A Comparative Kinetics Study between Cu/SSZ-13 and Fe/SSZ-13 SCR Catalysts

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Abstract:

Cu- and Fe/SSZ-13 catalysts with the same Cu(Fe)/Al ratios are synthesized using the same parent SSZ-13 starting material. The catalytic performance for both fresh and hydrothermally aged catalysts is tested with NO and NH₃ oxidation, and standard SCR reactions under steady-state conditions, and standard and fast SCR under temperature-programmed conditions. For standard SCR, Cu/SSZ-13 shows much better low-temperature performance which can be explained by NH₃-inhibition of Fe/SSZ-13. During hydrothermal aging, both catalysts undergo dealumination but Fe/SSZ-13 dealuminates more severely. For aged catalysts, Cu/SSZ-13 gains oxidation activities due to formation of CuO_x. However, Fe/SSZ-13 loses oxidation activities although formation of FeO_x clusters and FeAlO_x species also occur. Because of such physical properties differences, aged Cu/SSZ-13 loses while Fe/SSZ-13 maintains high-temperature SCR selectivities. A physical mixture of aged catalysts provides stable SCR performance in a wide temperature range and is able to decrease N₂O formation at high reaction temperatures. This suggests that Fe/SSZ-13 can be used as a cocatalyst for Cu/SSZ-13 for transportation applications. During temperature-programmed SCR reactions, weak hysteresis is found during standard SCR due to NH₃ inhibition. For fast SCR, hysteresis caused by NH₄NO₃ inhibition is much more significant. NH₄NO₃ deposition is greatly enhanced by Brønsted and Lewis acidity of the catalysts.

Key words: Selective catalytic reduction, chabazite, SSZ-13, diesel engine, emission control.

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1. Introduction

Zeolite-based selective catalytic reduction (SCR) catalysts, notably Cu/Chabazite and Fe/Beta, have received intensive recent research interest since they meet the requirements for commercialization as part of diesel engine exhaust aftertreatment catalytic systems [1-6]. Cu/CHA (including Cu/SSZ-13 and Cu/SAPO-34) has been especially well studied in the past few years [7-23]. Under certain circumstances, e.g., at relatively low Cu/Al ratios and for dehydrated samples, the nature and positioning of Cu ions in Cu/SSZ-13 are now well-understood. It is generally agreed that Cu^{2+} ions prefer faces of 6-membered rings (6MRs) with coordination to two Al associated ion-exchange sites. Several studies have suggested that these are the SCR active centers under reaction conditions [7-9]. However, from our recent detailed SCR reaction kinetics study, catalytically active Cu^{2+} ions are not located in faces of 6MRs at relatively low temperature reaction conditions ($\leq 250\text{ }^{\circ}\text{C}$) due to strong solvation effects from H_2O and/or NH_3 [23], and might be in the form of $[\text{Cu}(\text{OH})]^+$ [24] or even Cu dimers (e.g., $[\text{Cu}-\mu(\text{OH})_2-\text{Cu}]^{2+}$) [23] instead of naked Cu^{2+} . Only at high reaction temperatures ($\geq 350\text{ }^{\circ}\text{C}$) do Cu^{2+} ions lose their H_2O and/or NH_3 solvation shell, and then migrate to faces of 6MRs and serve as active centers. Standard NH_3 -SCR is characterized with high apparent activation energies of $\sim 140\text{ kJ/mol}$ in this high-temperature regime, much higher than low-temperature activation energies obtained for Cu/CHA catalysts (typically $< \sim 80\text{ kJ/mol}$) [9,10,23].

In contrast, not much work has focused on Fe/CHA catalysts. Recently, we published the first detailed characterization and SCR performance study of freshly prepared and hydrothermally aged (HTA) Fe/SSZ-13 catalysts [25]. Using Mössbauer and FTIR spectroscopies, the likely monomeric and dimeric ferric ions in the hydrated fresh sample were determined to be $[\text{Fe}(\text{OH})_2]^+$ and $[\text{HO}-\text{Fe}-\text{O}-\text{Fe}-\text{OH}]^{2+}$, although their precise positioning is not yet known. Following a harsh HTA treatment at $800\text{ }^{\circ}\text{C}$ for 16 h in the presence of 10% H_2O , the

majority of Fe-containing moieties convert to FeAlO_x and FeO_x cluster species, yet the Chabazite structure and a portion of extra framework cationic Fe species are still present. From the application point of view, Fe/SSZ-13 maintains high-temperature SCR activity and selectivity after hydrothermal aging, suggesting that it certainly holds the potential for practical application.

The different characteristics for Cu and Fe/zeolite SCR catalysts make direct comparison an interesting subject. In brief summary, previous literature has discovered the following differences between the two catalysts [26-30]: (1) Fe/zeolites typically have low standard SCR activities at temperatures below 250 °C due to strong NH_3 inhibition effects at such low temperatures. In contrast, Cu/zeolites can be highly active even at ~200 °C. (2) Cu/zeolites are much less sensitive to NO_2/NO_x ratios in the reactant feed. NO_x conversion differences between standard ($\text{NO}_2/\text{NO}_x = 0$) and fast ($\text{NO}_2/\text{NO}_x = 0.5$) SCR are often rather marginal for Cu/zeolite catalysts. In contrast for Fe/zeolites, $\text{NO}_2/\text{NO}_x = 0.5$ is clearly the preferred ratio for low-temperature reactivity. (3) Fe/zeolites are typically less selective in N_2O formation, especially at $\text{NO}_2/\text{NO}_x \leq 0.5$.

