cu/zeolite SCR catalysts are sensitive to sulfur poisoning [3,18,19] and even with ultra-low sulfur fuels, sulfur species can accumulate over time leading to decreased performance.

Diesel oxidation catalysts (DOCs) are typically used in diesel exhaust applications and are located upstream of the SCR catalyst. Therefore, depending on temperature primarily, at least a portion of the SO$_2$ will be oxidized to SO$_3$, and with water ever-present, H$_2$SO$_4$ formation is also likely. Previous work has suggested that sulfur poisoning by SO$_2$ differs from that of SO$_3$. For example, Ramachandran et al. have found that V–ZSM-5 is relatively stable for the SCR reaction in the presence of H$_2$O and SO$_2$, but in the presence of SO$_3$ rapid deactivation was observed. In terms of the mechanism, the authors concluded that ammonium bisulfate formed when both NH$_3$ and SO$_3$ were present [19]. Cheng et al. compared deactivation

of a Cu/BEA catalyst by SO$_2$ and SO$_3$ and found that SO$_3$ was more significant than SO$_2$, and the authors proposed that CuSO$_4$ formed upon SO$_3$ exposure, resulting in deactivation [18]. Their analysis also showed that even after the sulfate formed, the Cu remained in a highly dispersed state, at its initial ion-exchange locations. Jiang et al. [20] studied the poisoning effects of SO$_2$ over a Fe-Mn/TiO$_2$ catalyst, and concluded that SO$_2$ inhibition was due to surface sulfate formed, which in turn affected NO adsorption. Xu et al. [12] investigated a Ce/TiO$_2$ SCR catalyst and proposed that the SO$_2$ could react with the catalyst to form thermally stable Ce(SO$_4$)$_2$ and Ce$_2$(SO$_4$)$_3$, which in turn affected redox cycling between Ce(IV) and Ce(III) and inhibited nitrate formation.

Overall, based on the literature, different sulfur poisoning mechanisms of NH$_3$-SCR catalysts have been proposed. And thus far, the SO$_2$ deactivation mechanism of Cu/SAPO-34 has not been clearly explained. In the present study, the impact of SO$_2$ exposure on the SCR performance of a commercial Cu-SAPO-34 sample was characterized. The standard SCR reaction was chosen to examine the impact, with the assumption that the apparent ever-decreasing exhaust temperatures will put more emphasis on the standard SCR reaction over the fast and NO$_2$-SCR reactions.

2. Experimental methods

The Cu-SAPO-34 catalyst was supplied by Cummins Inc. The Cu-SAPO-34 catalyst sample had a Si/(Al + P) ratio of 0.2. The Cu loading was 0.95 wt.%, as detailed previously [11]. Also, this commercial

Table 1
Gas phase composition of different adsorption phase during TPD experiments.

Experiment	Adsorption phase (balance N_2)
SO_2-TPD	200 ppm SO_2 + 10% O_2
NH_3-TPD	500 ppm NH_3
SO_2 + NH_3-TPD	500 ppm NH_3 + 200 ppm SO_2 + 10% O_2
NO_x-TPD	500 ppm NO + 10% O_2
SO_2 + NO_x-TPD	200 ppm SO_2 + 500 ppm NO + 10% O_2

catalyst contains ceria as an additive, on the order of 2 wt.%. For SCR activity tests, a monolithic-supported sample was used, 1.4″ long and 0.8″ in diameter, which was placed in a quartz tube reactor placed inside a Lindberg temperature-controlled furnace. Before testing, the catalyst was pretreated at 550 °C for 4 h in 10% O_2/N_2. For the reactor experiments, all gases except balance N_2 were supplied by Praxair and were metered by MKS mass flow controllers. Balance N_2 was produced by a N_2 generator manufactured by On-Site. The effluent gas concentrations were measured using a MultiGas 2030 FTIR analyzer. For SCR activity tests, the simulated exhaust gas contained 500 ppm NO, 500 ppm NH_3, and 10% O_2, with a balance of N_2. The total flow rate was 5 L/min, and the corresponding gas hourly space velocity (GHSV) was 28,000 h^{-1}. For SO_2 oxidation, the reaction gas mixture consisted of 200 ppm SO_2, 10% O_2 and a N_2 balance.

To evaluate the performance of the sample with some or all sulfur removed (deSO$_x$), the S-laden samples were exposed to 10% O_2/N_2 and temperature programmed experiments were carried with a heating rate of 5 °C/min at a flow rate of 5 L/min. The samples were heated to different temperatures and left at those for 12 h.

Temperature-programmed desorption (TPD) experiments were carried out after the catalyst was exposed to SO_2, NH_3, SO_2 + NH_3, NO_x, or SO_2 + NO_x, using the same reactor described above. Typically, the sample was pretreated in 5 L/min of 10% O_2/N_2, while heating from room temperature to 600 °C with a heating rate of 25 °C/min, and was held at 600 °C for 0.5 h and then cooled back to room temperature in 10% O_2/N_2. For the TPD experiments, the adsorption phase was run at 150 °C and with a total flow rate of 5 L/min. This was followed by a purge phase in N_2 for 1 h, and then the temperature was increased from 150 to 735 °C at a rate of 10 °C/min. The gas compositions of each adsorption phase for the different experiments are listed in Table 1. Note, for SO_2 adsorption/desorption experiments, a sulfur mole balance was obtained, within 5% error.

