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Deactivation of Cu-SSZ-13 by SO_2 exposure under SCR conditions

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A deactivation study of Cu-SSZ-13 has been conducted using SO_2 exposure under SCR conditions and examining its effect on different reactions involving NH_3-SCR. Several reactions, including NH_3 storage/TPD, NO/NH_3 oxidation, standard SCR, fast SCR and SCR with 75% NO_2, as well as NH_3–NO_2 storage/TPD, were investigated at a temperature range of 100–400 °C after exposing the catalyst to 30 ppm SO_2 under SCR conditions at 300 °C for 90 min. The catalyst was characterized using XRD, BET, ICP-SFMS and H_2-TPR. The BET surface area and pore volume decreased after the sulfur treatment presumably due to blocking by sulfur and/or ammonium–sulfur species. It was found that sulfur was not uniformly deposited along the monolith channel. The deposition occurred from the inlet towards the outlet, as evident from ICP-SFMS measurements. Part of the sulfur was removed after an SCR experiment up to 400 °C. However, this removal was observed only in the inlet half of the sample and not in the outlet. Ammonia TPD experiments revealed that the sulfur poisoning resulted in additional sites that were capable of adsorbing ammonia, resulting in increased ammonia storage. Moreover, standard SCR was significantly deactivated by SO_2 poisoning under SCR conditions. Due to the site-blocking effect of the ammonium–sulfur species, fewer copper sites are likely available for the redox SCR cycle. Furthermore, the effect of sulfur poisoning on NH_3 oxidation and NO_2-SCR as well as N_2O production in various SCR reactions were observed. Finally, it was found that the conditions for the sulfur poisoning were critical in which SO_2 deactivation under SCR conditions (NH_3 + NO + O_2 + H_2O) was more severe compared to SO_2 poisoning in O_2 + H_2O alone.

1. Introduction

Diesel engines are more efficient than their gasoline counterpart and are, therefore, crucial for the transportation sector. However, excess air is used in the combustion of diesel, which unfortunately results in a difficulty in reducing NO_x. Since NO_x can cause acid rain and air pollution, it is therefore critical to remove NO_x from the exhausts. In one of the most practiced technologies, the so-called NH_3-SCR, NO_x is reduced to N_2 and H_2O using aqueous urea as a reducing agent.[1,2] Among those investigated, metal-exchanged zeolite-based catalysts have shown high activity under a broad range of temperatures.[3–5] Unfortunately, considering that in a typical NH_3-SCR after-treatment system the diesel particulate filter (DPF) placed upstream needs high temperatures for regeneration, hydrothermal susceptibility is a major drawback of several catalysts.[6,7]

Lately, there has been a great deal of attention paid to copper-exchanged molecular sieves with chabazite (CHA)

structure, such as Cu-SSZ3-13 and Cu-SAPO-34, as they showed excellent hydrothermal stability.[8–12] The reason for the high hydrothermal stability of the Cu-CHA structure is that its narrow pore structure makes it difficult for aluminium moieties, which are products of dealumination, to leave.[9] Further, it was found that Cu-SAPO-34 is more resistant than Cu-SSZ-13 towards harsh aging treatments.[9,13,14] After a long-term aging at 800 °C, the number of active Cu^{2+} sites in Cu-SSZ-13 was significantly decreased and the CHA structure collapsed, whereas the structure remained intact for Cu-SAPO-34.[14] As the Cu/Al ratio became higher due to the fact that the Cu^{2+} in a CHA cage might form CuO_x species, thermal deactivation of Cu-SSZ-13 became more severe. These CuO_x species might grow and then destroy the cage and channel of the zeolite.[15]

It is believed that isolated Cu^{2+} ions in the six-membered rings of the Cu-CHA are the active sites for the reduction of NO.[16,17] As suggested by Kwak et al.,[18] the Cu ion may have different positions in the zeolite framework, depending on the ion exchange level. In the case of Cu-SSZ-13 which has a low copper content, the Cu ions primarily reside in the six-membered rings, whereas for high exchange levels, copper is associated with the large cages of CHA structure. In a recent study, we developed a multi-site kinetic model using these

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two different copper species and the model could successfully describe the experiments across a wide temperature range.[19] Further, Bates et al.[20] stated that the Cu_xO_y species, which is not active for standard SCR, might form when the ratios of Cu/Al_{tot} are above 2.

While hydrothermal stability has been extensively discussed, the stability towards sulfur is another issue that should also be taken into account. Even though the sulfur content in fuels is legislated to be less than 10 ppm in most developed countries, some developing countries still use high sulfur content fuel. In addition, even when low sulfur content fuel is used, the accumulation of sulfur over years in use of the SCR catalyst might affect its performance. It is well known that copper-zeolites are more prone to sulfur poisoning than are Fe-zeolites.[21–23] Zhang et al.[24] investigated SO_2 poisoning over commercial Cu-SAPO-34 and suggested that the inhibiting effect mainly occurs at low temperatures because of the formation of ammonium sulfate, which might poison the active sites and block the zeolite pores. Another possible factor for the deactivation is the metal sulfate species formed as the result of SO_2 adsorption on the catalyst sites, which competes with NO_x adsorption.[24] In our recent study,[25] a substantial impact on the activity of standard SCR was found upon SO_2 treatment using Cu-SAPO-34, but the deactivation was less for the fast and NO_2-SCR, suggesting a different mechanism for SCR in the presence of NO_2. We also observed pore blocking by sulfur as indicated by decreasing the zeolite pore volume. In addition, fewer available copper sites after sulfur treatment were observed during our H_2-TPR experiment. The impact of sulfur poisoning on a small-pore Cu-zeolite at different temperatures was studied by Kumar et al.[26] showing that at 200 °C, the SO_2 and SO_3 poisoning showed similar deactivation effects on the catalyst functions. In contrast, poisoning at 400 °C resulted in a more severe deactivation when using SO_3 compared to SO_2 and in addition, it proved more difficult to regenerate the catalyst after SO_3 poisoning.

Despite the presence of the sulfur poisoning studies described above, the impact of SO_2 poisoning over Cu-SSZ-13 in an SCR environment has, to our knowledge, not been investigated. It is important to study this impact since the poisoning and SCR reactions occur simultaneously in a real application. The objective of the present study is to examine the effect of SO_2 treatment in the presence of NH_3, NO, O_2 and H_2O towards SCR reactions with different NO_2/NO_x ratios and adsorption–desorption behavior, as well as oxidation reactions. Further, the characterization of the catalyst was performed using ICP-SFMS, BET method, and H_2-TPR.

2. Experimental

2.1 Catalyst synthesis

Na-SSZ-13 was synthesized based on the method described by McEwen et al.[27] and then underwent an ion-exchange process which consisted of two steps. First, a solution of 0.25 M NH_4NO_3 (99%, Sigma Aldrich) was used followed by a

solution of 0.025 M $Cu(NO_3)_2$ (98%, Alfa Aesar GmbH) applied three times. Both the ammonium and copper exchange were conducted at 80 °C for 75 min. A detailed description of the Cu-SSZ-13 synthesis procedure is found in Olsson et al.[19] The resulting Cu-SSZ-13 powder was then washcoated onto cordierite monoliths possessing a cell density of 400 cpsi and a size of 21 mm in diameter and 20 mm in length using the same procedure as in our previous publication.[25] A thin layer of alumina was applied by immersing the monolith several times into a solution of 5 wt% of solid-phase boehmite (Disperal P2, Sasol, Gmbh) and 95 wt% of liquid phase (ratio of water to ethanol 1:1) followed by drying for 2 min in air at 90 °C. Thereafter, calcination was performed at 500 °C for 2 h. This procedure was followed by catalyst washcoating using a slurry of 20 wt% of solid phase (catalyst/boehmite ratio of 5:95) and 80 wt% of liquid phase (equal amount of water and ethanol). After the monolith had been dried in hot air at 90 °C for 2 min, the dipping procedure was repeated several times until the desired amount of catalyst washcoat had been reached. The monolith was then calcined in air at 600 °C for 2 h. The monolith catalyst had a 67 mg alumina layer and a 780 mg zeolite washcoat (which includes 5% binder). This monolith was used for flow reactor experiments and for fresh conditions and sulfur poisoning under SCR conditions. In addition, a second monolith was prepared and used for SO_2 poisoning in the presence of water and oxygen alone. For this sample, the alumina layer was 77 mg and the Cu-SSZ-13 layer was 778 mg. Further, three additional monoliths were synthesized from the same batch of Cu-SSZ-13 powder and were used for different characterization experiments for fresh and sulfur poisoned samples.

2.2 Catalyst characterization

2.2.1 BET surface area and ICP-SFMS. The BET surface area and pore volume of the Cu-SZZ-13 were measured using N_2 physisorption at −195 °C by a Micromeritics ASAP 2010 instrument after the powder had been degassed at 240 °C for 3 h under vacuum. An elemental analysis was performed using an inductively coupled plasma sector field mass spectrometer (ICP-SFMS) by ALS Scandinavia AB. In order to examine the zeolite structure, a Bruker AXS D8 advance diffractometer operating at 40 kV and 40 mA with nickel-filtered Cu Kα radiation (λ = 1.5418 Å) was used to obtain an X-ray diffractogram in the range of 5° < 2θ < 40° with a step size of 0.029°s^{-1}.

