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Comparative Study of SO_2 and SO_2/SO_3 Poisoning and Regeneration of Cu/BEA and Cu/SSZ-13 for NH_3 SCR

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Abstract
Two copper-exchanged zeolites, Cu/SSZ-13 and Cu/BEA, were studied as catalysts for the selective reduction of NO_x by NH_3 (NH_3-SCR). Their activities for standard SCR ($NO_x = NO$) and fast SCR ($NO_x = 50\%$ NO + 50% NO_2) were measured before and after sulfur poisoning at 250 °C. The effect of 30 ppm SO_2 and a mixture of 24 ppm SO_3 + 6 ppm SO_2 was evaluated. The repetition of subsequent activity measurements served as regeneration method in SCR conditions. SO_2 deactivated Cu/SSZ-13 whereas Cu/BEA was only moderately affected. SO_3 led to stronger deactivation of both catalysts than SO_2. However, also for this case, the Cu/BEA was significantly less affected than Cu/SSZ-13, even though Cu/BEA contained larger amount of stored sulfur. One possible reason for this could be the large pores of Cu/BEA, where the sulfur species possibly resulted in less sterical hindrance than in the small pore SSZ-13 structure. NH_3 temperature-programmed desorption (NH_3-TPD) showed no loss of storage sites upon sulfur treatment and subsequent regeneration. Partial activity recovery was observed after a period in SCR conditions at 400 °C and 500 °C. Temperature at 300 °C was insufficient to regenerate the catalysts. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of NO adsorption suggested that SO_2 interacts with the ZCuOH sites on Cu/SSZ-13, causing the strong poisoning.

Keywords NH_3 SCR · Poisoning · SO_2 and SO_3 · Cu/zeolites

1 Introduction

Diesel and lean-burn gasoline engines present the advantage to be more fuel-efficient and to emit less CO_2 than gasoline engines. However, these combustion systems also produce nitrogen oxides (NO_x). NH_3-SCR is an efficient process to reduce NO_x by NH_3 over a metal-exchanged zeolite or V_2O_5-based catalyst. For automotive applications, NH_3 can be produced in situ through decomposition and hydrolysis of a solution of urea sprayed in the exhaust gas.

The exhaust gas contains other chemical compounds that can interfere with the NH_3-SCR process and deactivate the widely used, efficient, Cu-exchanged zeolite catalyst. Sulfur oxides (SO_x) are impactful poisons which are therefore widely studied. Even at low concentration, the SO_x store and accumulate on the catalyst. They can block the active sites for the NO_x reduction reaction and decrease the catalytic performance with time [1–5]. This accumulation process requires periodic regeneration of the catalyst. Reducing conditions and high-temperature treatment can readily decompose the stored SO_x species. However, such reducing conditions at a high temperature may permanently damage the Cu-exchanged zeolite catalyst [6]. To preserve the catalyst, it is important to further develop regeneration strategies for SO_x-poisoned SCR catalysts.

Most of the SO_x poisoning and regeneration studies solely focus on the impact of SO_2 as SO_x species and thermal regeneration [3, 5, 7–12], sometimes carried out under reducing atmosphere. However, the SO_2 present in the exhaust of a modern vehicle passes through an oxidation catalyst before reaching the SCR catalyst. The oxidation catalyst is a noble metal-based catalyst which oxidizes CO and hydrocarbons into CO_2 and water vapor. It also oxidizes a large fraction of NO to NO_2 and SO_2 to SO_3 [13–16]. The oxidation of SO_3 occurs also on the Cu/SSZ-13 SCR catalyst itself from 450 °C [9]. Therefore, it is relevant to study the

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impact of a SO_2/SO_3 mixture on SCR catalysts because it is more representative of the real conditions. SO_3 reacts readily with NH_3 to form a solid salt that decomposes at a high temperature. Moreover, SO_3 has shown a higher potential to store and deactivate the SCR catalyst than SO_2 [17–19]. Simultaneous sulfur poisoning and thermal aging was studied by Wijayanti et al. [12] using SO_2 and Tang et al. [20] using a SO_x mixture containing a large amount of SO_3. Tang et al. [20] found that a hydrothermal pretreatment prior to sulfur exposure can decrease the deactivation of the SCR catalyst.

The zeolite structure also affects the sulfur aging for Cu/zeolites as found in one of our earlier studies, where Cu/SSZ-13 and Cu/LTA were compared during sulfur poisoning with SO_2 [11]. However, there are according to the best of our knowledge no studies available where the effect of zeolite structure in Cu/zeolites is examined for sulfur poisoning using both SO_2 and SO_3 as a SO_x source. In this work, we therefore performed the comparative poisoning of two kinds of Cu-exchanged zeolites with SO_2 and a mixture of SO_2/SO_3. The influence of the zeolite structure (SSZ-13 and BEA) was thus studied and the impact of SO_3 was determined and compared with the impact of SO_2. The regeneration of poisoned catalyst was performed at various temperatures under realistic SCR conditions. Both the standard SCR and fast SCR activities were evaluated. The fresh and poisoned catalysts were characterized by XRD, ICP, and BET surface measurement.

2 Experimental Methods

2.1 Catalyst Synthesis

Two zeolite types were studied, where the BEA zeolite was commercial (Zeolyst International, Si/Al = 19) while the SSZ-13 (chabazite structure) was synthesized. The SSZ-13 was chosen since Cu/SSZ-13 has been used for removing NO_x from diesel vehicles for several years [21]. In order to aid the understanding of the poisoning and regeneration ability of Cu/SSZ-13, we compare it with another Cu/zeolite, namely Cu/BEA due to the high activity of Cu/BEA for SCR with NH_3. It should be noted that Cu/BEA is not commercially applicable due to thermal degradation [22] and hydrocarbon poisoning [23] issues and was chosen in this work for mechanistic reasons together with Cu/SSZ-13.

The chabazite structure was obtained by hydrothermal conversion of a faujasite zeolite. NaOH pellets (Sigma-Aldrich > 98% anhydrous pellets) were dissolved in deionized water (Millipore) to prepare a 1 M NaOH solution. Sodium trisilicate (Na_2SiO_3, VWR) and deionized water were added to the NaOH solution under stirring. The respective proportions used were 250 g and 320 g for a 200 mL NaOH solution. After 15 min stirring, 25 g of faujasite zeolite were added (Zeolyst International, CBV720). The solution was stirred for 30 min at room temperature before addition of 105 g of the structure-directing agent (SDA), N,N,N-trimethyl-1-adamantanamine iodide (TMAAI, Zeo-Gen SDA 2825). After 30 min under stirring at room temperature, the mixture was transferred to the Teflon liner of a stainless-steel autoclave (Parr Instrument Company) for hydrothermal treatment. The autoclave was then placed in a static oven at 140 °C for 6 days. The mixture was centrifugated to collect the solid zeolite. The zeolite was then washed with deionized water and again collected by centrifugation. The pH of the liquid after washing was measured and the washing process was repeated until this pH was neutral. The zeolite was dried at room temperature for at least 12 h and calcined for 8 h at 550 °C with a slow heating rate of 0.5 °C/min. The sodium form of the zeolite (Na/SSZ-13), where Na^+ cations counterbalance the negative charge of the aluminum, was thus obtained.

The next step in the catalyst preparation was ion exchange. Similar ion exchange procedure was applied to both BEA and CHA zeolites. Sodium ions were exchanged by ammonium ions with a solution of ammonium nitrate (2 M) prepared by dissolving NH_4NO_3 (Sigma-Aldrich, > 99.0%) in deionized water. The zeolite powder was poured into the ammonium nitrate solution (33.33 mL/g of zeolite) and heated in an oil bath at 80 °C for 15 h under stirring. The powder was collected and washed as described previously. After drying at room temperature for at least 12 h, a second exchange with NH_4NO_3 was performed in the same way. After washing and drying (12 h at room temperature), the zeolite was added to a copper nitrate solution (0.2 M, 33.33 mL/g of zeolite) for the copper exchange stage. The copper nitrate solution was prepared by dissolving copper nitrate hemi(penta-hydrate) ($CuN_2O_6{\cdot}2.5H_2O$, Sigma-Aldrich) in deionized water. The mixture was maintained under vigorous stirring at 80 °C in an oil bath for 2 h. After washing and drying, the Cu-exchanged zeolite was calcined for 4 h at 550 °C with a heating rate of 5 °C/min.

For activity studies and poisoning in synthetic gas bench reactor (SGB), catalyst-coated monoliths were prepared. The cordierite honeycomb substrate (Corning) had a channel density of 400cpsi and was calcined at 600 °C for 2 h prior to coating. The monoliths were 20 mm long with a diameter of 15 mm for a volume of ca. 3.5 mL. The washcoat was made of 5wt% boehmite (Disperal P2, Sasol) and 95wt% catalyst. The washcoat powder was dispersed in a solution of 50 wt% deionized water and 50 wt% spectroscopic purity grade ethanol (Merck) with a liquid-to-solid mass ratio of 4. The cordierite substrate was dipped into the slurry to fill up the channels. The solvent was evaporated under a hot air gun while rotating manually the sample to ensure homogeneous coating. The process was repeated until 300 mg washcoat

was loaded on the substrate. Finally, the samples were calcined in air at 500 °C for 2 h.

2.2 Characterization Methods

The crystalline structure of the zeolites was examined by X-ray diffraction with a powder diffractometer (Siemens D5000) operating at 40 kV, using the $K\alpha_1$ emission ray of a Cu anode as the X-ray source ($\lambda = 1.54060$ Å). The X-ray diffraction angle was measured in the Bragg–Brentano geometry. The elemental composition of the catalyst was determined by ICP-AES (ALS Scandinavia). The specific surface area was measured by physisorption of N_2 at 77 K with a Micromeritics Tri-Star 3000 and calculated according to the BET method.

