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Nature of SO_3 poisoning on Cu/SAPO-34 SCR catalysts

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ABSTRACT

To reveal the nature of SO_3 poisoning of Cu/SAPO-34 selective catalytic reduction (SCR) catalysts, CHA structure, copper species, and NO_x conversion were probed. The Cu/SAPO-34 catalyst was treated with different ratios of SO_3 to SO_x (0, 6, 13, and 20%) at 250 °C. The breakage of Si—O(H)—Al bonds takes place and leads to aluminum sulfate formation upon SO_x sulfation. More isolated Cu^{2+} transform to copper sulfate with an increment of the SO_3/SO_x ratio. Catalysts poisoned with SO_x show lower NO_x conversion at 150–300 °C, the reason for which is a reduced number of isolated Cu^{2+} sites, as their turnover frequencies (TOFs) are identical. The loss of isolated Cu^{2+} and Si—O(H)—Al bonds is responsible for the inferior activity above 300 °C. The presence of SO_3 cannot be ignored because of the irreversible reaction with Cu/SAPO-34 when diesel oxidation catalysts are applied upstream of the SCR.

1. Introduction

The selective catalytic reduction (SCR) of NO_x with NH_3 is currently a promising technology for abatement of NO_x from diesel engine emissions. The Cu/SAPO-34 catalyst, a chabazite (CHA) with 3.8–4.3 Å pore zeolite-based material, is among the best-performing candidates, because it can resist to hydrothermal treatment and has excellent NH_3 SCR turnover rate and high selectivity to N_2 formation [1–5].

However, Cu/SAPO-34 catalyst poisoning by sulfur species has been recognized as a substantial barrier to its wide practical application. To understand sulfur's effect on Cu/SAPO-34, pioneering studies on the subject have used SO_2 as a poisoning agent [6–11]. However, in real-world applications, diesel oxidation catalysts (DOCs) will be applied upstream of the SCR catalysts to remove CO and HCs and to oxidize the NO partially into NO_2 to benefit SCR reaction efficiency. In such a peroxidation process, a portion of SO_2 will be oxidized into SO_3.

As yet the poisoning mechanism for different sulfur oxides (SO_2 and SO_3) on Cu/zeolites has rarely been studied. To date, Cheng [12,13], Luo [14], and Kumar [15] have attempted to focus on this issue. Cheng [12] has investigated the different impacts of SO_2 and SO_3 on Cu/beta SCR catalysts. They found that NO_x activity of catalysts was significantly reduced for the samples sulfated by SO_3 in comparison with those sulfated by SO_2 because of more sulfur deposition and stable sulfate formation on SO_3 sulfated samples. But the poisoning mechanism of SO_3 is not clearly shown in this study, because of the failing correlation between numbers of active sites, catalyst crystallinity, and NO_x conversion. Luo [14] focused on the response of Cu sites in Cu/SSZ-13 to SO_x poisoning. They found that two types of active sites in Cu/SSZ-13 had different responses to SO_x exposure, and $Cu[OH]^+$ species disappeared. However, the structural integrity of CHA was not mentioned. Kumar [15] studied the effect of SO_2 and SO_3 on Cu/SAPO-34 catalysts. They found that SO_3 has a substantial effect on catalytic activity due to some temperature-activated chemical reactions with catalyst material taking place at 400 °C. However, a few important questions, such as what reactions occur and how these reactions affect the activity of Cu/SAPO-34, were not involved. In a word, the variation of copper species, CHA structure, sulfate species, and extra-framework species with the NO_x reaction rate is a foundation for obtaining the poisoning mechanism of different sulfur oxides on Cu/SAPO-34.

In this work, we report the effect of SO_3 poisoning on Cu/SAPO-34 catalysts as a function of the SO_3/SO_x ratio (the ratio of SO_3 to SO_x varies from 0 to 20% under the same SO_x flux). Through characterization with X-ray diffraction (XRD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and nuclear magnetic resonance (NMR), the deterioration mechanism of the CHA

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structure in Cu/SAPO-34 catalysts was revealed. The poisoning mechanism of the specific catalytic sites was determined by thermogravimetric analysis (TGA), temperature-programmed reduction (TPR), electron paramagnetic resonance (EPR), and kinetics. This study shows different poisoning mechanisms for SO_2 and SO_3 on Cu/SAPO-34 and provides information to improve the sulfur resistance.