In order to characterize the catalyst after sulfur poisoning, we used a separate monolith. First, the catalyst was degreened with 400 ppm NH_3, 400 ppm NO, 8% O_2 and 5% H_2O at 650 °C for 4 h using a flow reactor system as will be described in section 2.3. Following this procedure, standard SCR was performed with equal amounts of NH_3 and NO (400 ppm) exposed to the catalyst, in the presence of 8% O_2 and 5% H_2O from 100 up to 600 °C. The catalyst was then poisoned with 30 ppm SO_2 under SCR conditions (400 ppm NH_3, 400 ppm NO, 8% O_2, 5% H_2O) at 300 °C for 90 min. Thereafter, the monolith was cut into two parts along the

axial direction; one part was left as it was, whereas the other part underwent a standard SCR reaction (400 ppm NH_3, 400 ppm NO, 8% O_2, 5% H_2O) from 100 to 400 °C in several temperature steps. Each of these pieces was then cut perpendicularly to the flow direction of the gas and these samples were then denoted as poisoned inlet, poisoned outlet, poisoned + SCR 400 inlet and poisoned + SCR 400 outlet. Inlet and outlet refer to the position of the monolith in the flow reactor according to the gas flow. The procedure for the poisoned monolith used for characterization is schematically described in Fig. 1. It should be noted that in addition to this monolith, another fresh monolith was used for characterization for comparison purposes. The small pieces of the monoliths were then crushed and used for measuring its BET surface area and pore volume using a similar procedure as mentioned before. An ICP-SFMS analysis was also performed to determine the sulfur content of the samples.

2.2.2 H_2-TPR experiment. In order to examine the redox behavior of the fresh and sulfur poisoned catalyst, hydrogen temperature programmed desorption (H_2-TPR) experiments were conducted over scraped washcoat from monolith catalysts. A separate monolith was used for the H_2-TPR experiments employing the exact same poisoning procedure as for the monolith used for BET and ICP-SFMS (see section 2.2.1). The same notation as described in section 2.2.1 was used. The H_2-TPR experiments were conducted using the calorimeter set-up, which has been described in an earlier study.[25] The inlet gas flow was controlled using several Bronkhorst mass flow controllers (MFCs) and a Hiden HPR-20 QUI mass spectrometer (MS) was used for analyzing the outlet gas concentration. Two quartz tubes were mounted into the DSC during the measurement; one tube was used to place the powder

sample on a sintered plate and another tube was used as a reference. The total flow of 20 ml min^{-1} was used for the experiments and argon was the inert balance. 30 mg of scraped off monolith powder was used and prior to the experiments, the catalyst was exposed to 8% O_2 for 20 min at 400 °C to clean the surface and remove the moisture content. The temperature was then reduced to 50 °C. Thereafter, 3000 ppm H_2 was introduced for 50 min at 50 °C, followed by increasing the temperature to 800 °C with a ramp speed of 10 °C min^{-1} while exposing the sample to the H_2 flow. The temperature was then maintained at 800 °C for 40 minutes in the presence of H_2. For the fresh sample, degreening in 400 ppm NH_3, 400 ppm NO and 8% O_2 at 650 °C for 4 h was performed before the experiment.

2.3 Flow reactor measurement

The activity of the catalyst was measured using a flow reactor set-up as described in.[25] Briefly, it consisted of a gas mixing system with several Bronkhorst mass flow controllers, a CEM (controlled evaporation and mixing) system for water flow and a horizontal quartz tube reactor into which the monolith catalyst was placed. A thermocouple was used to measure the gas temperature and another was placed inside a channel measuring the temperature of the catalyst. The outlet gas was analyzed with a FTIR spectrometer (MKS Multigas 2030) for monitoring concentrations of NH_3, NO, NO_2 and N_2O. The total flow used for all experiments was 3500 ml min^{-1}, resulting in a space velocity of 30 300 h^{-1}, with argon used as inert balance.

The catalyst was first degreened in 400 ppm NH_3, 400 ppm NO, 8% O_2 and 5% H_2O at 650 °C for 4 h in order to obtain stable activity during the measurement. Prior to all experiments with the fresh catalyst, the sample was exposed to 8% O_2 and 5% H_2O for 20 min at 600 °C. The NH_3 storage experiments were conducted at two adsorption temperatures of 50 and 150 °C using 400 ppm NH_3 and 5% H_2O for 90 minutes, followed by 75 min with 5% H_2O in argon, and the temperature was then increased to 600 °C with a ramp speed of 10 °C min^{-1}. The standard SCR reaction was studied by exposing the sample to 400 ppm NH_3, 400 ppm NO, 8% O_2 and 5% water and increasing the temperature stepwise from 100 to 600 °C, with a ramp speed of 20 °C min^{-1} between each step. For fast and NO_2-SCR, NO_2 was also fed during reactions in which the NO_2/NO_x ratios were 50% and 75%, respectively. This procedure resulted in a feed of 400 ppm NH_3, 200 ppm NO, 200 ppm NO_2, 8% O_2 and 5% H_2O for fast SCR and 400 ppm NH_3, 100 ppm NO, 300 ppm NO_2, 8% O_2 and 5% H_2O for NO_2-SCR. These reactions were investigated in temperature steps from 200 to 600 °C. The reason for starting at a higher temperature, 200 compared to 150 °C, was to decrease the ammonium nitrate formation in the presence of NO_2. In another experiment (data not shown here) fast SCR was studied from 150 °C, and we observed a substantial deactivation at low temperature due to this effect. Ammonium nitrate formation at low temperature in the presence of NO_2
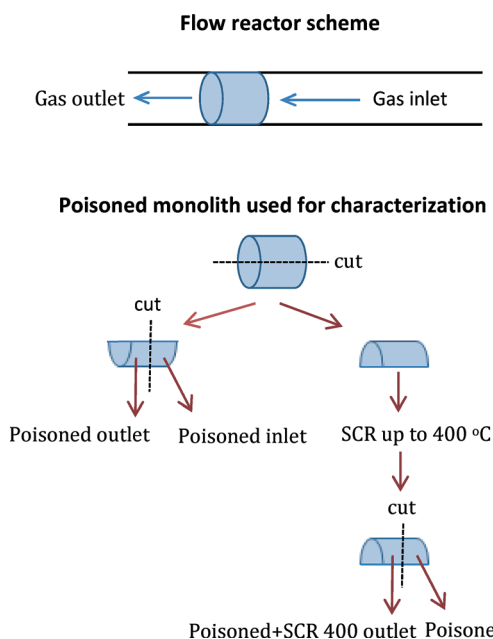

Fig. 1 Schematic description of the experimental procedure for the poisoned monolith used for characterization.

and NH_3 is in line with several studies in the literature, such as work by Devadas *et al.*,[28] Tronconi *et al.*[29] and Chigada *et al.*[30] The oxidation reactions of NO/NH_3 were investigated using 400 ppm NH_3/NO, 8% O_2 and 5% H_2O and increasing the temperature in steps from 150 to 600 °C. Finally, the ammonium nitrate formation and decomposition were investigated by exposing the catalyst to 400 ppm NH_3, 400 ppm NO_2 and 5% H_2O at 150 °C for 60 min. Thereafter, the catalyst was flushed with 5% H_2O in Ar for 30 minutes before the temperature was ramped to 600 °C, using a speed of 10 °C min^{-1}.

After the fresh activity measurement was finished, the sample underwent sulfur poisoning by exposing it to 30 ppm SO_2 in the presence of 400 ppm NH_3, 400 ppm NO, 8% O_2 and 5% H_2O at 300 °C for 90 min. The sulfur poisoned catalyst activity was then evaluated with eight repeated standard SCR experiments using 400 ppm NH_3, 400 ppm NO, 8% O_2 and 5% H_2O, while increasing the temperature in steps from 100 up to 400 °C. The reason for repeating the same experiments several times was to examine the gradual removal of the sulfur species and to reach stable activity. The fast and slow NO_2-SCR, NO/NH_3 oxidation, NH_3 storage/TPD experiments and NH_3–NO_2 storage/TPD experiments were thereafter conducted using the same procedure as described above for the fresh catalyst. However, the maximum temperature used for the sulfur poisoned sample was only 400 °C, compared to 600 °C for the fresh catalyst. The reason for the lower temperature was that if 600 °C would instead have been used, it would have resulted in the removal of much more of the sulfur species and it would have been difficult to study the poisoning in the following experiments. The catalyst was pretreated with 8% O_2 and 5% H_2O at 400 °C before each experiment with the sulfur-treated catalyst, except for the first experiment after SCR poisoning, where no pre-treatment was performed.