2.3 DRIFT Spectroscopy of NO Adsorption

NO adsorption was conducted on degreened and SO_2-poisoned monolithic catalysts treated in the flow reactor described below. The monoliths were crushed into a powder and then sieved to keep the particles fraction between 40 and 80 µm. The catalyst was placed in the sample holder of a heated Praying Mantis DRIFT cell (Harrick Scientific Products, Pleasantville, NY, USA) equipped with ZnSe windows and mounted on a Vertex 70 FTIR spectrometer (Bruker, Billerica, MA, USA) equipped with a liquid N_2-cooled MCT detector. The spectra were recorded with a resolution of 4 cm^{-1}. Before NO adsorption, the sample was firstly pretreated with 8% O_2 at 500 °C for 45 min and cooled to 30 °C. Ar was then flushed over the sample for 60 min at 30 °C and a background spectrum was recorded under these conditions (32 scans). The total gas flow rate was always 50 mL/min with Ar as balance gas. A total of 500 ppm NO in Ar was then fed to the catalyst bed at 30 °C for 60 min. Spectra (12 scans) were recorded with a 5-min interval during NO adsorption.

2.4 Reactor Setup

These experiments were performed in a reactor made of a horizontal quartz tube heated by a resistance coil. The assembly was wrapped in quartz wool for insulation. The monolith was placed at ca. 9 cm from the tube outlet and wrapped in a layer of quartz wool to fill the void between the monolith and the reactor wall and thus avoid gas bypassing. Two thermocouples were inserted from the reactor outlet to record the intra-catalyst temperature and the inlet gas temperature (ca. 0.5 cm in front of the monolith). The thermocouple measuring the inlet gas temperature was used as feedback to regulate the reactor temperature. The gases were delivered by mass flow controllers (Bronkhorst) and the water vapor flow was generated by a controlled evaporator mixer (Bronkhorst). The outlet gas composition was quantitatively determined by a gas FTIR spectrometer equipped with a liquid N_2-cooled MCT detector, a gas cell with a 5.11 m effective pathlength, and ZnSe windows (MultiGas 2030, MKS Instruments). The operating temperature of the spectrometer and of the inlet and outlet gas lines was 191 °C.

2.5 Activity Measurements

The samples were first subjected to a degreening step at 600 °C for 3 h. The gas flow composition for the degreening was 400 ppm NO, 400 ppm NH_3, 8% O_2, and 5% H_2O balanced in Ar. After this, activity measurement was done in standard SCR conditions (400 ppm NO, 400 ppm NH_3, 8% O_2, 5% H_2O balanced in Ar) and fast SCR conditions (200 ppm NO, 200 ppm NO_2, 400 ppm NH_3, 8% O_2, 5% H_2O balanced in Ar). Prior to the standard and fast SCR activity measurements, the catalyst was pre-treated at 500 °C for 20 min in a gas flow of 8% O_2 and 5% H_2O balanced in Ar. This pre-treatment was not applied after poisoning to observe solely the effect of the regeneration in SCR conditions. The standard SCR activity was measured stepwise with a 30-min-long step at each temperature. When necessary, the steps were extended to 45 min to ensure steady-state measurement. For the degreened catalysts, the activity was measured at 100, 125, 150, 175, 200, 250, 300, 350, 400, 450, and 500 °C. The fast SCR activity was measured at 175, 200, 250, 300, 350, 400, 450, and 500 °C with 45-min-long steps. In all experiments, argon was used as carrier gas and the total flow rate was 1.2 L/min (GHSV = 20,400 h^{-1}).

2.6 NH_3 TPD

After degreening and activity measurement, temperature-programmed desorption of NH_3 was conducted in the same reactor to measure the amount and strength of the different NH_3 storage sites. The catalyst was exposed to 400 ppm NH_3 and 5% H_2O in Ar for 90 min at 200 °C. The catalyst was then flushed with 5% H_2O in Ar for 1 h at 200 °C before ramping the temperature at 10 °C/min up to 600 °C. NH_3 TPD was also carried out after SO_x poisoning and regeneration (Fig. 1).

2.7 Poisoning

SO_2 and SO_2/SO_3 poisoning was carried out for 6 h at 250 °C with a gas flow containing 30 ppm SO_x, 400 ppm NO, 8% O_2, and 5% H_2O balanced in Ar. NH_3 was preadsorbed on the catalyst for 30 min at 250 °C (800 ppm NH_3, 5% H_2O balanced in Ar). SO_3 was produced by oxidation of SO_2 over a 7.7 wt% Pt/Al_2O_3 catalyst that was placed in a separate tubular reactor fed with SO_2, O_2 flows, and Ar. During SO_2/SO_3 poisoning, all gases passed through

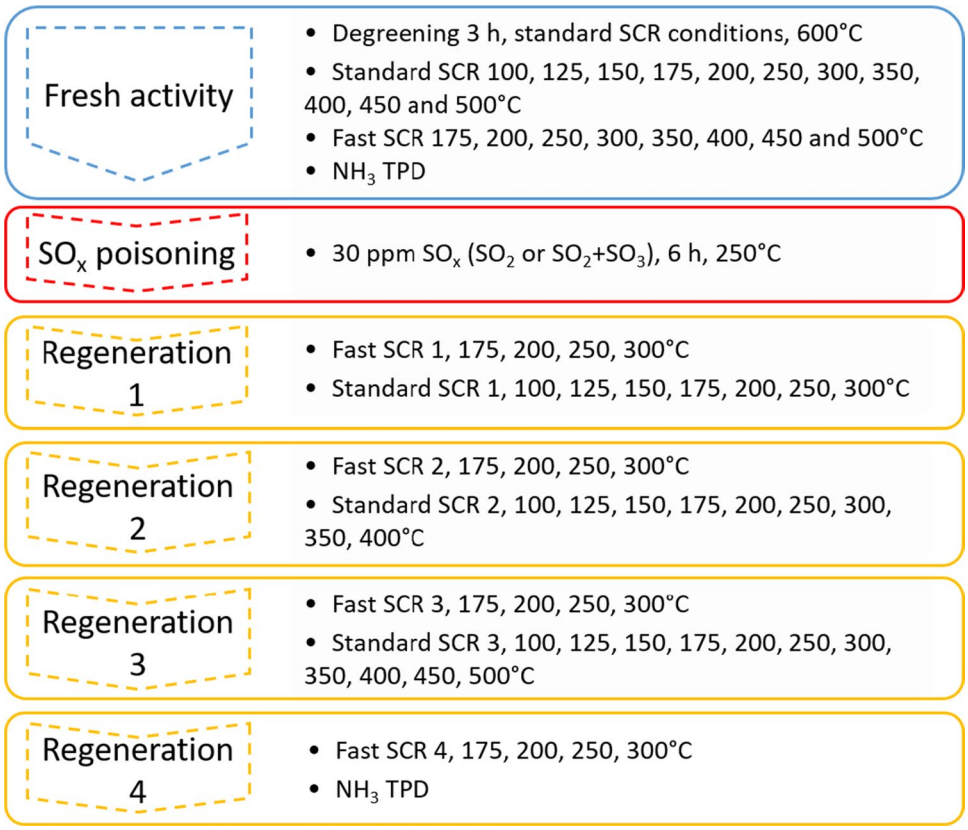

Fig. 1 Schematic diagram of the experimental procedure conducted on monolithic catalysts in SGB reactor. SO_x poisoning: 30 ppm SO_x, 400 ppm NO, 8% O_2, 5% H_2O balanced in Ar. Standard SCR: 400 ppm NO, 400 ppm NH_3, 8% O_2, 5% H_2O balanced in Ar. Fast SCR: 200 ppm NO, 200 ppm NO_2, 400 ppm NH_3, 8% O_2, 5% H_2O balanced in Ar

the SO_3 generator except NO, water vapor, and argon used to carry water vapor. The SO_3 generator temperature was set to 550 °C corresponding to a thermodynamic equilibrium of 80% SO_3. Assessment of the SO_2 oxidation was made in an empty reactor. The concentrations measured at the outlet were 24 ppm SO_3 and 6 ppm SO_2 for a feed containing 30 ppm SO_2 and 8% O_2 in Ar. The system was therefore able to generate SO_3 according to the thermodynamic levels. The SO_3 generator outlet was connected to the inlet line of the main reactor as close as possible to the reactor inlet and all lines were carefully heated with electrical heating bands. Ultra-low sulfur diesel (ULSD) contains a maximum mass fraction of 15 ppm sulfur (in the USA). The combustion of such fuel emits SO_2 in a concentration that inherently depends on the air-to-fuel ratio (A/F) and can be calculated. For diesel vehicles, A/F varies a lot depending on driving conditions and engine load. Assuming A/F = 25, the combustion of ULSD yields SO_2 = 0.518ppmv. In these conditions, our poisoning corresponds to the sulfur emission of a ca. 300 h driving cycle. It should be noted that the assumed A/F is rather low so the engine out SO_2 concentration can be even lower.

2.8 Regeneration

The regeneration procedure consisted in repeating the standard and fast SCR activity measurements described previously. However, at each repetition of standard SCR, measurement steps were added at a higher temperature. Thus, the effect of the added temperature step, in SCR conditions, could affect the subsequent fast SCR and standard SCR activity measurements. A complete diagram of the experiments is shown in Fig. 1.