2. Experimental

2.1. Catalyst preparation

Cu/SAPO-34 catalysts were synthesized using the one-pot method [16] and a H/SAPO-34 molecular sieve was synthesized by the hydrothermal method. The synthesis gel consisted of 1 Al_2O_3, 0.9 P_2O_5, 0.7 SiO_2, 0.2 or 0 CuO, 2 morpholine (MOR), 0.2 or 0 tetraethylenepentamine (TEPA), and 5.69 H_2O (molar basis). The material sources for Si, P, Al, and Cu are silica sol (40 wt.% SiO_2, Qingdao Jiyida Silica Reagent Factory, China), orthophosphoric acid (85 wt.% H_3PO_4, Tianjin Kemiou Chemical Reagent Co., Ltd., China), pseudoboehmite (68 wt.% Al_2O_3, Shangdong Aluminium Industry Co., Ltd., China), and copper (II) sulfate pentahydrate (purity above 99 wt.%, Tianjin Kemiou Chemical Reagent Co., Ltd., China), respectively. MOR (purity 99 wt.%, Tianjin Kemiou Chemical Reagent Co., Ltd., China) was used as a templating agent and TEPA (purity 90 wt.%, Tianjin Kemiou Chemical Reagent Co., Ltd., China) as a complexing agent for copper (II). The resulting gel was sealed in a 200 ml Teflon-lined stainless steel pressure vessel and heated in a static oven at 200 °C under autogenic pressure for 48 h. After the crystallization process, the sediment was separated from the mother liquid via centrifugation, washed with distilled water, and then filtered. Finally, the powder was dried at 120 °C in an oven for 12 h and calcined at 650 °C in an oven with air for 5 h.

2.2. Sulfation treatment

The resulting powders (catalysts and supports) were hydrothermally aged with 10% H_2O in air at 750 °C for 4 h and are named fresh Cu/SAPO-34 (F-Cu) and fresh H/SAPO-34 (F-SAPO).

The fresh catalysts were sulfated with SO_x-containing streams in the presence or absence of SO_3 under the same sulfur oxide flux (50 ppm). For SO_3-free (0% SO_3/SO_x) sulfation, the catalysts were sulfated at 250 °C with a feed containing 50 ppm SO_2 and 5% H_2O in air (total flow 1 L/min). For sulfation with SO_x, the sulfation was conducted at 250 °C with a feed containing 50 ppm SO_x (the ratio of SO_3 to SO_x was 6, 13, or 20%), 5% H_2O in air (total flow 1 L/min). In both cases, the sulfation lasted 16 h with a total sulfur throughput of 68.6 mg S/g catalyst. In order to get stable SO_3 input for 16 h, a 2% V_2O_5/10% WO_3/TiO_2 catalyst rather than a noble metal catalyst was used. The ratio of SO_3 to SO_x (6–20%) was controlled by adjusting the temperature of the V_2O_5/10% WO_3/TiO_2 catalyst from 550 to 600 °C; detailed information about the sulfation equipment is shown in Fig. S1 in the Supporting Information. A description of sulfation conditions and their corresponding catalyst nomenclatures is shown in Table 1. The sulfated catalysts are denoted as S-*x*-Cu, where S stands for sulfation and *x* for the ratio of SO_3 to SO_x. For comparison, the F-SAPOs were also treated with the same feeds at 250 °C, denoted as S-*x*-SAPO. In order to monitor the change of CHA structure and confirm sulfate species formation during SO_x sulfation, H/SAPO-34 was further treated with a feed containing 20% SO_3/SO_x, 5% H_2O in air at 250 °C for 48 h (sulfur oxide flux was 50 ppm). The corresponding catalyst nomenclatures are also shown in Table 1.