Finally, another sulfur poisoning method was examined using the second monolith. The catalyst was degreened using the same procedure as used for the first monolith. Thereafter, various SCR experiments were conducted (results not shown here) followed by the poisoning. For the poisoning, the catalyst was exposed to 30 ppm SO_2 in the presence of 8% O_2 and 5% H_2O at 300 °C for 90 min. Following this step, the activity was measured by exposing the catalyst to 400 ppm NH_3, 400 ppm NO, 8% O_2, and 5% H_2O in Ar and increasing the temperature in steps from 100 to 600 °C.

3. Results and discussion

3.1 Catalyst characterization

The result of our elemental analysis using ICP-SFMS on the prepared Cu-SSZ-13 before washcoating showed that the copper content was 3.1 wt% and the Si/Al ratio was 3.56. The Cu to Al molar ratio was 0.16, which is why the zeolite can be considered under-exchanged. In addition, a small amount of Fe (0.06 wt%) was also detected. The textural characteristics of the sample were examined using N_2-physisorption analysis

which resulted in a BET surface area of 438 m^2 g^{-1} and a pore volume of 0.22 cm^3 g^{-1}. The synthesized SSZ-13 zeolite structure was identified using XRD and the diffraction data illustrated in Fig. 2 and shows good agreement with the scientific literature.[27,31,32] A similar pattern between the Na-SSZ-13, the ammonium formed zeolite, as well as the Cu-SSZ-13 was observed which confirmed that despite the acid condition and relatively high temperature used during the ion exchange, the crystalline structure of the sample was well preserved.

Crushed monoliths of the fresh and sulfur poisoned samples were characterized with the help of nitrogen adsorption analysis (BET method). The poisoned samples refer to those that underwent sulfur poisoning (30 ppm SO_2 under SCR conditions at 300 °C for 90 min), whereas poisoned + SCR 400 samples are those that had been treated with SO_2 under SCR conditions followed by an SCR reaction of up to 400 °C. Inlet and outlet determine the position of the catalyst in the reactor and refer to the direction of the gas flow. As depicted in Table 1, the sulfur treatment decreased both the surface area and the pore volume of the catalyst, which is likely due to the blocking effect of the sulfur species. This finding is in accordance with our previous investigation,[25] which showed that both surface area and pore volume of Cu-SAPO-34 were decreased by sulfur poisoning. In addition, Shen *et al.*[33] found a small decrease in surface area of Cu-SAPO-34 after sulfur exposure, where it decreased from 571 to 538 m^2 g^{-1} for fresh and sulfur poisoned sample (35.6 μmol sulfur per gram Cu-SAPO-34), respectively. Further, our crushed monolith samples were analyzed with ICP-SFMS to measure the sulfur content and the results are presented in Table 1. Sulfur was deposited non-uniformly in the catalyst and the deposition of sulfur occurred from the inlet moving towards the outlet, yielding a higher sulfur content in the inlet part of the monolith. A similar result was obtained by Cheng *et al.*[34] who observed a distribution of sulfur as a function of the
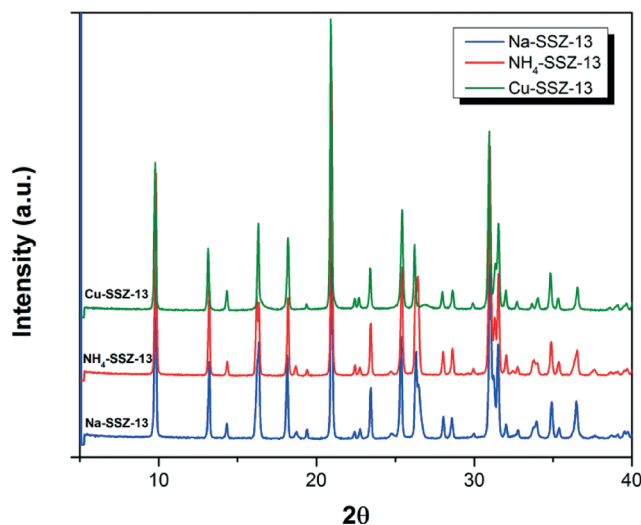

Fig. 2 X-ray diffractograms of the synthesized Na-SSZ-13, NH_4-SSZ-13 and Cu-SSZ-13.

Table 1 BET surface area, pore volume and sulfur content of the samples

Cu–SSZ-13 monolith sample	$S_{BET}{}^a$ (m² g⁻¹)	$V_p{}^a$ (cm³ g⁻¹)	Sulfur^a (wt%)
Fresh	387	0.24	—
Sulfur poisoned inlet	316	0.20	1.28
Sulfur poisoned outlet	327	0.20	0.63
Sulfur poisoned + SCR 400 inlet	336	0.21	1.03
Sulfur poisoned + SCR 400 outlet	337	0.22	0.70

^{a} Based on estimated amount of washcoat.

Fig. 3 H_2-TPR over fresh, sulfur poisoned and sulfur poisoned + SCR 400 Cu-SSZ-13 samples.

distance from the inlet of the catalyst after being poisoned by SO_2. Moreover, there is a small difference in sulfur content in the outlet part of the monolith before and after the SCR experiment, but this difference is only minor and is probably within the measuring error of analyzing crushed monoliths. However, the amount of sulfur left on the inlet parts of the catalyst significantly decreased after the SCR reaction up to 400 °C. It is possible that SCR conditions are beneficial for the removal of the sulfur and at high temperature a full conversion of ammonia and NO occurs; thus, only the front part of the monolith is exposed to SCR conditions. Spatially resolved MS experiments using Cu-BEA revealed that only 25% of the catalyst length is used at 400 °C to obtain full conversion.[35] Thus, a possible explanation for the observed sulfur removal in the front of the catalyst was the presence of SCR conditions; meanwhile no removal was observed in the outlet part which could be due to the lack of SCR conditions in the outlet part.

3.2 H_2-TPR

An H_2-TPR experiment was performed to study the redox behavior of the fresh and sulfur-treated catalyst. The H_2 consumption over the fresh, sulfur poisoned, and sulfur poisoned + SCR 400 scraped washcoat samples, during the temperature ramp from 50 to 800 °C, is illustrated in Fig. 3. A major peak from the fresh sample appeared at around 413 °C and the integration of this peak up to 650 °C results in a H_2/Cu ratio of 0.44, indicating that the reduction of the Cu^{2+} ions was incomplete and had probably undergone one-electron reduction. This hypothesis was supported by a calculation of the molar ratio of H_2 consumption of Cu to amounts up to 800 °C in the sample and was only 0.49, denoting that a higher temperature than 800 °C was needed to fully reduce Cu^{2+} to C^0. A previous investigation by Kwak et al.[18] has shown that H_2-TPR over Cu-SSZ-13 might show a different number of peaks at varying temperatures depending on the degree of ion exchange (% IE) and the environment in which the experiment was performed (presence/absence of H_2O). A prominent peak at 340 °C was for instance observed from a sample of 20% IE (corresponding to a Cu/Al ratio of 0.1) which was assigned as copper in the six-membered rings. At a higher copper loading of 60% IE, another peak at lower temperature appeared to indicate that Cu-SSZ-13 might have
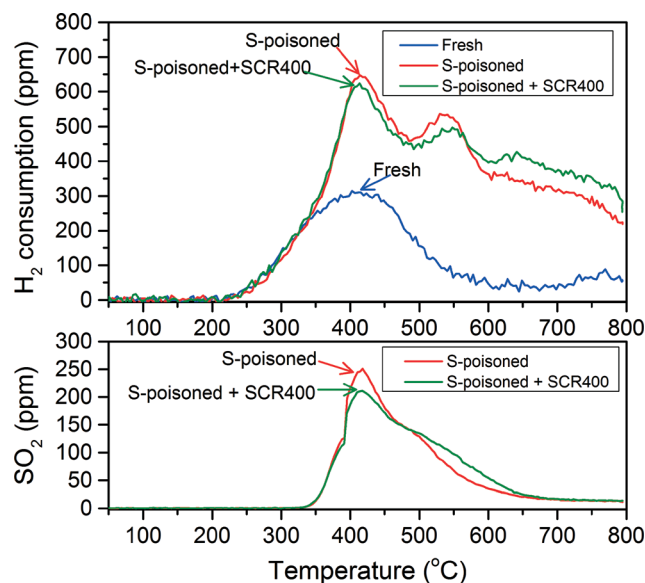
more than one active site, which was later denoted as copper in a larger cage of CHA structure. Since our Cu-SSZ-13 sample has a Cu/Al ratio of only 0.16, i.e. it is under-exchanged, and likely only has small amounts of copper in the larger cages, we did therefore not observe any low temperature reduction peak, which is in line with the study by Kwak et al.[18]

The sulfur poisoned samples (before and after SCR reaction) show significantly higher H_2 consumption than the fresh Cu-SSZ-13 samples as displayed in Fig. 3. The highest peak of both sulfur-treated samples occurred at approximately the same temperature as the fresh sample (413 °C) which is also the case for the SO_2 signal detected by the MS. Total H_2 consumptions per mole Cu for both sulfur-treated catalysts were similar: 1.32 and 1.40 for sulfur poisoned and sulfur poisoned + SCR 400 samples, respectively. It is expected that H_2 was consumed not only by the reduction of copper but also by sulfates or other sulfur species formed during the SO_2 treatment to form SO_2. Further, the H_2S signal detected during the experiment (data not presented here) indicated that some of the hydrogen was consumed to form H_2S. The H_2S was formed simultaneously as the SO_2, as well as at higher temperature, which might be a reason for the high temperature consumption of H_2 in the TPR. Zhang et al. suggested[24] that sulfur is mainly stored as either sulfates or surface SO_2 groups. Our previous study[25] using Cu-SAPO-34 showed that after the catalyst had been poisoned with SO_2 + O_2 + H_2O, less copper was available on the surface that might undergo the redox cycle, which is likely the case also in the present investigation. However, the main SO_2 release occurs at the same temperature as the main copper reduction peak for Cu/SSZ-13, resulting in the fact that the reduction of copper and sulfur species overlaps, which is why it is not possible to resolve the hydrogen consumption owing to copper reduction in the sulfur poisoned samples.