3 Results and Discussion

3.1 Catalyst Characterization

Table 1 shows the Cu loading and the Si and Al content of the catalysts according to ICP-AES measurements. Cu/SSZ-13 exhibited a Cu loading of 1.7 wt% and a Si/Al molar ratio of 17 which corresponds to a Cu/Al ratio of 0.30. The Cu loading of Cu/BEA was 1.9 wt% and its Si/Al ratio was 19, corresponding to a Cu/Al ratio of 0.39. The sulfur loading

Table 1 Elemental composition of Cu/SSZ-13 and Cu/BEA determined by ICP-AES

Fresh powder	Cu/BEA	Cu/SSZ-13
Copper loading (wt%)	1.9	1.7
Si/Al ratio	19	17
S content after SO_2 poisoning (wt%)		
Crushed monolith (measured, based on crushed monolith)	0.11	0.01
Catalyst washcoat (calculated, based on only washcoat weight)	0.45	0.04

Table 2 BET surface area of fresh and SO_2-poisoned Cu/SSZ-13 and Cu/BEA

BET surface area (m^2/g)	Cu/BEA	Cu/SSZ-13
Fresh calcined powder	621	692
Degreened monolith*	128	167
Poisoned monolith*	124	163

*Crushed monolith, including both washcoat and cordierite

after SO_2 poisoning was also measured on crushed monolithic samples specially prepared for characterization. They were degreened and treated with SO_2 in the same reactor and according to the same procedure as the other samples used for activity measurements. It is clear that the Cu/BEA contained significantly more sulfur after poisoning compared to Cu/SSZ-13 (see Table 1).

Table 2 reports the BET surface area of the calcined fresh powders and the degreened and SO_2-poisoned monoliths which were crushed for the analysis. For the calcined powders, the Cu/SSZ-13 exhibited a slightly higher BET surface area. Crushed monoliths had significantly lower surface area than its corresponding catalyst powder. This is due to the dilution of the catalyst with crushed cordierite, since the specific surface area of cordierite substrate was negligible (0.7 m^2/g). Moreover, the surface area before and after SO_2 poisoning was similar for both catalysts, suggesting no significant blocking of the pores by sulfur deposits (Table 2). The sulfur content measured after SO_2 poisoning confirmed the sulfur deposition on both catalysts.

Figure 2 shows the X-ray diffractograms obtained with the Cu/SSZ-13 (a) and the Cu/BEA (b) catalysts. The diffractograms of the fresh powders are shown to evaluate the structure and the crystallinity. The diffractograms of the respective degreened and poisoned crushed monolith are shown with an offset. The diffractogram of the cordierite substrate is also given as a reference. Figure 2a shows sharp peaks at 2θ = 9°, 13°, 16°, 18°, 21°, 25°, and 31° corresponding to the chabazite structure [5, 6, 24]. Those characteristic peaks were detected with the degreened and SO_2-poisoned monoliths which shows that the zeolite structure was not altered by the coating process, the degreening, and the poisoning. The results also clearly show that all FAU was converted to CHA during synthesis, since the peak at 6.3° [25] is absent. Crystalline copper was not detected by XRD which rules out the presence of large copper particles. It rather suggests that copper is well-dispersed, as desired. Figure 2b shows analogous results in the case of Cu/BEA. The fresh powder shows a broad feature at 2θ = 7.6°, 22.5° corresponding to the BEA zeolite structure. No other diffraction peaks were detected, indicating that the copper was well-dispersed. The BEA zeolite is partially disordered which is confirmed by the large width of the peaks measured. Like for SSZ-13, the degreening and the SO_2 poisoning did not damage the structure of the BEA zeolite, which is in line with the surface area measurements (Table 2).

Figure 3 reports the NH_3 release during NH_3-TPD for the degreened, SO_2-poisoned, and SO_3-poisoned catalysts.

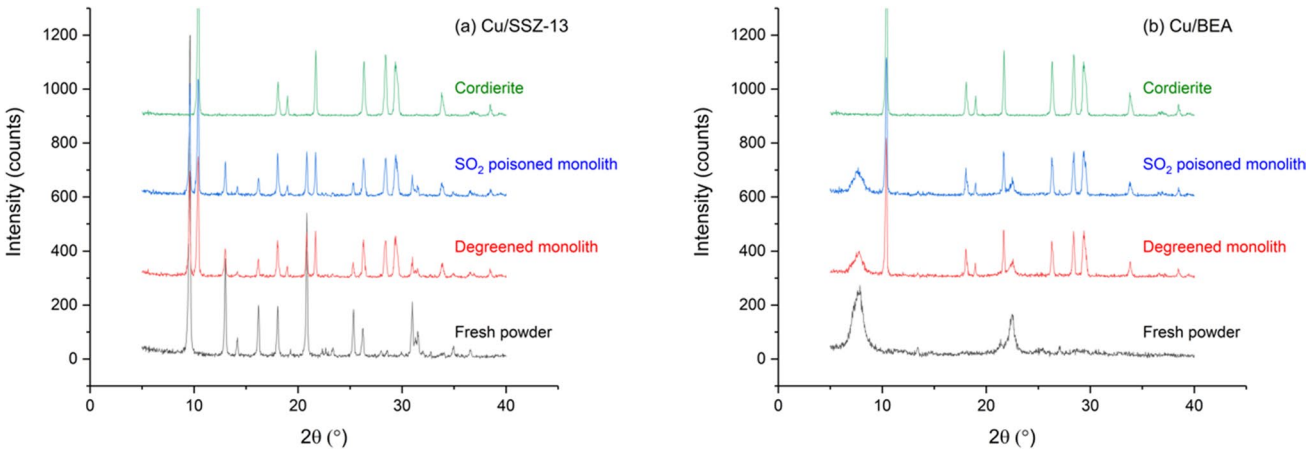

Fig. 2 XRD patterns of the fresh powders, the degreened crushed monoliths, and the SO_2-poisoned crushed monoliths. **a** Cu/SSZ-13 and **b** Cu/BEA

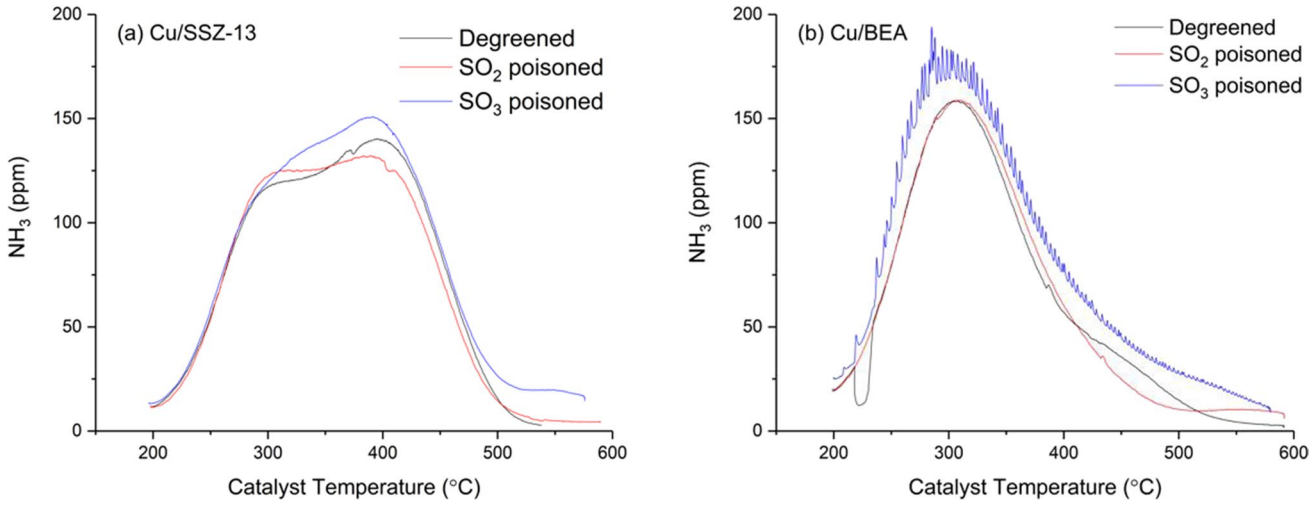

Fig. 3 NH_3-TPD profiles of degreened, SO_2-poisoned (and regenerated), and SO_3-poisoned (and regenerated) **a** Cu/SSZ-13 and **b** Cu/BEA. Feed: 5% H_2O in Ar, flowrate = 1.2L/min, ramping rate: 10 °C/min. During SO_2 poisoning, 30 ppm SO_2 was used, and during SO_3 poisoning, 24 ppm SO_3 and 6 ppm SO_2, in the presence of 400 ppm NO, 8% O_2, 5% H_2O for both cases

Figure 3a presents the typical binodal NH_3 profile of Cu/SSZ-13, constituted of two main peaks. The low-temperature release, centered at 300 °C, was assigned to NH_3 adsorbed on exchanged copper ions which are Lewis acid sites [6, 26]. The high-temperature peak was assigned to NH_3 adsorbed on the stronger sites, i.e., the Brønsted acid sites of the zeolite and, in lesser extent, the strongest of the Lewis sites [6, 27]. The NH_3 TPD after SO_2 and SO_3 poisoning was performed after all regeneration steps (see Fig. 1); thus, a large amount of sulfur was likely already removed. After SO_2 poisoning and regeneration, the amount of NH_3 stored was similar. However, SO_2 poisoning slightly changed the binding strength, indicated by the larger low-temperature peak and the smaller high-temperature peak. Wijayanti et al. [5] found that sulfur adsorption could induce new ammonia storage sites in Cu/SSZ-13, and this might be the reason for the small shift in binding strength of the ammonia in our results (see Fig. 3a). Interestingly, SO_3 poisoning and regeneration increased the NH_3 storage, which is in line with the results by Wijayanti et al. [5] and Brookshear et al. [8] using SO_2. In addition, a desorption feature at 555 °C was observed and was correlated to a sulfur release (Fig. 4a). The additional stored ammonia can have formed ammonium sulfate or ammonium bisulfate with the adsorbed sulfur [8, 28]. As shown in Fig. 4a, SO_2 was released during the NH_3-TPD. Both Cu/SSZ-13 samples showed one peak at 400 °C and