Table 1
Sulfation conditions and BET surface areas.

Catalysts	Poisoned conditions	Surface area (m^2/g)	$\triangle S$ (%)[a]
F-Cu	–	477	–
F-SAPO		485	–
S-0-Cu	50 ppm SO_2 at 250 °C for 16 h	430	0
S-0-SAPO		483	0
S-6-Cu	50 ppm SO_x (6% SO_3) at 250 °C	420	2
S-6-SAPO	for 16 h	471	3
S-13-Cu	50 ppm SO_x (13% SO_3) at 250 °C	378	12
S-13-SAPO	for 16 h	418	13
S-20-Cu	50 ppm SO_x (20% SO_3) at 250 °C	308	28
S-20-SAPO	for 16 h	330	32
S-20-SAPO_48	50 ppm SO_x (20% SO_3) at 250 °C for 48 h	223	54

Notes: Base feed: 5% H_2O in air. Total flow rate: 1000 ml/min.
[a] $\Delta S\ (\%) = \frac{S_{SO_2\ poisoning} - S_{SO_X\ poisoning}}{S_{SO_2\ poisoning}} \times 100\%$.

2.3. Catalyst characterization

The XRD spectra was collected using an X'Pert Pro diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5418 Å), operating at 40 kV and 40 mA in the range of 5–50° with a step size of 0.01°. The relative crystallinity of samples was calculated as the normalized total areas of five peaks (201, 003, 211, 104 and 220) relative to that for a fresh sample [16,17].

BET surface areas were measured by N_2 adsorption–desorption at −196 °C using a Beijing F-Sorb 2400 automatic physisorption analyzer after degassing samples at 150 °C for at least 5 h under pressure 0.133 Pa.

Ex situ DRIFTS (Nicolet 6700 spectrometer) were used to monitor the intensity variation of Si—O(H)—Al bonds and isolated Cu^{2+} ions upon sulfation. Before each measurement, sulfated samples were dried at 250 °C for 30 min. The spectra were recorded at 200 °C, and the KBr (purity 99.9 wt.%, Guangfu Fine Chemical Research Institute, China) spectrum under the same conditions was used as the background. The DRIFTS were recorded in the range from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1}.

NH_3 TPD experiments were performed to reveal the acidity of Cu/SAPO-34 catalysts or H/SAPO-34s. The catalysts/supports were dehydrated at 250 °C for 30 min under 5% O_2/N_2 and then cooled to 100 °C under N_2 (purity 99.999%, Tianjin Best Gas Co., Ltd., China). The samples were purged by 500 ppm NH_3/N_2 (Tianjin Best Gas Co., Ltd., China) at 100 °C until the NH_3 concentration was stable. Then the samples were purged with N_2 at 100 °C to remove any weakly absorbed NH_3. When the NH_3 concentration was lower than 10 ppm, the samples were heated from 100 to 550 °C at a ramping rate of 10 °C/min.

To identify the deactivating agents formed on the catalyst surface and their amounts [18,19], the sulfated catalysts (15 mg) was examined with a Mettler Toledo TGA. TGA patterns were obtained within the temperature range from 40 to 850 °C at a ramping rate of 10 °C/min in a gas flow containing N_2 (47.5 ml/min, purity 99.999%, Tianjin Best Gas Co., Ltd., China) and O_2 (2.5 ml/min, purity 99.9%, Baoding North Special Gases Co., Ltd., China).

SO_2 TPD measurements were used to monitor the SO_2 desorption. Prior to the TPD experiment, samples was heated to 250 °C and kept at this temperature for 30 min under a flow of 5% O_2 in N_2 (Baoding North Special Gases Co., Ltd., China). Then the samples were measured in a flow of N_2 (500 ml/min^{-1}, purity 99.999%, Tianjin Best Gas Co., Ltd., China) from 100 to 600 °C at a ramp rate of 10 °C/min. FTIR (MKS 2030) was used to measure the concentrations of SO_2, SO_3, and H_2SO_4.