3.3 Ammonia storage and desorption

Ammonia adsorption/desorption plays a significant role in the SCR system, especially during transient operations;[36] it is therefore crucial to examine this behavior over the zeolite catalysts. Ammonia was first adsorbed on the catalyst by exposing the sample to 400 ppm NH_3 in the presence of 5% H_2O in Ar at 150 °C for 90 min. The NH_3 inlet was then switched off while maintaining the feed stream with 5% H_2O in Ar for 75 min; hence, the loosely bound ammonia was released. The temperature was then linearly increased to 600 °C at a heating rate of 10 °C min^{-1} during which the main desorption occurred. The desorption peak has a maximum temperature of about 300 °C, which is displayed in Fig. 4. In another experiment, the adsorption step instead was carried out at 50 °C, which resulted in larger amounts of ammonia stored than in the previous experiment. Following saturation, the catalyst was flushed with 5% H_2O in Ar at 50 °C and it was found that more loosely bound ammonia was released than when the adsorption temperature was 150 °C because of the larger adsorption of loosely bound ammonia at a low temperature. This result is in good agreement with a previous investigation[6] using a micro-calorimetry technique so that the more strongly bound ammonia is adsorbed on the catalyst sites at higher temperature. In addition, shoulders were seen on the desorption profile of the low temperature storage experiment that may be attributable to the presence of more than one site on the catalyst. Further, the amount of NH_3 desorbed at temperatures higher than 340 °C is similar for the two different adsorption cases.

After the catalyst had been sulfur poisoned, the NH_3 storage experiments were repeated along similar lines; however, the TPD step was performed up to 400 °C. It should be noted that prior to the TPD experiments the catalyst was pre-treated with 8% O_2 and 5% H_2O at 400 °C and 600 °C for the sulfur

poisoned and fresh sample, respectively, in order to remove any residual stored ammonia. The ammonia desorption peak *versus* the temperature during the TPD is presented in Fig. 5. As seen in Fig. 5A, the catalyst desorbed more ammonia after sulfur poisoning than the fresh catalyst. This result is consistent with the adsorption step by which increased ammonia storage is noted for the sulfur poisoned catalyst as clearly shown in Table 2. During poisoning, different sulfur species were formed, most of them stable, which was observed by using ICP-SFMS (see Table 1), whereby a large part of the sulfur was still present after SCR conditions of up to 400 °C. Further, SO_2 has higher affinity for copper sites than for acid sites of the zeolite;[33] thus, it is likely that a large number of the sulfur species are associated with the copper sites. These sulfur species are probably capable of binding more ammonia, which may explain the higher ammonia storage of the sulfur poisoned sample. In addition, the ammonia is desorbed at a higher temperature during the TPD; thus, the ammonia stored on the sulfur sites is more strongly bound. The desorption of ammonia stored at 50 °C before and after catalyst poisoning is presented in Fig. 5B. Similar to what was observed when the NH_3 adsorption occurred at 150 °C, increased ammonia storage was observed for the sulfur poisoned sample and a greater amount of stable ammonia stored on the sulfur sites was visible. However, larger desorption was also found at low temperature, indicating that at such a low temperature as 50 °C, ammonia was also bound very loosely to the sulfur sites.

3.4 NH_3 oxidation

Ammonia oxidation is a competitive reaction that occurs during NO_x reduction, which usually decreases the overall conversion, especially at high temperatures.[36–38] Ammonia oxidation was examined for the fresh catalyst by exposing it to 400 ppm NH_3, 8% O_2 and 5% H_2O while increasing the temperature stepwise from 150 to 600 °C (see Fig. 6). The NH_3 oxidation activity started at 250 °C and increased with increasing temperature; however, the conversion at 400 °C was slightly lower than that at 350 °C. Thereafter, the conversion again increased up to 600 °C. Gao et al.[39] found two different levels of energy activity for NH_3 oxidation over Cu-SSZ-13 at low and high temperatures. It has been suggested that for Cu-SSZ-13 with low copper loading, the Cu mainly occupies the sites in the six-membered rings, whereas for samples featuring high ion-exchange levels, the Cu is primarily attached to the larger cages of the CHA structure[18] or in the form of Cu_xO_y.[20] Even though Cu-SSZ-13 in the present study had a low exchange level (Cu/Al = 0.16), we suggest that those two different sites were present in the sample considering that besides its high activity of NO_x reduction, which will be described later in section 3.6, it was also active for NO oxidation (see section 3.5). According to Bates et al.,[20] copper in the six-membered ring of Cu-SSZ-13 is inactive for NO oxidation. Thus, since our catalyst possesses NO oxidation activity, it likely also contains some copper in the larger zeolite cages.
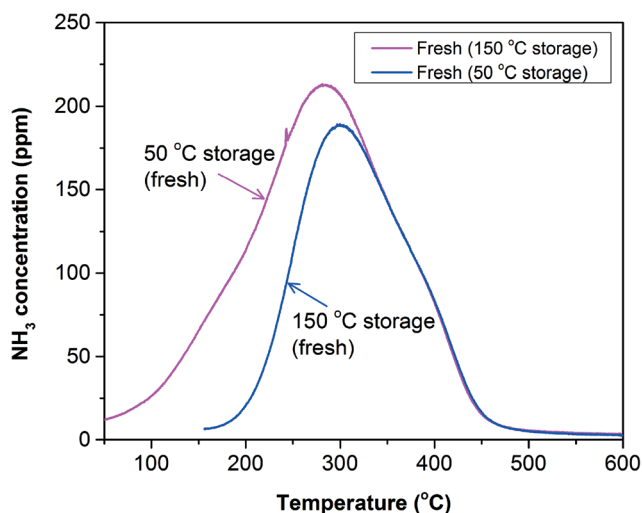

Fig. 4 NH_3 desorption profiles of the fresh Cu-SSZ-13. The catalyst was exposed to 400 ppm NH_3 + 5% H_2O for 90 min at 50 or 150 °C followed by flushing using 5% H_2O for 75 min. The temperature was then increased to 600 °C with a ramp rate of 10 °C min^{-1}.
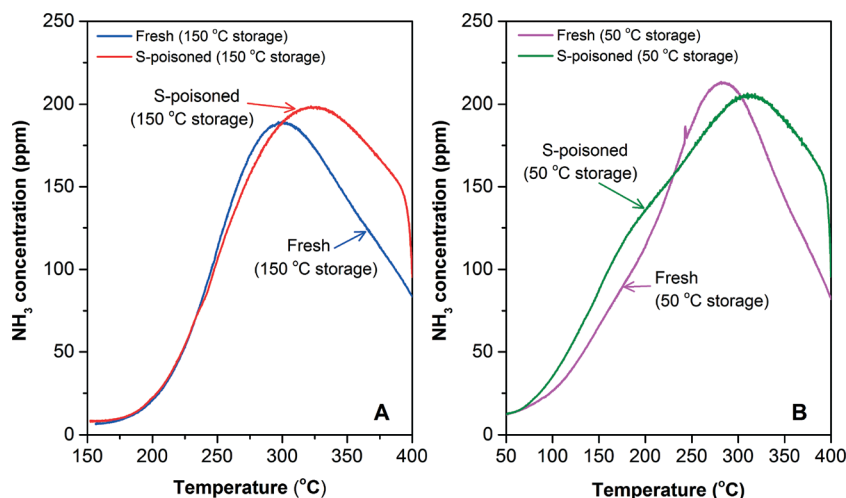
Fig. 5 NH$_3$ desorption profiles of the fresh and sulfur poisoned Cu-SSZ-13. The catalyst was exposed to 400 ppm NH$_3$ + 5% H$_2$O for 90 min at 150 °C (A) or 50 °C (B) followed by flushing with 5% H$_2$O for 75 min. The temperature was then increased at a ramp rate of 10 °C min^{-1}.