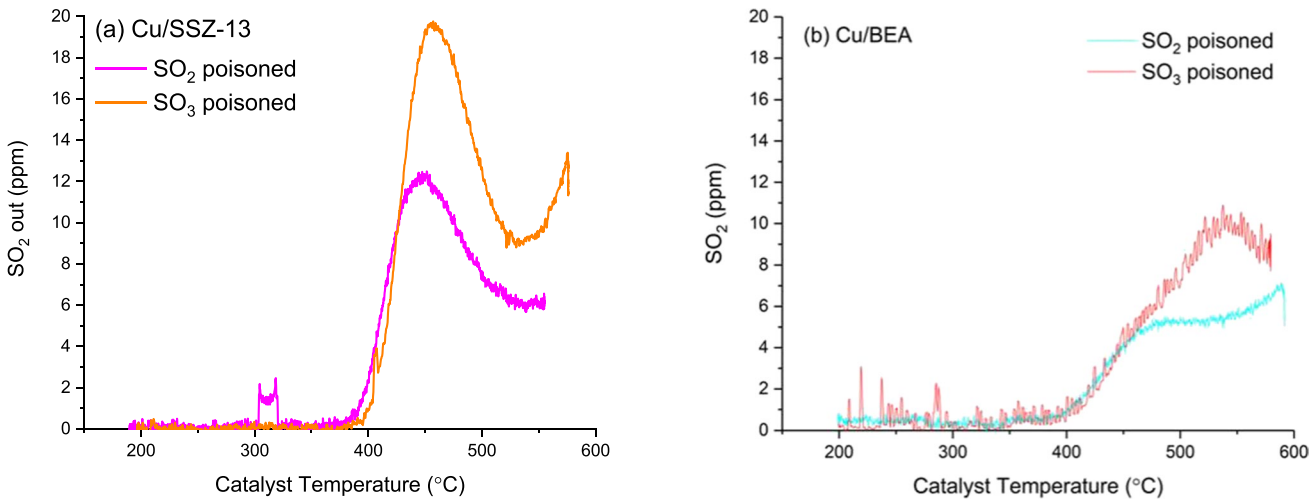

Fig. 4 SO_2 desorption during NH_3-TPD carried out on SO_2-poisoned (and regenerated) and SO_3-poisoned (and regenerated) **a** Cu/SSZ-13 and **b** Cu/BEA. Feed: 5% H_2O in Ar, flowrate = 1.2L/min, ramping rate: 10 °C/min. During SO_2 poisoning, 30 ppm SO_2 was used, and during SO_3 poisoning, 24 ppm SO_3 and 6 ppm SO_2, in the presence of 400 ppm NO, 8% O_2, 5% H_2O for both cases

the SO_3-poisoned catalyst showed an additional incomplete peak starting to form at 550 °C. This is consistent with the SO_2 desorption observed by Wijayanti et al. [12] at 540 and 780 °C, after SO_2 poisoning of Cu/SSZ-13. The SO_2 release measured was greater for the SO_3-poisoned catalyst, indicating larger sulfur storage for the SO_3 poisoned case. However, it should be noted that it is possible that the sulfates also are released as SO_3 or H_2SO_4, but these species were not measured. The study of the stored sulfur species by Su et al. [4] revealed three distinct types of sulfur species, the thermal decomposition of which releases SO_2. They observed desorption features peaking at 545, 632, and 772 °C, assigned to H_2SO_4, $CuSO_4$, and $Al_2(SO_4)_3$, respectively. Since we observe a sulfur desorption starting from 550 °C, it could possibly be related to the decomposition of H_2SO_4 adsorbed on the catalyst, in line with the work by Su et al. [4].

The NH_3-TPD of Cu/BEA showed one main peak at 310 °C and the degreened catalyst showed a shoulder at 450 °C which was absent after SO_2 poisoning. A weak peak at 560 °C can be observed on the SO_2-poisoned catalyst and a shoulder at 530 °C was present after SO_3 poisoning. In general, the NH_3 storage was not decreased with sulfur poisoning and regeneration. Like for Cu/SSZ-13, the NH_3 release was even enhanced with SO_3 exposure and small amounts of SO_2 were released from 400 °C (Fig. 4b). A first SO_2 peak appeared at 475 °C on the SO_2-poisoned Cu/BEA. This peak appeared as a shoulder on the SO_3-poisoned Cu/BEA and was probably due to ammonium sulfate decomposition. A second peak was observed at 540 °C on the SO_3-poisoned Cu/BEA and at a temperature higher than 600 °C on the SO_2-poisoned Cu/BEA. These peaks demonstrated the formation of different sulfate species such as H_2SO_4, $CuSO_4$ depending on the sulfur feed used during poisoning. This result is consistent with the influence of SCR conditions and H_2O on the amount and partition of sulfate species demonstrated by Su et al. [4].

To summarize, the catalyst characterization indicates that the physical properties of the catalysts were almost unaffected by the SO_x treatments. The SO_2 desorption observed during NH_3-TPD at the end of the poisoning and regeneration procedure indicates that some stored sulfur species remained despite the regeneration.

3.2 Standard SCR Activity for Degreened and Poisoned Samples

Figure 5 is a comparative graph reporting the steady-state conversion of NO measured at several temperatures in the range of 100–500 °C. The curves depict the standard SCR activity for the degreened catalysts, after SO_2 poisoning and after SO_3/SO_2 poisoning (denoted SO_3 poisoning). The activity of Cu/SSZ-13 is reported in Fig. 5a, which also includes the results for the degreened Cu/BEA. Both degreened catalysts show similar activity characterized by a low NO conversion below 150 °C, a conversion greater than 90% between 250 and 350 °C, and the slight decline of the conversion at T > 350 °C. After SO_2 poisoning, the light-off temperature increased, but even more so after SO_3 poisoning. For example, the NO conversion was 51% at 250 °C and 81% at 300 °C for SO_2 poisoned Cu/SSZ-13, while after SO_3/SO_2 poisoning, the NO conversion at 300 °C was only 44%. The results in Fig. 5a clearly demonstrate the high sensitivity of Cu/SSZ-13 to SO_2 and, to a greater extent, to SO_3. It should be noted that N_2O was also formed during SCR, even more so during fast SCR, and that SO_2 and SO_3 significantly decreased the N_2O formation (data not shown).

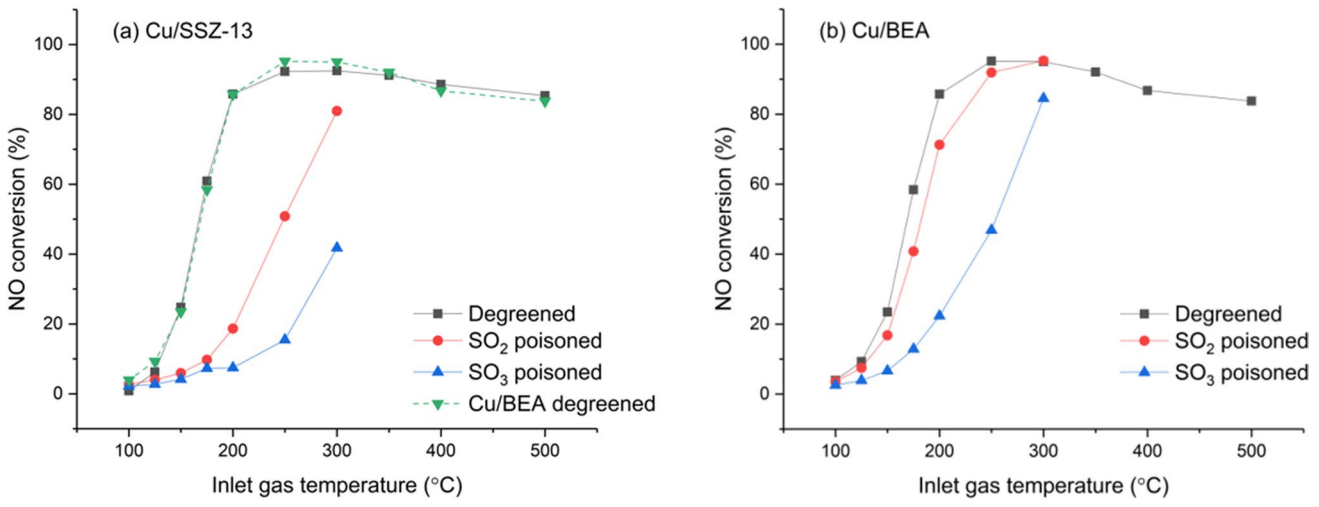

Fig. 5 Standard SCR activity (NO conversion) of degreened, SO_2-poisoned, and SO_3-poisoned **a** Cu/SSZ-13 and **b** Cu/BEA. Feed: 400 ppm NO, 400 ppm NH_3, 8% O_2, 5% H_2O in Ar, flowrate = 1.2L/min. During SO_2 poisoning, 30 ppm SO_2 was used, and during SO_3 poisoning, 24 ppm SO_3 and 6 ppm SO_2, in the presence of 400 ppm NO, 8% O_2, 5% H_2O for both cases

The impact of SO_2 and SO_3 poisoning on the SCR activity of Cu/BEA is compared in Fig. 5b. Also, for this catalyst, the NO conversion dropped at 175 and 200 °C after SO_2 poisoning. However, the general impact of SO_2 was moderate on Cu/BEA and much less pronounced than on Cu/SSZ-13 despite the greater SO_2 storage of Cu/BEA (Table 1). One possible reason for this could be that since BEA has significantly larger pores, the adsorbed sulfur species causes less sterical hindrance for the reactants to access the Cu sites. Like for Cu/SSZ-13, SO_3 poisoning was more detrimental than SO_2 poisoning on Cu/BEA. The SO_3-poisoned Cu/BEA was again more active than the SO_3-poisoned Cu/SSZ-13 with 86% NO conversion at 300 °C, compared with 44% for Cu/SSZ-13.