Surface species formed during catalyst exposure to SO_2, NO_x and NH_3 were characterized with in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). A Nicolet 6700 FT-IR spectrometer equipped with a Harrick Scientific Praying Mantis DRIFTS cell and a mercury-cadmium-telluride (MCT) detector was used. The powder sample was scraped from the monolith sample and was pressed into a 60 mg pellet of 6.5 mm diameter and placed in the sample cup with a porous screen at the bottom surface, allowing the gas to pass through the catalyst from top to bottom. A feed gas mixture, controlled using MKS mass flow controllers, was supplied at a flow rate of 50 mL/min. The samples were first treated in a flow of 10% O_2/He at 500 °C for 0.5 h and then cooled to room temperature. At the temperatures used for analysis, a background spectrum was recorded in flowing He, and it was subtracted from the sample spectrum obtained at the same temperature. The DRIFTS spectra were collected from 4000 to 650 cm^{-1}, accumulating 100 scans at a 4 cm^{-1} resolution. Nicolet OMNIC software was used to convert the absorbance data into Kubelka-Munk (KM) format. The experimental details for the DRIFTS experiments are described below.

The interactions between SO_2 and the surface of the Cu-SAPO-34 catalyst were studied by collecting DRIFTS spectra during exposure
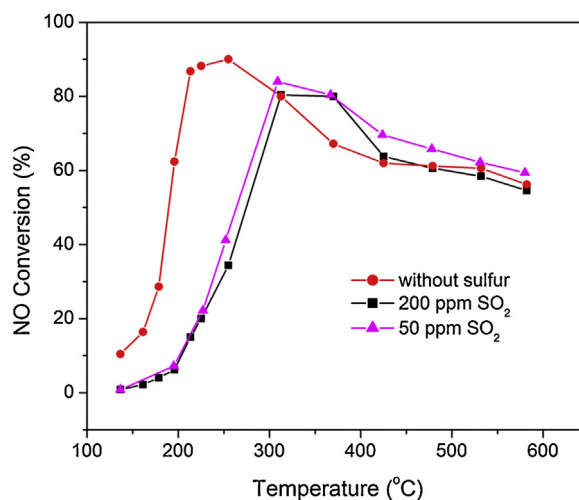

Fig. 1. SCR reaction activity in the absence and presence of SO_2. Reaction conditions: 500 ppm NH_3, 500 ppm NO, 0, 50 or 200 ppm SO_2, 10% O_2 and a balance of N_2, total flow rate 5 L/min, SV = 28,000 h^{-1}.

to 200 ppm SO_2 and 10% O_2 at 150 °C, with He as the carrier gas. In investigating the interactions between NH_3 and SO_2 adsorbed on the surface of catalyst, the sample was exposed to 500 ppm NH_3 and 500 NH_3 + 200 ppm SO_2, in the presence of 10% O_2, at 150 °C.

The interactions between SO_2 and NO_x on the surface of the catalyst were also investigated. First, DRIFTS spectra were obtained during catalyst exposure to 500 ppm NO + 10% O_2 and then exposing the sample to 200 ppm SO_2 at 150 °C. Second, the effects of SO_2 on NO_x adsorption were also investigated by exposing the sample to 200 ppm SO_2 + 10% O_2 at 150 °C for 60 min, followed by purging in He for 30 min, and then exposing the sample to 500 ppm NO for 60 min. In the third experiment, DRIFTS spectra were obtained while the sample was exposed to 500 ppm NO or 500 ppm NO + 200 ppm SO_2, in the presence of 10% O_2, at 150 °C.

3. Results and discussion

3.1. SO_2 exposure impact on NH_3-SCR

The standard SCR reaction activity was evaluated over the monolith-supported Cu-SAPO-34 catalyst from 130 to 580 °C, and the NO conversion results in the absence and presence of SO_2 as a function of temperature are shown in Fig. 1. Under the conditions tested, appreciable NH_3-SCR activity was observed in the absence of SO_2 between 130 and 580 °C. About 90% NO conversion was achieved at 200 °C. With increasing temperature, the conversion decreased because of competitive NH_3 oxidation at high temperatures, as evidenced by 100% NH_3 conversion at these temperatures. In addition, very little N_2O (<5 ppm) was detected during these tests, indicating a high selectivity of NO to N_2 was achieved.

The effect of SO_2 on the SCR activity is also illustrated in Fig. 1. Low temperature catalytic activity (130–300 °C) significantly decreased with the addition of 50 ppm SO_2. For example, the NO conversion dropped from 90% to 15% at 200 °C. On the other hand, at temperatures above 300 °C, there is a slight improvement or no impact observed. When 200 ppm SO_2 was added to the system instead of 50 ppm, the poisoning effects on NO conversion were similar, indicating that different concentrations do not lead to different poisoning mechanisms. These inlet SO_2 concentration values are admittedly higher than those found in vehicle exhaust, however, the higher concentrations were used to achieve steady-state conditions in a timely manner. Furthermore, the lack of difference