In a previously developed kinetic model,[19] we proposed that ammonia oxidation occurs at different rates on copper in the six-membered ring and in the larger cages. At low temperatures, NH$_3$ oxidation took place at a low rate on the sites representing the copper located in the six-membered rings. When the temperature increased, the NH$_3$ coverage on these sites decreased, which resulted in a decreasing conversion between 350 and 400 °C. At higher temperatures, the reaction mostly related to the exchanged sites in the larger cage as the conversion of NH$_3$ was again observed to increase up to 600 °C.

After the catalyst had been sulfur poisoned, the NH$_3$ oxidation substantially changed, as seen in Fig. 6. For example, at 400 °C, the conversion of NH$_3$ decreased from 35% to 15% after sulfur poisoning of the sample. The ammonia oxidation activity was severely influenced by the sulfur species, especially at lower temperatures. Since we consider the reaction to have mainly occurred on Cu sites in the six-membered rings at low temperature, we suggest that these sites should be strongly deactivated due to sulfur poisoning under SCR conditions. The reactions after sulfur treatment had been performed up to 400 °C to prevent the removal of large amounts of sulfur and hence, the effect of sulfur above 400 °C could not be resolved using these experiments.

3.5 NO oxidation

NO oxidation over Cu-SSZ-13 was investigated by exposing the fresh catalyst to 400 ppm NO and 8% O$_2$ in the presence

of 5% H$_2$O between 150 and 600 °C. As depicted in Fig. 7, the catalyst shows NO oxidation activity, whereby the conversion was increased as the temperature increased. The maximum conversion of about 5.6% was reached at the highest temperature (600 °C). The oxidation of NO to NO$_2$ is a reversible reaction in which the NO$_2$ production usually decreases at high temperatures due to thermodynamic constraints.[40–42] However, since the NO$_2$ concentration was quite low and far from equilibrium, such a condition was not observed in the present study. Since the NO$_x$ reduction is faster given the presence of NO$_2$, some may argue that NO oxidation is the rate-determining step of the SCR reaction over metal-zeolite catalysts.[37,43,44] However, small-pore zeolite catalysts have shown good NO$_x$ reduction capability despite the low concentration of NO$_2$ detected during NO oxidation.[25,38] These results indicate that the NO oxidation is likely not a crucial step for NO$_x$ reduction over copper zeolites. Despite the literature debate
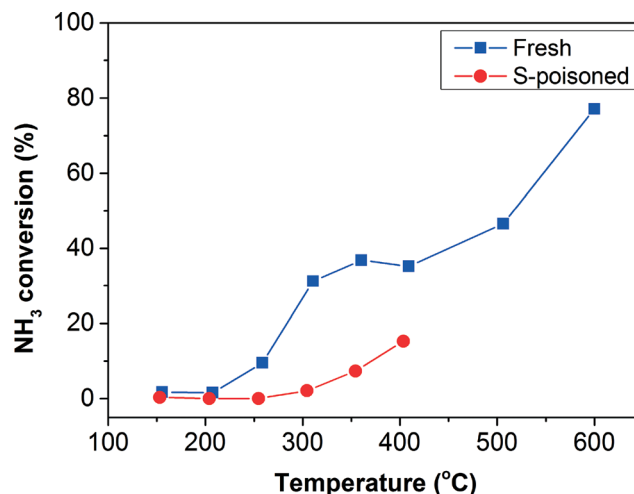
Table 2 NH$_3$ storage on fresh and sulfur poisoned Cu-SSZ-13 during adsorption at 50 and 150 °C, respectively

Catalyst	Amount of NH$_3$ stored (mmol g^{-1} washcoat)	
	150 °C	50 °C
Fresh sample	1.17	1.66
Sulfur poisoned sample	1.30	1.80

Fig. 6 NH$_3$ oxidation over fresh and sulfur poisoned Cu-SSZ-13. The catalyst was exposed to 400 ppm NH$_3$, 8% O$_2$ and 5% H$_2$O during these experiments.
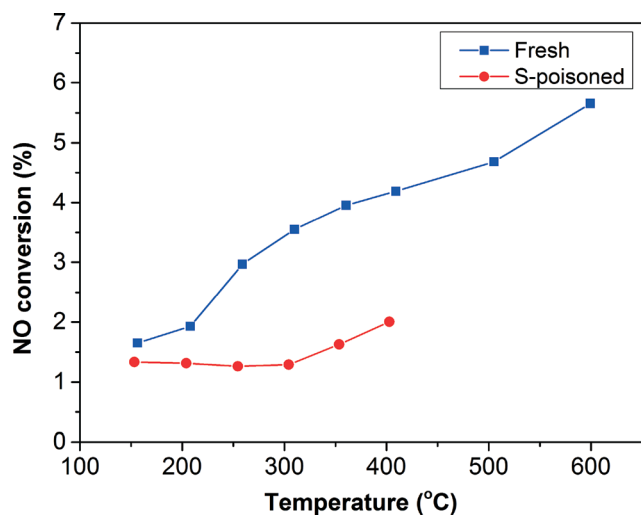
Fig. 7 Steady state conversion of NO during NO oxidation over fresh and sulfur poisoned catalyst. The catalyst was exposed to 400 ppm NO, 8% O_2, and 5% H_2O with Ar balance.

on this issue, it is still interesting to study the NO oxidation reaction in order to gain a fundamental understanding of the effect of sulfur poisoning on different reactions and active sites.

NO oxidation was decreased over the sulfur poisoned catalyst as displayed in Fig. 7, where for example NO conversion decreased from 4.2% to 2% at 400 °C. However, it should be noted that the concentrations were very low. Kumar *et al.*[26] who investigated the SO_2 impact on commercial copper-exchanged catalysts did not detect any measurable difference on NO oxidation activity after exposing a catalyst to 33 ppm

SO_2 for 8 h at 200 °C; however, after sulfur poisoning at 400 °C for 24 h, a deactivation was observed. As described above, NO oxidation likely takes place on copper sites in the large cages or on Cu_xO_y species. Thus, copper sites in the larger cages are probably also influenced by the sulfur poisoning since after sulfur poisoning, we observed a decrease in NO oxidation even though the conversion for the NO oxidation reaction is small.

3.6 Standard SCR

The reduction of NO in NH_3-SCR was studied by exposing the catalyst to 400 ppm NH_3, 400 ppm NO, 8% O_2 and 5% H_2O while simultaneously increasing the temperature stepwise from 100 to 600 °C. Fig. 8 presents the steady state conversions of NO_x (A) and NH_3 (B), whereas the N_2O concentration is displayed in the lower panel (Fig. 8C). As shown in Fig. 8A, NO reduction was observed already at 150 °C (33% conversion), which thereafter increased as the temperature was increased and reached full conversion at 250 °C. At 350 °C, the conversion of NO_x started to decline because of the non-selective NH_3 oxidation at high temperatures, in agreement with the experimental results described in section 3.4 and as also found in earlier investigations.[6,38,45] Further, NO and NH_3 were consumed in similar amounts during reactions up to 350 °C (Fig. 8A and B), which is characteristic of standard SCR over copper-exchanged zeolites.[46,47]

After sulfur poisoning under SCR conditions, the standard SCR reaction was repeated eight times until a stable activity was reached. In order to prevent the removal of a large amount of sulfur from the catalyst surface, the reaction was only performed up to 400 °C. The NO_x conversion of the first
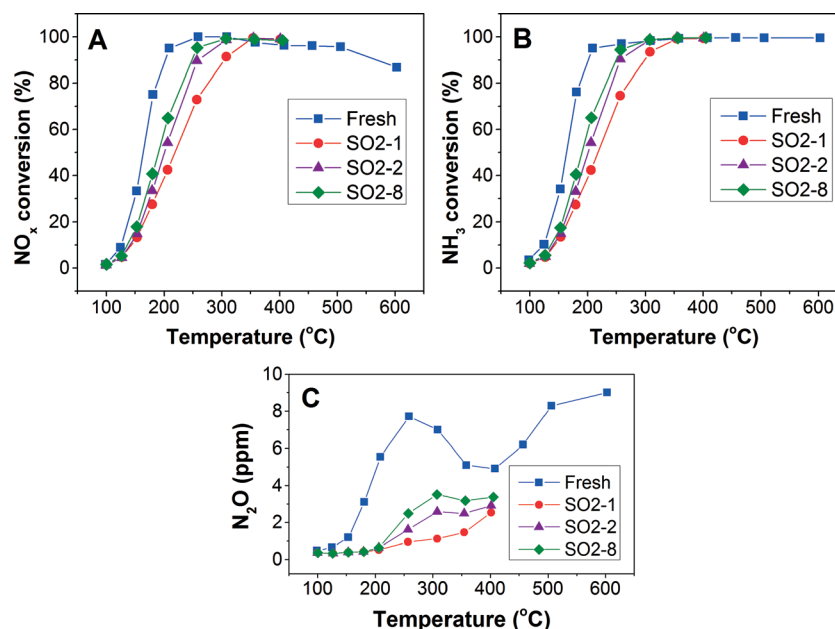