3.3 Fast SCR Activity for Degreened and Poisoned Samples

The selective reduction of an equimolar mixture of NO and NO_2 with NH_3 in presence of O_2 is known as fast SCR due to its faster kinetics. These conditions are aimed by the upstream oxidation catalyst which converts NO to NO_2 for a more efficient NO_x removal process. However, at a high temperature, this catalyst also converts SO_2 to SO_3. The fast SCR reaction was studied, and the activity is reported in Fig. 6 for Cu/SSZ-13 (a) and Cu/BEA (b). The NO conversion of the degreened Cu/SSZ-13 was close to 80% at 175 °C and increased to higher than 90% between 200 and 400 °C. The activity declined below 80% at 500 °C. Similar observations can be made for Cu/BEA as seen in Fig. 6. It can be noted that the NO conversion at low temperature was higher for the fast SCR than for the standard SCR. The NO_2 conversion (not shown) was high (above 90% and for mid-range temperatures 100%). The SO_2 exposure led to a significant activity decrease of Cu/SSZ-13 below 200 °C. However, the fast SCR was less impaired than the standard SCR. The SO_3 poisoning led to an even greater deactivation of Cu/SSZ-13 with a maximum NO conversion of only 80% at 300 °C. As opposed to Cu/SSZ-13, Cu/BEA was only mildly deactivated by SO_2 and SO_3 exposure (Fig. 6b). The lowest conversion for Cu/BEA, noted at 175 °C, was 65% and 82% after SO_2 poisoning and SO_3 poisoning, respectively. It appeared clearly that Cu/SSZ-13 is more sensitive than Cu/BEA to both SO_2 and SO_3 exposure. Cu/SSZ-13 is prone to severe deactivation when exposed to sulfur compounds, especially SO_3. BEA is a type of zeolite characterized by wide channels constituted of 12-membered rings interconnected and forming cages [29]. SSZ-13, on the other hand, is a narrow-pore zeolite which consists of 6-membered rings forming hexagonal prisms (d6r) and chabazite cages (cha). The widest window of the chabazite cages is made of 8-membered rings with a 3.8 Å diameter. The smaller channel opening and cage volume could be one reason why Cu/SSZ-13 is more prone to pore blocking by sulfate species than BEA and more subjected to deactivation by SO_2 and SO_3. Cu/SSZ-13 is preferred as an SCR catalyst for its better hydrothermal stability and lower hydrocarbon storage than Cu/BEA. However, our results show that SSZ-13 is more subjected to sulfur-induced deactivation than Cu/BEA. Since SO_3 has a much larger effect than SO_2 on Cu/SSZ-13, it would be beneficial to produce as little SO_3 as possible. For a durable and optimal NO_x reduction, it is crucial to operate

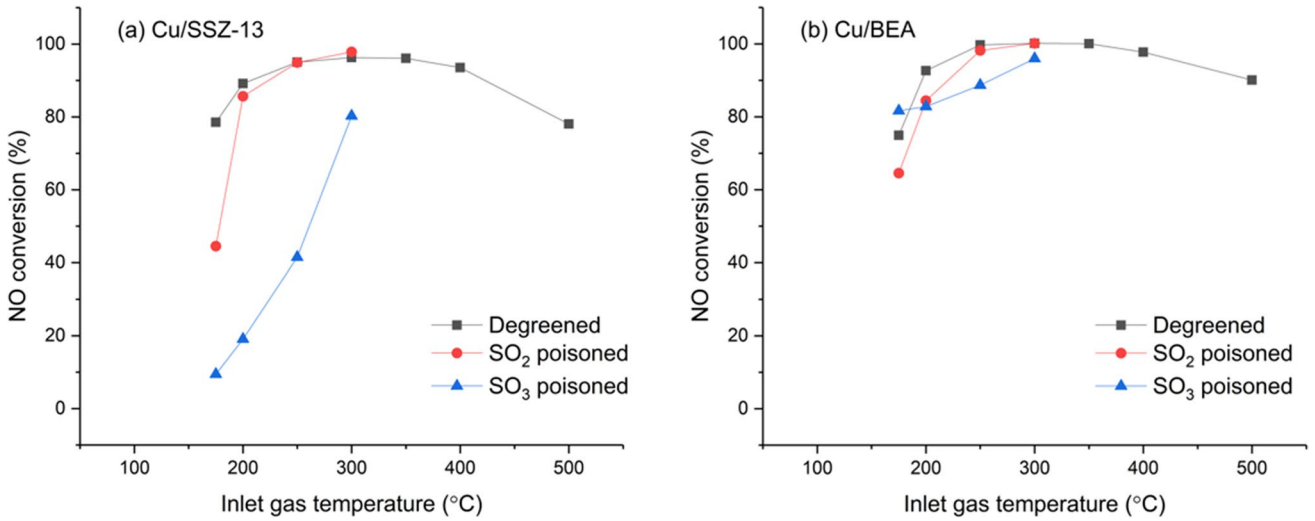

Fig. 6 Fast SCR activity (NO conversion) of degreened, SO_2-poisoned, and SO_3-poisoned **a** Cu/SSZ-13 and **b** Cu/BEA. Feed: 200 ppm NO, 200 ppm NO_2, 400 ppm NH_3, 8% O_2, 5% H_2O in Ar, flowrate = 1.2L/min. Note: only NO conversion is shown, the NO_2 conversion was 100% at all temperature steps. During SO_2 poisoning, 30 ppm SO_2 was used, and during SO_3 poisoning, 24 ppm SO_3 and 6 ppm SO_2, in the presence of 400 ppm NO, 8% O_2, 5% H_2O for both cases

in fast SCR conditions since Cu/SSZ-13 is less sensitive to SO_2 and SO_3 in fast SCR conditions than in standard SCR conditions.

The impact of SO_2 exposure on fast SCR activity is moderate compared to its impact on standard SCR when the SCR unit is considered. However, taking the whole aftertreatment system into account that consists of an oxidation catalyst followed by the SCR converter, SO_2 will affect the oxidation catalyst and inhibit its ability to oxidize NO to NO_2 [14] which is necessary to perform the fast SCR on the SCR catalyst. Overall, SO_2 exposure will decrease the NO_2/NO_x ratio which will lower the amount of NO_x that can react in the fast SCR reaction. This will lead to an overall lower rate since a higher amount of NO needs to react in the slower standard SCR reaction.

3.4 Regeneration in SCR Conditions: Standard SCR

To desorb sulfur and restore the initial activity, hydrothermal treatment at a high temperature is usually advocated [9, 19]. A reductive atmosphere is also beneficial to decompose the stored sulfur oxides [30]. However, such treatments affect the zeolite structure and the dispersion of active copper centers. High temperature in presence of water vapor is known to degrade the crystallinity of the zeolite structure, and at very high temperatures, the structure collapses [2, 31], which urges the development of highly stable zeolites. The detrimental effect of reducing treatment on the copper dispersion and the subsequent SCR activity has been revealed by Auvray et al. [6, 32]. It was shown that exchanged copper ions tend to agglomerate in larger particles under the action of hydrogen. Therefore, in this study, the regeneration in lean SCR conditions at temperatures up to 500 °C was investigated. The stepwise activity measurement for standard and fast SCR was used and repeated after sulfur poisoning as a regeneration procedure. Each time the standard SCR activity was measured, the upper temperature boundary was increased from 300 °C for the first measurement after poisoning to 400 and 500 °C for the second and third measurements, respectively. Figure 7 presents the standard SCR activity of Cu/SSZ-13 (a) and Cu/BEA (b) after SO_2 poisoning and regeneration in standard SCR conditions. For Cu/SSZ-13 (Fig. 7a), the NO conversion measured during the first repetition (denoted regeneration 2) was similar to the NO conversion measured after SO_2 poisoning (denoted regeneration 1). Since the maximum temperature of the regeneration 1 stage was 300 °C, this result indicates that no regeneration occurred in SCR conditions at 300 °C. However, a significant NO conversion improvement was noted for the second measurement repetition (regeneration 3) between 200 and 300 °C. Before the regeneration 3 experiment, the poisoned catalyst was exposed to SCR conditions at 400 °C during the regeneration 2. This result shows that partial regeneration of SO_2-poisoned Cu/SSZ-13 occurred under SCR conditions at 400 °C.