Fig. 8 Conversion of NO_x (A), NH_3 (B), and N_2O production (C) during standard SCR reaction over fresh and sulfur poisoned Cu-SSZ-13. The catalyst was exposed to 400 ppm NH_3, 400 ppm NO, 8% O_2, and 5% H_2O with Ar balance. SO2-1 denotes the first SCR experiment after poisoning, SO2-2 the second, and so on. Note: poisoning was only carried out prior to SO2-1.

two and final SCR experiments are plotted in Fig. 8A, where SO2-1 denotes the first SCR experiment after SO_2 exposure, SO2-2 the second, and so on. Experimental results show that the activity was significantly affected by sulfur treatment (SO2-1) but gradually recovered after repeated experiments (SO2-2) and was finally stabilized after eight SCR experiments (SO2-8). This progression is due to the removal of loosely bound sulfur species that attach to catalyst sites. The sulfur poisoned catalyst could reach approximately the same maximum conversion as the fresh catalyst; however, it should be noted that the activity at low temperatures showed a substantial decrease. At around 200 °C, for example, the conversion in the fresh catalyst was 95% and then declined to 42% after sulfur poisoning (SO2-1). Thereafter, the conversion again increased because of the sulfur removal and reached 54% *versus* 65% for SO2-2 and SO2-8, respectively. This result is consistent with previous studies[24] that demonstrated that the impact of the sulfur treatment was mainly visible at low temperatures. One of the reasons why deactivation is difficult to observe at high temperature is that the ammonia conversion is 100% (see Fig. 8C). Using spatially resolved MS experiments, we have previously found that for a Cu-BEA catalyst, 100% conversion was reached already after 25% of the catalyst length.[48] These results show that only a small fraction of the catalyst is used for the SCR reaction at high temperature and this is also likely the case in the present study. Thus, even though sites are poisoned, it is difficult to observe the deactivation at high temperature because of the large number of excess sites at these temperatures. The fact that the activity after eight SCR experiments was lower than the fresh activity shows that even after reaching a stable level and repeating the standard SCR experiments up to 400 °C, there are some sulfur species left on the catalyst. These results are in agreement with the ICP-SFMS results presented in Table 1, where it was found that the amount of sulfur in the catalyst was decreased after a single SCR experiment but that a large amount of sulfur remained in the sample. It is also worth mentioning that at 350 and 400 °C, the activity of the sulfur poisoned catalyst was slightly higher than that of the fresh catalyst, which might be attributable to the decreasing activity of NH_3 oxidation (section 3.4).

As seen in Fig. 8C, nitrous oxide (N_2O) was detected during the experiments; however, the concentration was low (less than 10 ppm) for the fresh sample. This result is in accordance with previous studies,[13,25,38] which showed that small-pore zeolite catalysts show high selectivity for N_2, as they produce only minor amounts of N_2O. After sulfur treatment under SCR conditions, the N_2O formation significantly decreased and after repeated SCR experiments, the N_2O concentration gradually increased, although it never returned to its initial concentration (Fig. 8C).

It is likely, as described above, that Cu is primarily located in the six-membered rings of our present sample, while at the same time small amounts are occupying positions in the larger CHA cages. Mihai and co-workers[5] have proposed that two different copper sites were present in Cu-BEA, where Cu

for the low-exchange level was coordinated to two Al, while for the high exchange level, Cu was coordinated to one Al and the charge was balanced by an OH group. Mihai *et al.*[49] observed that when increasing the copper-loading, the N_2O selectivity significantly increased and therefore ascribed the N_2O formation to primarily occur on the over-exchanged sites. In line with these results, kinetic models for N_2O formation were developed over Cu-BEA[50] and Cu-SSZ-13,[19] where the N_2O production was related to copper sites that started to form when the copper loading was increased, which means Cu in the larger cages for Cu-SSZ-13. Furthermore, considering the results of the sulfur poisoned sample and the decreasing activity of both NO oxidation and N_2O formation, those copper sites were most likely affected by sulfur treatment. In addition, copper in the six-membered rings is also poisoned by sulfur, which results in deactivation of the standard SCR reaction (see Fig. 8A). A recently published study by Shen *et al.*[33] suggested that the declining amount of Cu^{2+} ions in a sulfated sample of Cu-SAPO-34 might be attributed to the formation of cupric sulfites. Another possibility was that sulfate species might be formed by catalytic oxidation of SO_2 into SO_3 which then formed sulfates on the copper site.[51] Moreover, the XPS result conducted by Cheng *et al.*[34] also revealed the presence of sulfate species after the zeolite catalyst had been poisoned by SO_2. Further, Zhang *et al.*[24] proposed that $(NH_4)_2SO_4$ was the main reason for the degradation of low temperature activity in a commercial Cu-SAPO-34. During sulfur treatment, the catalyst was poisoned with 30 ppm SO_2 in an SCR environment (with the presence of 400 ppm NH_3, 400 ppm NO, 8% O_2 and 5% H_2O). It was therefore likely that the formation of ammonium sulfur species occurred that may foul catalyst sites and limit the interaction between reactants. Interestingly, Kumar *et al.*[26] found that the sulfur poisoning was more severe and in addition, the sulfur species were more difficult to regenerate if the poisoning at 400 °C was performed using SO_3 rather than SO_2. These results indicate that with SO_3, more stable sulfates are formed and thus, SO_2 poisoning likely forms different sulfur species (of which parts might be sulfates).

Further, in order to clarify the different behaviors of the catalyst after SO_2 treatment with or without SCR conditions (NH_3 + NO), an experiment was performed during which the catalyst was only poisoned with 30 ppm SO_2 + 8% O_2 + 5% H_2O at 300 °C for 90 min. As seen in Fig. 9, sulfur treatment under SCR conditions results in a greater decrease in NO_x reduction activity than in the case without NH_3 + NO, for instance at 250 °C in which the fresh catalyst possessed complete conversion, the NO_x conversion decreased to 73% and 89% for sulfur poisoning under SCR conditions and for the case without NH_3 + NO, respectively. Zhang *et al.*[52] observed that after SO_2 + NH_3 + O_2 and SO_2 + O_2 TPD experiments more sulfur was adsorbed in the presence of NH_3. The reason for this could be a larger storage of different ammonium–sulfur species compared to sulfur only species, and this would explain the larger deactivation that we observe during sulfur poisoning under SCR conditions.
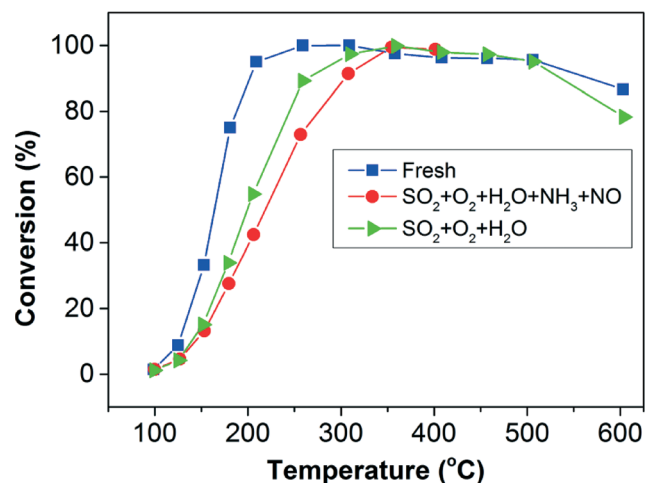
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Fig. 9 Effect of different sulfur poisoning treatments on the standard SCR over Cu-SSZ-13. Sulfur poisoning was performed prior to the SCR experiment by exposing the catalyst to (30 ppm SO_2) or (30 ppm SO_2 + 400 ppm NH_3 + 400 ppm NO) + 8% O_2 + 5% H_2O for 90 min at 300 °C.

3.7 Fast SCR

When the composition of NO_2/NO_x is 50%, the rate of NO_x reduction can be improved and follows well-known fast SCR.[53] This reaction was investigated by exposing the catalyst to 400 ppm NH_3, 200 ppm NO, 200 ppm NO_2 in the presence of 8% O_2 and 5% water in the temperature range of 200–400 °C as depicted in Fig. 10. For the fresh catalyst, initially at 200 °C, a high consumption of NH_3 was observed and the conversion of NO_x increased over time. Even though a stable outlet concentration of NO_x was not achieved at the end of the step, we perceived a high conversion of NO_x at this temperature. Upon increasing the gas temperature to 250 °C and above, complete conversion of NO_x was observed. Further, when the standard SCR conversion declined at 350 and 400 °C (96% conversion at 400 °C) attributable to the contribution of NH_3 oxidation, fast SCR still resulted in full conversion; however, the differences were minor. This result was similar to the study by Metkar *et al.*[54] who observed a similar NO_x conversion between standard and fast SCR using a Cu-CHA catalyst. It should be noted that as the NO_x conversion during fast SCR in our study decreased at 500 and 600 °C; the conversion at 600 °C of 78% (the data are not presented here) was even lower than for the standard SCR case, which may be attributed to NH_3 consumption by NO_2 producing NO as suggested by Watling *et al.*:[55]

$$2NH_{3\ ads} + 3NO_2 \rightarrow 3NO + N_2 + 3H_2O \qquad (1)$$
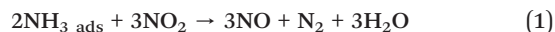
This is supported by the fact that the outlet concentration of NO was much higher than that of NO_2 at 500 and 600 °C.

Nitrous oxide concentration during our experiment is presented in Fig. 10C in which the production of N_2O started at 200 °C and increased up to 300 °C, where it reached about 14 ppm for the fresh catalyst; thereafter, the N_2O concentration leveled out. The small-pore zeolite catalysts, such as Cu-SSZ-13 and Cu-SAPO-34, have proven to possess low selectivity
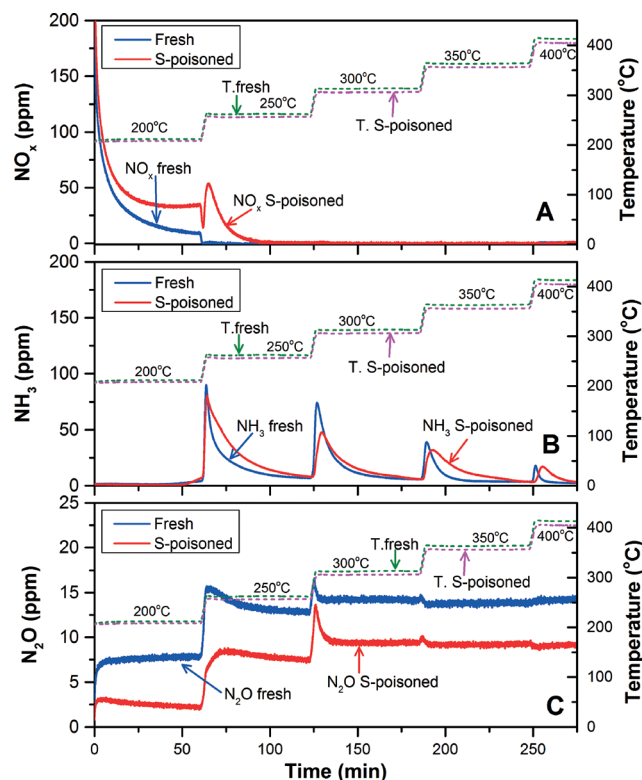

Fig. 10 Concentrations of NO_x (A), NH_3 (B) and N_2O (C) as a function of time during the fast SCR reaction for the fresh and sulfur poisoned sample. The catalyst was exposed to 400 ppm NH_3, 200 ppm NO and 200 ppm NO_2 at 200–400 °C with a ramping step of 20 °C min^{-1} between the temperature steps.

towards N_2O production;[56] however, when comparing those two catalysts, Cu-SSZ-13 produced more N_2O than Cu-SAPO-34.[13] N_2O production at low temperatures is suggested to be produced from the formation and decomposition of ammonium nitrate surface species,[5] while at high temperatures, a slow reaction between NH_3 and NO_2 may result in undesired N_2O.

Referring to the results depicted in Fig. 10A, the impact of the sulfur poisoning under SCR conditions on the fast SCR reaction was discernible at a low temperature of 200 °C and the effect was hardly witnessed at a higher temperature up to 400 °C. However, it should be noted that at these temperatures (250–400 °C), full conversion was achieved; hence, it was difficult to determine the deactivation. Previous investigations[21,25] showed that the impact of deactivation by SO_2 can be minimized when the ratio of NO_2/NO_x is 0.5 which is likely the case in the present study. The production of N_2O was affected by sulfur poisoning, as seen in Fig. 10C, where the concentration of N_2O was observed to be lower than that of the fresh case, which is probably caused by the deactivation of active sites in which the N_2O formation takes place, as observed for N_2O in the standard SCR case.

3.8 SCR with NO_2/NO_x ratio of 0.75

The NO_2 presence in the feed has proven to significantly affect the rate of reaction,[53] and it is therefore important to

examine Cu-SSZ-13 activity with a high fraction of NO_2/NO_x and a ratio of 0.75 used for this study. The catalyst was exposed to 400 ppm NH_3, 100 ppm NO, 300 ppm NO_2, 8% O_2 and 5% H_2O from 200–600 °C and 200–400 °C for the fresh and sulfur-treated sample, respectively. Outlet concentrations of NO_x, NH_3 and N_2O are depicted in Fig. 11.

Initially at 200 °C for the fresh sample, a total uptake of NH_3 was observed and the NO_x consumption simultaneously increased before it exhibited a minimum of NO_x concentration and then increased again. The reason for the initial increase in NO_x conversion was that the ammonia coverage on the surface was slowly building up, and since the reaction rate for NO_2-SCR depended on the NH_3 coverage,[50,57] the SCR rate was increasing with increasing NH_3 coverage. Thereafter, a minimum in NO_x conversion was observed and we noticed a similar minimum in our previous investigation using Cu-SAPO-34.[25] This experimental feature might be due to blocking of sites by ammonium nitrate species, hindering the SCR reaction.[58] Moreover, an increase in N_2O production to about 13 ppm was noticeable at 250 °C followed by a significant peak of N_2O during the temperature ramping from 250 to 300 °C (Fig. 11C) presumably caused by decomposition of ammonium nitrate species on the surface. At 300 °C, very high conversion of NO_x was achieved, denoting that the ammonium nitrate species had been removed from the surface. Previous studies[53,59] had found a correlation

Fig. 11 Measured outlet concentrations of NO_x (A), NH_3 (B) and N_2O (C) for SCR with 0.75 NO_2/NO_x. The fresh and sulfur poisoned sample was exposed to 400 ppm NH_3, 100 ppm NO, 300 ppm NO_2, 8% O_2, 5% H_2O and balance Ar.

between the NO_2 fraction and the N_2O production, whereby a high ratio of NO_2/NO_x resulted in additional N_2O produced which was also the case in the present study. Similar to what was observed at fast SCR, substantially higher amounts of NO were detected at high temperatures compared to NO_2, denoting that the production of NO through reaction (1) occurred. In addition, the NO_x conversion at 75% NO_2/NO_x was lower than that of the fast and standard SCR. Lowering NO_x conversion at a high NO_2/NO_x fraction was also found in our previous study using Cu-SAPO-34 (ref. 25) and was in line with the investigation conducted by Metkar and co-workers[54] attributable to the so-called slow NO_2-SCR.

After the catalyst had been sulfur poisoned under SCR conditions, as seen in Fig. 11, a noticeable impact at low temperatures was perceived. A similar NO_x profile trend was shown, albeit with a higher concentration than the fresh catalyst. Thus, the activity of the NO_x reduction was affected by the SO_2 treatment. At a gas temperature of 250 °C, for example, the fresh catalyst exhibited 71% NO_x conversion, whereas a 63% conversion was demonstrated by the sulfur poisoned catalyst. However, the degree of overall deactivation of the SCR with 75% NO_2/NO_x was not as large as in the standard case. This result revealed that the presence of NO_2 lowered the deactivation caused by sulfur treatment as suggested by previous studies.[21,25] In addition, a lower concentration of N_2O was detected over the sulfur poisoned sample compared to the fresh case at low temperature. It has been suggested that low temperature production of N_2O is closely related to the formation and decomposition of ammonium nitrate species.[5,60] Thus, the decreased N_2O production might be attributed to a reduced ammonium nitrate species formation after sulfur poisoning of the catalyst.

3.9 Ammonium nitrate formation and TPD experiments

Ammonium nitrate formation may occur when NH_3 together with NO_2 is fed into the reactor according to the following reaction:[25,60]