The NO conversion was also improved by the poisoning and regeneration compared to the degreened one at temperatures higher than 350 °C. This has also been found for thermal aging [33] and could be due to larger deactivation of the ammonia oxidation reaction resulting in increased selectivity for the SCR reaction. The presence of SCR conditions is important for the sulfur regeneration, as previously

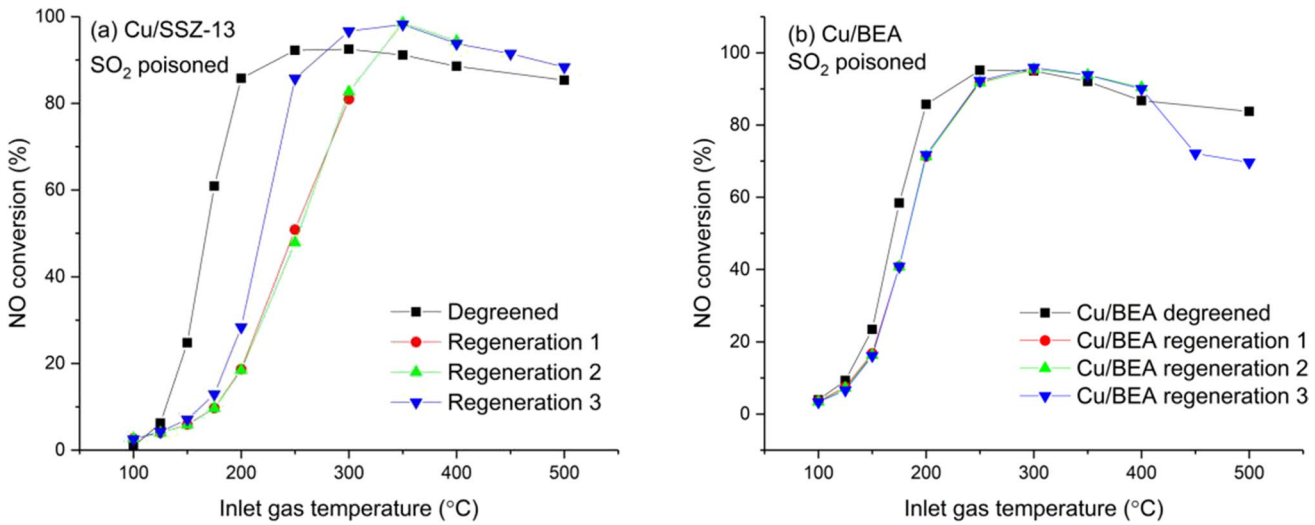

Fig. 7 Standard SCR activity (NO conversion) of degreened catalysts and during regeneration of SO_2-poisoned **a** Cu/SSZ-13 and **b** Cu/BEA. Feed: 400 ppm NO, 400 ppm NH_3, 8% O_2, 5% H_2O in Ar, flowrate = 1.2L/min. Regeneration 1 is performed directly after the poisoning, thus showing the poisoned catalyst. Note that regeneration 1 and 2 for Cu/SSZ-13 and regeneration 1, 2, and 3 for Cu/BEA are overlapping. During SO_2 poisoning, 30 ppm SO_2 was used in the presence of 400 ppm NO, 8% O_2, 5% H_2O

shown by Kumar et al. [30]. Moreover, Brookshear et al. [8] reported significant regeneration in lean conditions at 350 °C but obtained full activity recovery only with a DeSOx temperature of 500 °C. Hammershøi et al. [19] found almost full recovery after regeneration in SCR conditions at 550 °C. However, some remaining poisoning was still found after the 550 °C treatment in that study.

Sulfur poisoning and regeneration for Cu/BEA are shown in Fig. 7b. The results show that Cu/BEA was much less influenced by SO_2 poisoning compared to Cu/SSZ-13, but also that the Cu/BEA did not regain any activity during the regenerations up to 400 °C. This result can indicate an irreversible deactivation caused by the SO_2 poisoning to the catalyst or that higher temperatures are needed for the regeneration.

The effect of the regeneration of SO_3-poisoned catalysts is shown in Fig. 8. Like after SO_2 poisoning, the activity of Cu/SSZ-13 (Fig. 8a) was not recovered at all during the regeneration 2 (after SCR conditions up to 300 °C in regeneration 1) but was improved during the regeneration 3. This indicates that partial regeneration of a SO_3-poisoned Cu/SSZ-13 was possible at 400 °C. Like after SO_2 poisoning, the NO conversion at high temperatures (> 350 °C) was improved by the SO_3/SO_2 poisoning and the regeneration. After regeneration 3, the standard SCR activity of Cu/SSZ-13 was significantly lower when the poisoning was carried out with the SO_3/SO_2 mixture than with SO_2.

The SO_3 poisoning impaired significantly the activity of Cu/BEA. In these conditions, the regeneration had a greater impact than on the SO_2-poisoned Cu/BEA. Figure 8b shows the partial activity recovery during regeneration 3, indicating that SCR conditions at 400 °C were able to partly reactivate Cu/BEA. This observation is similar for both Cu/SSZ-13 and Cu/BEA after SO_3/SO_2 poisoning.

3.5 Regeneration in SCR Conditions: Fast SCR

The various sulfur species formed on the catalyst have different stability and affect different sites. The exchanged Cu attached to one Al center (ZCuOH) was reported to be strongly affected upon sulfation of Cu/SSZ-13 [34]. Jangjou et al. [28] suggested that copper bisulfites form preferentially on ZCuOH while ammonium sulfates tend to form on Cu^{2+} connected to a pair of framework Al (Z2Cu sites). These two sites present different reactivity and roles in oxidation reactions and SCR. Therefore, the impact of sulfation and regeneration on the fast SCR was studied. Fast SCR activity measurements were part of the regeneration procedure (see Fig. 1). However, since full conversion of NO_x was reached at a rather low temperature, the measurements were limited to 300 °C. Consequently, the impact of the fast SCR sequences on the sulfur regeneration was expected to be minor compared to the standard SCR steps. The fast SCR activity was measured four times after poisoning. It allowed us to probe the regeneration after each standard SCR step, whose maximum temperature was 300, 400, and 500 °C, respectively. Figure 9 shows the NO conversion during fast SCR of the SO_2-poisoned Cu/SSZ-13 (a) and Cu/BEA (b). Figure 9a shows that regeneration 1 and 2 were similar for Cu/SSZ-13, indicating no regeneration during SCR at 300 °C. However, fast SCR activity was regained during SCR at 400 and 500 °C, as suggested by the regeneration 3

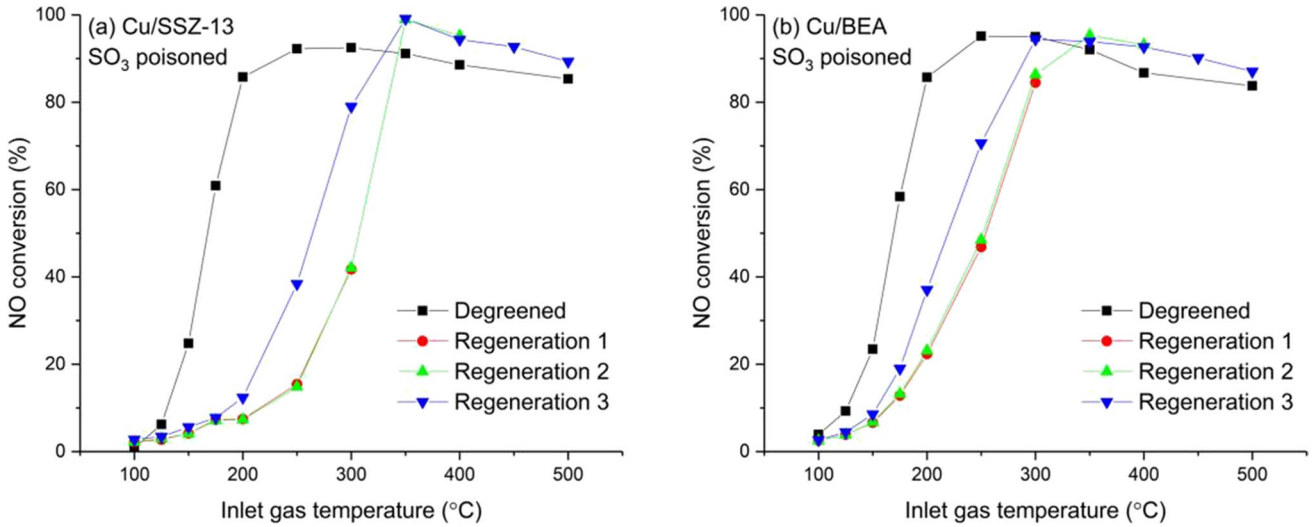

Fig. 8 Standard SCR activity (NO conversion) of degreened catalysts and during regeneration of SO_3-poisoned **a** Cu/SSZ-13 and **b** Cu/BEA. Feed: 400 ppm NO, 400 ppm NH_3, 8% O_2, 5% H_2O in Ar, flowrate = 1.2L/min. Regeneration 1 is performed directly after the poisoning, thus showing the poisoned catalyst. During SO_3 poisoning, 24 ppm SO_3 and 6 ppm SO_2, in the presence of 400 ppm NO, 8% O_2, 5% H_2O were used