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \qquad (2)$$
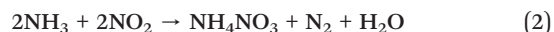
However, it should be noted that different types of ammonium nitrate precursors, species and complexes might form depending on the condition. The ammonium nitrate species formation and decomposition play an important role in the SCR system and it is therefore interesting to study the behavior of the catalyst towards this reaction. An experiment was performed exposing the catalyst to 400 ppm NH_3, 400 ppm NO_2 and 5% H_2O at 150 °C, followed by a temperature ramp (10 °C min^{-1}) to 600 and 400 °C for the fresh and sulfur poisoned sample, respectively. The resulting concentration of NH_3, NO_2, NO and N_2O is displayed in Fig. 12. As seen in Fig. 12, at the beginning of the experiment, a total uptake of NH_3 was observed attributable to the storage of NH_3, ammonium nitrate species formation, fast SCR and NO_2-SCR. These reactions also resulted in a consumption of NO_2 and NO. The
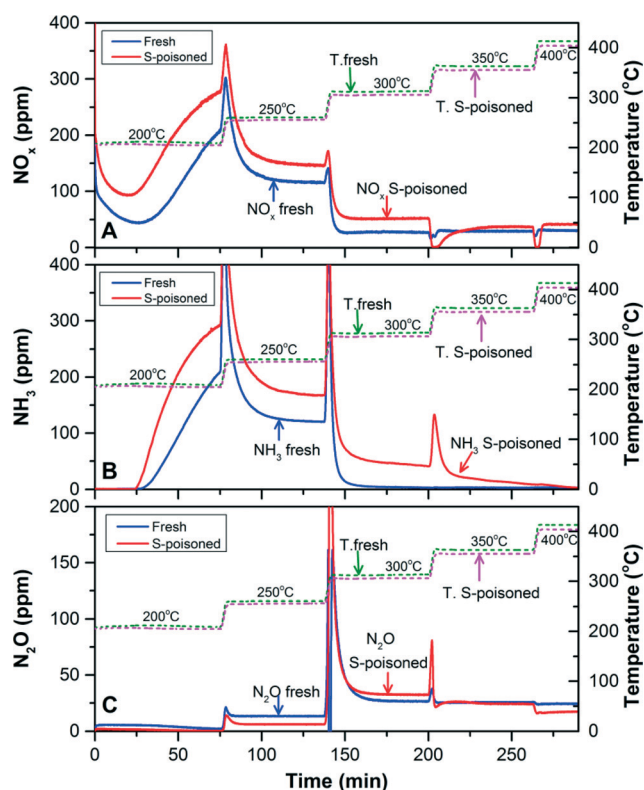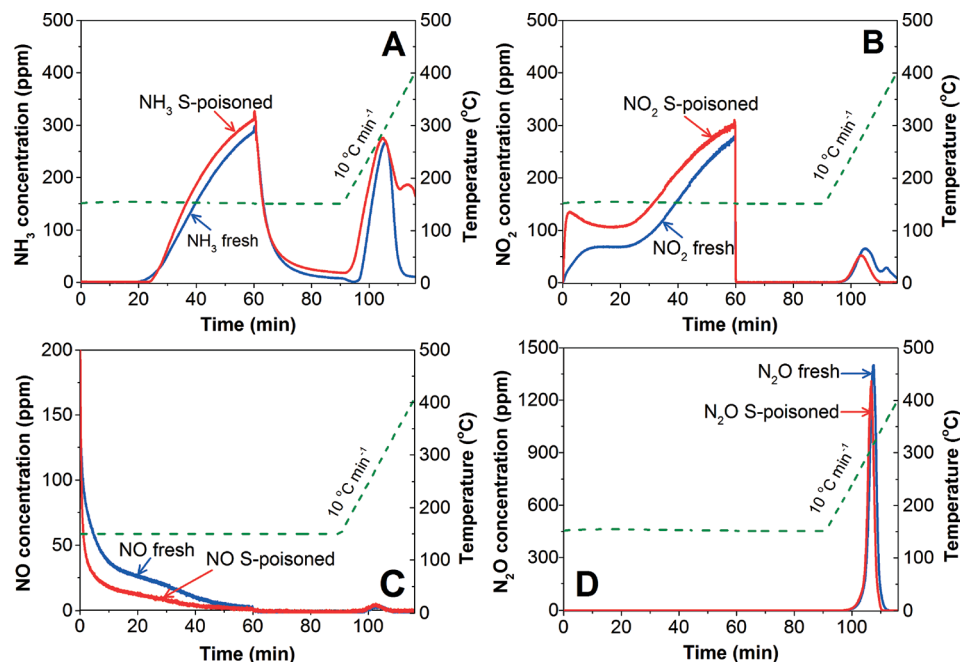
Fig. 12 Outlet concentrations of NH_3 (A), NO_2 (B), NO (C) and N_2O (D) during NH_3–NO_2 storage and TPD experiment.

NO_2 concentration profile exhibited a minimum because the formation of ammonium nitrate species most likely blocked the active copper sites in the same way as discussed in section 3.8 for the NO_2-SCR experiment. Further, when the temperature was ramped up, an N_2O peak appeared, which was attributed to the decomposition of ammonium nitrates.[5]

The sulfur poisoned catalyst exhibited a somewhat lower NH_3 consumption during the adsorption step as depicted in Fig. 12A; however, the gap was significantly smaller than that observed for the NO_2 concentration (Fig. 12B). Referring to the result from the SCR with an NO_2/NO_x ratio of 0.75 (section 3.8), it has been demonstrated that the sulfur treatment causes a decrease in the NO_2-SCR reaction, which means lowering the NH_3 and NO_2 consumption. In addition, the sulfur treatment resulted in lower NO formation (see Fig. 12C); thus, reaction (1) seemed to be inhibited, in which NO_2 reacted with NH_3 to produce NO. Further, our NH_3 TPD experiment (section 3.3) showed that the sulfur poisoned sample stored a greater amount of NH_3 than the fresh sample. These two facts, decreased NO_2-SCR and increased NH_3 storage after sulfur poisoning of the sample, explain the minor difference in NH_3 concentration between the fresh and the sulfur poisoned sample compared to that of the NO_2. When the temperature was linearly increased during the TPD, the NH_3 peak perceived was larger than that of the fresh sample, which was in accordance with previous findings that more NH_3 was stored for the sulfur poisoned sample. Further, the poisoned catalyst exhibited higher stability of the stored ammonia, as evident by the second ammonia peak, which was also in line with the NH_3 TPD experiment. In addition, less N_2O was produced after the catalyst had been sulfur poisoned. Nitrous oxide released from the fresh sample was 0.67 mmol, whereas the sample contained 0.38 mmol Cu. Since

one N_2O is formed for every ammonium nitrate created, the amount of ammonium nitrates on the surface is more than available Cu sites; thus, it is possible that the ammonium nitrates are attached to both acid and copper sites. This finding is in line with a previous investigation conducted by Mihai et al.[5] using a Cu-BEA catalyst, which showed that N_2O production can proceed either on acid or on copper sites. However, the binding strength of the ammonium nitrate species increased with increased copper loading, indicating the preferential binding to the copper sites. Furthermore, the experiment with the sulfur poisoned sample produced 0.56 mmol N_2O, which was slightly lower than that of the fresh case; hence, sites on which the N_2O was produced at low temperatures were poisoned by sulfur treatment. This fact was in accordance with the results of the standard SCR reaction (section 3.6) which demonstrates that the N_2O production at low temperatures was suppressed after the catalyst was poisoned with SO_2 in SCR conditions.

4. Conclusions

The deactivation of Cu-SSZ-13 owing to SO_2 treatment under SCR conditions in the NH_3-SCR system has been investigated. An activity measurement of the fresh and sulfur-treated catalyst was performed and in addition, a detailed catalyst characterization was conducted. The structure of the in-house synthesized Cu-SSZ-13 was examined using XRD, which showed that the structure of zeolite could be well preserved during the ion-exchange process. In addition, the catalyst possessed a high BET surface area and pore volume.

SO_2 treatment under SCR conditions decreased the BET surface area as well as the pore volume of the catalyst. Referring to ICP-SFMS analysis, sulfur loading was not uniform on

the monolith channel, denoting that the deposition of the sulfur occurred from the inlet moving towards the outlet. In addition, ICP-SFMS showed that some sulfur could be removed in the inlet part of the monolith during SCR conditions, but this was not the case for the outlet part of the monolith. H_2-TPR results showed that hydrogen usage was higher over the sulfur poisoned sample, presumably due to the fact that H_2 was also consumed by its reaction with the sulfur species formed on the catalyst surface, resulting in SO_2 production. In addition, a minor amount of H_2S was detected which also contributes to H_2 consumption. The H_2S was formed simultaneously with the SO_2 as well as at higher temperature, which might be a valid reason for the high temperature consumption of H_2 in the TPR. Another feature of the sulfur poisoned sample was that additional NH_3 was stored on this catalyst due to the capability of the sulfur species on the catalyst surface to store more NH_3. It is expected that sulfur was predominantly attached to the copper as opposed to the acid sites since the sulfur loading detected by ICP-SFMS was low.

Following the sulfur treatment using SO_2 under SCR conditions (NH_3 + NO + O_2 + H_2O) at 300 °C, the SCR reaction up to 400 °C was conducted and significant deactivation, particularly at low temperature, was observed. Some activity was regained by repeating the SCR reaction until a stable activity had been attained. However, the activity of the final SCR was much lower than the activity in the fresh case. The effect of SO_2 exposure under SCR conditions was mainly detected at low temperatures, probably due to complete conversion of ammonia at higher temperatures. Furthermore, the NH_3 and NO oxidation were reduced by SO_2 treatment of the catalyst under SCR conditions. Less deactivation was seen for SCR with NO_2/NO_x of 50% compared to the standard SCR case, which was in good agreement with our previous investigation using Cu-SAPO-34. From the NH_3 + NO_2 storage and TPD experiment, it can be concluded that the N_2O formation was suppressed by the sulfur poisoning. Finally, the impact of the sulfur poisoning conditions was investigated. It was established that SO_2 poisoning under SCR conditions (NH_3 + NO + O_2 + H_2O) was more severe than SO_2 exposure alone in the presence of O_2 and H_2O. This observation may be attributed to the formation of ammonium sulfur species on the catalyst under SCR conditions.

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