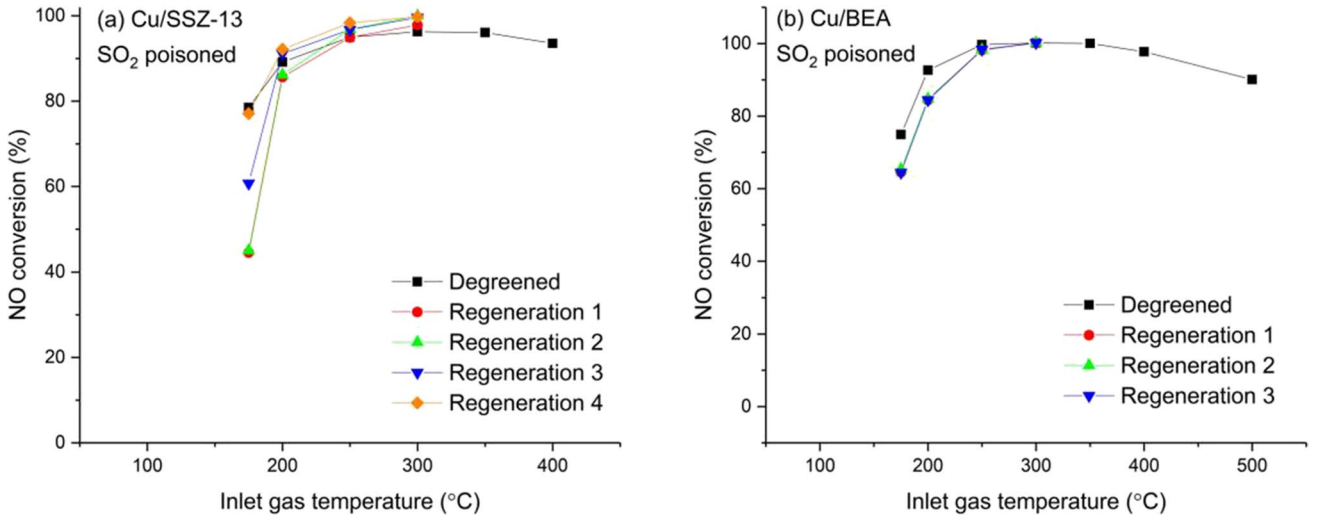

Fig. 9 Fast SCR activity (NO conversion) of degreened catalysts and during regeneration of SO_2-poisoned **a** Cu/SSZ-13 and **b** Cu/BEA. Feed: 200 ppm NO, 200 ppm NO_2, 400 ppm NH_3, 8% O_2, 5% H_2O in Ar, flowrate = 1.2L/min. Regeneration 1 is standard SCR up to 300 °C. During SO_2 poisoning, 30 ppm SO_2 was used in the presence of 400 ppm NO, 8% O_2, 5% H_2O

and regeneration 4 measurements. The full activity recovery at 175 °C can be noted during regeneration 4. The improvement of the degreened activity can be noted as well between 200 and 300 °C. As for the standard SCR, the regeneration up to 400 °C was inefficient for the fast SCR on Cu/BEA (Fig. 9b) after SO_2 poisoning; however, Cu/BEA was also significantly less poisoned compared to Cu/SSZ-13.

The regeneration effect after SO_3/SO_2 poisoning was then examined for the fast SCR (Fig. 10). SO_3 greatly decreased the fast SCR activity of Cu/SSZ-13 (Fig. 10a), but regeneration was possible in SCR conditions at 400 and 500 °C, whereas 300 °C was not sufficient to observe any improvement. After regeneration 4, full recovery was not obtained at 175 °C, indicating that some sulfur was remaining on the catalyst. Interestingly, the activity was greater than the degreened activity at a temperature between 200 and 300 °C. Sulfur poisoning results in the formation of different sulfur species such as H_2SO_4, $CuSO_4$, $Al_2(SO_4)_3$ [4], and also ammonium sulfates (in the presence of ammonia). During mild regeneration, such as our regeneration, it is likely that some of the ammonium sulfates, which are less stable [12], are decomposed, while the more stable copper sulfates

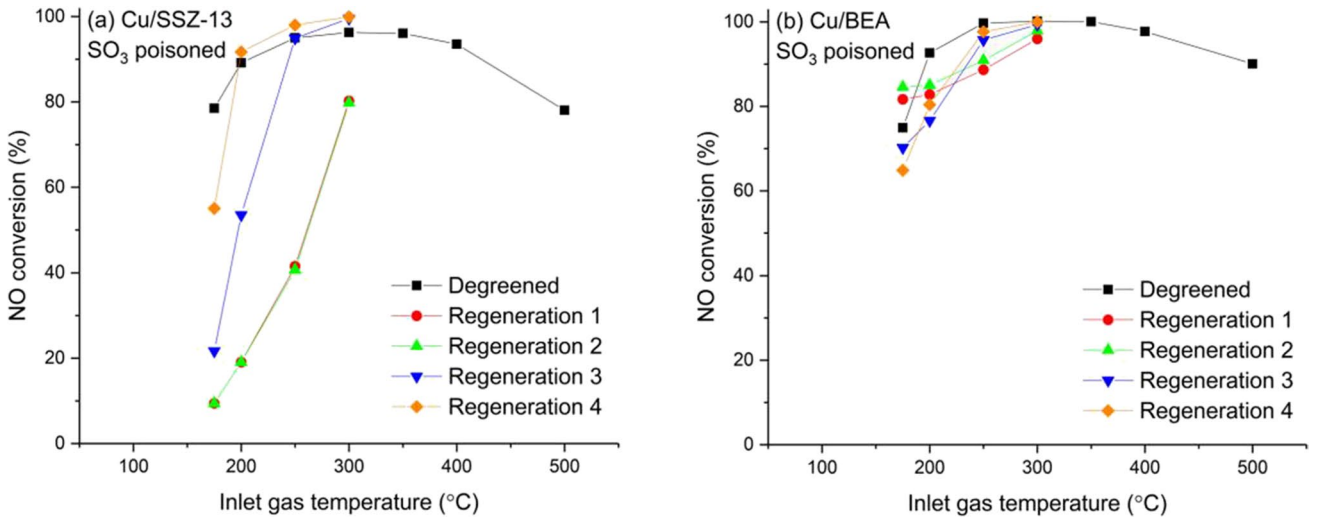

Fig. 10 Fast SCR activity (NO conversion) of degreened catalysts and during regeneration of SO_3-poisoned **a** Cu/SSZ-13 and **b** Cu/BEA. Feed: 200 ppm NO, 200 ppm NO_2, 400 ppm NH_3, 8% O_2, 5% H_2O in Ar, flowrate = 1.2L/min. Regeneration 1 is standard SCR up to 300 °C. During SO_3 poisoning, 24 ppm SO_3 and 6 ppm SO_2 were used in the presence of 400 ppm NO, 8% O_2, 5% H_2O for both cases

remain. The formation of copper sulfates is increased in the presence of copper oxides [12], and copper oxides also enhance the ammonia oxidation. It is possible that the presence of copper sulfates reduces the competitive ammonia oxidation reaction and thereby increases the selectivity in the SCR process. Separate ammonia oxidation experiments (data not shown) show that some ammonia oxidation occurs at 300 °C, which could explain the increased SCR activity at 300 °C, but not at 200 °C. However, the N_2O formation also decreased significantly during poisoning (data not shown), indicating that there is less ammonium nitrate formation after sulfur poisoning. Since ammonium nitrate formation hinders the SCR activity [35], we suggest that the reason for the increased SCR activity at low temperature could be related to that sulfur species blocks the ammonium nitrate formation, and thereby results in increased NO conversion. The SO_3/SO_2 exposure on Cu/BEA (Fig. 10b) had a dual effect with a promotion at 175 °C and poisoning at a higher temperature. These two features of the poisoned Cu/BEA tended to disappear with the regeneration. Figure 10b displays the global improvement during regeneration 2 and the degradation of the activity at 175 °C in regeneration 3 and 4. At the end of the process, however, the activity at 250 and 300 °C had retrieved its degreened level.

In general, Cu/SSZ-13 was more affected by SO_2 and SO_3/SO_2 poisoning than Cu/BEA. This was clearly evidenced with SO_2 poisoning since it only decreased moderately the SCR activity of Cu/BEA. However, in real conditions, SO_3 is formed over the diesel oxidation catalyst and our results demonstrated that SO_3 had a greater impact than SO_2 on both Cu/SSZ-13 and Cu/BEA. SO_3 exposure was able to decrease significantly the standard SCR of the SO_2-resistant Cu/BEA and the fast SCR activity of Cu/SSZ-13. Our results suggest the importance of adding SO_3 during poisoning studies of SCR catalysts and in addition that the zeolite used plays a major role in the poisoning and regeneration. These results emphasize the need to study in detail the SO_3 chemistry on the SCR catalysts. The regeneration in SCR operating conditions was possible to some extent whether the poisoning was performed using SO_2 or SO_3/SO_2, which indicates the chemical and reversible nature of the poisoning.

3.6 DRIFT Spectroscopy

NO adsorption was performed on degreened and SO_2-poisoned catalysts in a DRIFT cell. Figure 11 compares the FTIR spectra recorded after 55 min of NO exposure on Cu/SSZ-13 and Cu/BEA. On Cu/SSZ-13, the T-O-T structure vibration is disturbed by the exchanged Cu^{2+}. Upon adsorption of a probe molecule such as NO or NH_3 on Cu, the T-O-T vibration bands appear as negative bands at approximately 900 cm^{-1} and 950 cm^{-1}. These bands are known to correspond to the Z2Cu and ZCuOH centers, respectively [11]. The inset of Fig. 11a shows that the ratio ZCuOH/Z2Cu was lower on the sulfated Cu/SSZ-13 than the degreened sample. These results indicate that stable sulfates were formed preferentially on the copper coordinated to one framework Al and one hydroxyl group (ZCuOH). Thus, a part of these ZCuOH sites was blocked and unavailable to NO during the NO adsorption step. The decrease of the amount of ZCuOH upon sulfation was also observed by Tang et al. [20] and Luo et al. [34]. Shih et al. [3] reported on the higher S:Cu molar ratio of ZCuOH than Z2Cu sites indicating that ZCuOH was more prone to sulfation whereas Z2Cu was rather insensitive to SO_2 poisoning, which is in

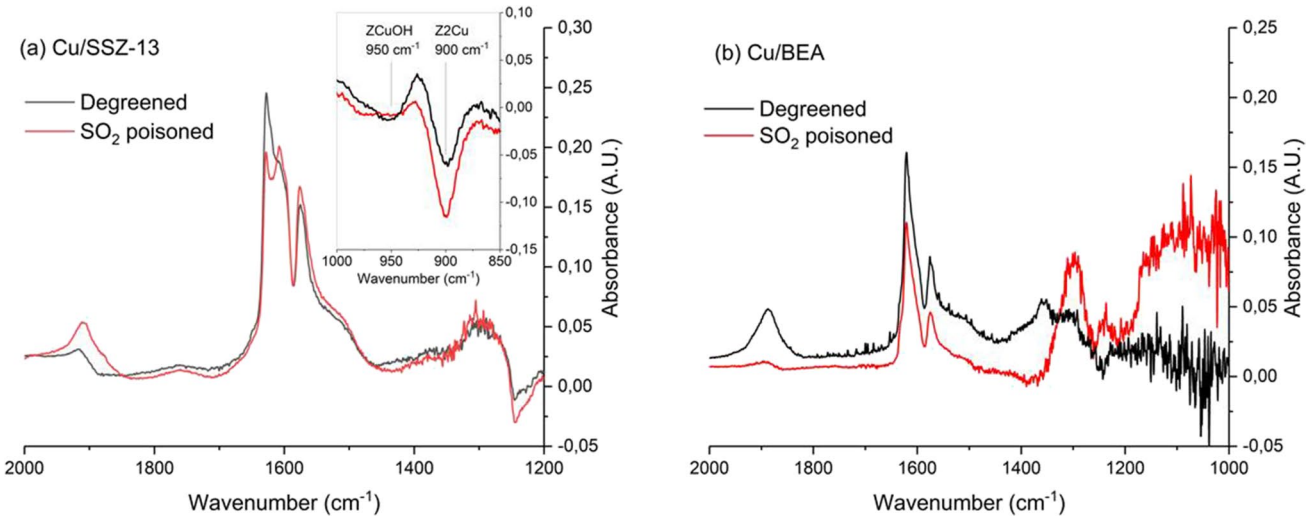

Fig. 11 DRIFT spectroscopy absorbance spectra of NO at 30 °C after oxidizing pretreatment at 500 °C of degreened and SO_2-poisoned **a** Cu/SSZ-13 and **b** Cu/BEA catalysts. The spectra were recorded after 55 min of NO exposure

line with our results. ZCuOH can readily form stable copper bisulfites and bisulfates in the presence of SO_2 alone while the sulfation of Z2Cu sites is obtained with cofeeding SO_2 and NH_3 to form ammonium sulfates [36]. Catalysts with a high Si:Al ratio present a higher ZCuOH:Z2Cu and therefore are prone to formation of stable copper bisulfites that oxidize further to bisulfates. Catalysts with low Si:Al are mainly deactivated by ammonium sulfates. Low-temperature deactivation occurs on Cu/SSZ-13 upon SO_2 poisoning regardless of the Si:Al ratio. However, the regeneration is greatly impacted by the nature of the inhibiting sulfate species. Therefore, regeneration of low Si:Al Cu/SSZ-13 can be achieved at relatively low temperature. Upon hydrothermal aging, Cu cations migrate through the CHA framework and it has been evidenced that ZCuOH is converted to the more stable Z2Cu [20, 23, 34] located in the 6-member rings. In particular, Wei et al. [37] have demonstrated a decrease in sulfur storage and the mitigation of SO_2 poisoning on mildly hydrothermally aged (750 °C) Cu/SSZ-13. The conversion of ZCuOH to Z2Cu offers a greater resistance to SO_2 poisoning and an improved SCR efficiency at high temperature because ZCuOH is active for NH_3 oxidation. However, the SCR activity is lost at low temperature, which is very problematic. After higher hydrothermal aging temperature (800 °C), Wijayanti et al. [12] also found a lower sulfur amount stored on the Cu/SSZ-13, but the formation of some copper oxides resulted in more stable copper sulfates being formed. In addition, copper oxides are less active for ammonia SCR reaction, which would reduce the catalyst efficiency.

The band at 1910 cm^{-1} could be assigned to NO adsorbed on Cu^{2+} (mononitrosyl group) [38–40]. It increased rapidly before decreasing slowly with time on the poisoned Cu/SSZ-13. The band at 1580 cm^{-1} can be assigned to a nitrate species adsorbed on Cu [38] while the bands at 1607 and 1628 cm^{-1} can be assigned to monodentate and bridging nitrates adsorbed on the zeolite framework, respectively [41]. SO_2 poisoning affected these latter two bands by switching their relative ratio, increasing the monodentate/bridged nitrate ratio. This result was consistent with the blocking of sites by sulfates since bridge nitrates required two sites.

NO adsorption on Cu/BEA showed similarities with Cu/SSZ-13 (Fig. 11b) concerning the monodentate nitrate band at 1619 cm^{-1} and the nitrate on Cu^{2+} band at 1575 cm^{-1}. The band assigned to NO adsorbed on Cu^{2+} was located at 1890 cm^{-1} on Cu/BEA. This band decreased rapidly when NO was turned off while the band at 1350 cm^{-1} kept growing. The latter band was tentatively assigned to nitrite species. On the poisoned Cu/BEA, the NO-Cu^{2+} band decreased during NO exposure after 30 min. In addition, new bands at 1320 cm^{-1} and 1240 cm^{-1} and a broad band at 1100 cm^{-1} appeared. The bands at 1320 and 1240 cm^{-1} are tentatively assigned to different kinds of nitrates, which were more likely to form than nitrites on an oxidized surface. Negri et al. [42] observed a band at 1310 cm^{-1} during NO adsorption at 50 °C on Cu-CHA that they assigned to a type of monodentate chelating nitrate on Cu. The broad band at 1100 cm^{-1} is in the spectral region of sulfates [43–45]. This result suggests the conversion of sulfate species during NO adsorption on SO_2-poisoned Cu/BEA. The growth of this sulfate species can be due to the mobility of a different sulfate species or the interaction with the adsorbed NO. This was not observed on poisoned Cu/SSZ-13 which indicates the more difficult reactivity and/or mobility of the sulfate species on Cu/SSZ-13 than on Cu/BEA. This result agrees with the activity measured after SO_2 poisoning which showed a great negative impact on Cu/SSZ-13 and only a moderate activity loss on Cu/BEA.

4 Conclusions

The poisoning of Cu/BEA and Cu/SSZ-13 with SO_2 and a mixture of SO_3 and SO_2 (SO_3:SO_2 = 4) was studied on washcoated monoliths. After a degreening, Cu/SSZ-13 and Cu/BEA showed similar SCR activities. It should be noted that Cu/BEA is not commercially applicable and is used to compare with Cu/SSZ-13 for mechanistic reasons. The XRD analysis showed that the structure of the zeolites was not damaged by sulfur treatment. XRD analysis did not detect any large Cu particles either, which confirmed the absence of structural damages. The number and strength of acidic sites, determined by NH_3-TPD, were not strongly affected after poisoning and subsequent regeneration. Several regeneration treatments in SCR conditions were attempted in order to measure the degree of recovery.

There are both similarities and differences between the poisoning and regeneration of Cu/SSZ-13 and Cu/BEA. Firstly, both catalysts exhibited a decreased standard SCR activity after poisoning by SO_2; however, Cu/SSZ-13 was significantly more deactivated. Interestingly, the Cu/BEA contained more adsorbed sulfur after poisoning compared to Cu/SSZ-13. These results indicate that even though there were more sulfur available in Cu/BEA, it did not affect the activity equally much. One possible reason for this could be that the Cu/BEA has significantly larger pores, so there could be less sterical hindrance by the sulfur addition. Moreover, the deactivation noted after SO_3/SO_2 poisoning was much more intense for both catalysts. Cu/BEA, however, was again less poisoned compared to Cu/SSZ-13.

Evaluation of standard SCR after regeneration revealed that 300 °C was not enough to regain any activity, while some regeneration was found for Cu/SSZ-13 after regeneration at 400 °C. It should be noted that no regeneration was observed for this condition for Cu/BEA, but on the other

hand, it was only mildly poisoned. SO_3 poisoning was much more severe for both catalysts, but especially Cu/SSZ-13. Both catalysts now exhibited some regeneration capabilities in SCR conditions at 400 °C. Examining the fast SCR after different regenerations in standard SCR after SO_2 poisoning showed that Cu/SSZ-13 could regain its full activity after regeneration at 500 °C. After SO_3 poisoning, much of the fast SCR activity was regained for both catalysts after 500 °C regeneration, but not all. Both catalysts exhibited less activity after SO_3 poisoning and regeneration compared with fresh catalysts.

DRIFT spectroscopy revealed the interaction between sulfates and the ZCuOH sites of Cu/SSZ-13 which can explain the strong deactivation by blocking the active sites. Moreover, Cu/BEA showed clear sulfate bands in DRIFT, which is consistent with the large amount of stored sulfur species by ICP measurements.

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Declarations

Conflict of Interest The authors declare that they have no competing interests.

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