In the following, we for the first time present a detailed comparison between fresh and aged Cu- and Fe/SSZ-13 catalysts with respect to SCR kinetics obtained at both steady-state and with temperature-programmed reaction conditions. To make a fair comparison, catalysts were prepared with the same Cu(Fe)/Al ratio of 0.2, using the same SSZ-13 substrate ($\text{Si}/\text{Al} = 12$). Some of the results for Fe/SSZ-13 have been published recently [25] but are included here for the purpose of comparison.

2. Experimental

2.1 Catalyst synthesis

A Na/SSZ-13 sample with Si/Al = 12 was hydrothermally synthesized using a method modified slightly from a protocol developed recently by Deka, et al. [9]. Composition of the gel was the following: 10SDA:10NaOH:4Al₂O₃:100SiO₂:2200H₂O. The gel was prepared by first dissolving NaOH (99.95%, Aldrich) in deionized water and adding the SDA (TMAda-OH, Sachem ZeoGen 2825). Following this, Al(OH)₃ (containing ~54% Al₂O₃, Aldrich) and fumed silica (0.007 μ m average particle size, Aldrich) were added sequentially under vigorous stirring until the gel was homogenized. The gel (with a stir bar in) was then sealed into a 125 ml Teflon-lined stainless steel autoclave. Subsequently, the autoclave was placed in a salt bath on top of a hot plate stirrer to carry out hydrothermal synthesis at 160 °C for 96 h under continuous stirring (300 rpm). After synthesis, Na/SSZ-13 was separated from the mother liquid via centrifugation and washed with deionized water for 3 times. Finally, the zeolite powders were dried at 120 °C under flowing N₂, and calcined in static air to remove the SDA. In this latter process, a thin layer of powder sample well-dispersed in a ceramic plate was heated to 550 °C at 2 °C/min and maintained at 550 °C for 8h. Si and Al contents of the product powders were measured with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at Galbraith Laboratories (Knoxville, TN, USA). Prior to measurements, the sample was dehydrated at 150 °C for 2 h in vacuum to remove adsorbed moisture.

Cu/SSZ-13 was prepared using a two-step solution ion exchange protocol [16]. First, Na/SSZ-13 was exchanged to NH₄/SSZ-13 using a 0.1 M NH₄NO₃ solution at 80 °C. After separation, washing with deionized water and drying in flowing N₂ at 120 °C to obtain the NH₄/SSZ-13 powder, a second ion exchange was performed using a 0.01 M CuSO₄ solution at 80 °C for 1 h at a pH of ~3.0. After that, Cu/SSZ-13 was collected, washed and dried. Fe/SSZ-13 was prepared similarly using NH₄/SSZ-13 and FeSO₄; however, care must be taken to avoid Fe²⁺ oxidation to Fe³⁺ which leads to bulky Fe-complexes during ion exchange. This was achieved by

N₂ protection during ion exchange and more details can be found elsewhere [25]. The as-prepared powders were first calcined in static air at 550 °C for 8 h. Samples thus obtained are denoted as “fresh” here. A portion of fresh samples were hydrothermally aged at 800 °C for 16 h in flowing air containing 10% H₂O (denoted as “HTA” samples). In order for a fair comparison to be made, Cu/Al and Fe/Al ratios were both chosen as 0.2 for the Cu/SSZ-13 and Fe/SSZ-13 catalysts. Cu and Fe contents of the catalysts were also determined via ICP-AES.

2.2 NO/NH₃ oxidation and standard/fast NH₃-SCR reaction tests

NO/NH₃ oxidation and NH₃-SCR reaction kinetics were measured using a plug-flow reaction system described elsewhere [16]. Powder samples were pressed, crushed and sieved (0.177–0.25 mm) prior to use. For “standard” SCR ($4\text{NO} + 4\text{NH}_3 + \text{O}_2 = 4\text{N}_2 + 6\text{H}_2\text{O}$), the feed gas contained 350 ppm NO, 350 ppm NH₃, 14% O₂, ~2.5% H₂O, and balance N₂. For “fast” SCR ($\text{NO} + \text{NO}_2 + 2\text{NH}_3 = 2\text{N}_2 + 3\text{H}_2\text{O}$), the feed gas contained 175 ppm NO and 175 ppm NO₂, and other components were the same as standard SCR. NO (NH₃) oxidation reaction was conducted in the same manner, without adding NH₃ (NO) to the feed. Some kinetic measurements were carried out at steady-state. In this case, measurements were conducted from high to low reaction temperatures, and samples were maintained at each target temperature for ~50 min to reach a steady-state before moving to the next (lower) temperature. Some temperature-programmed reaction measurements were also performed by linearly heating the samples from 100 to 500 °C and cooling back to 100 °C at 2 °C/min. All of the gas lines were heated to over 100 °C to avoid water condensation. The total gas flow was 300 sccm, and the gas hourly space velocity (GHSV) was estimated to be ~200,000 h⁻¹ for a catalyst amount of 60 mg. Concentrations of reactants and products were measured by an online Nicolet Magna 560 FTIR spectrometer with a 2 m gas cell maintained at 150 °C. In this study, catalytic performance is mainly reported as conversion

versus temperature (i.e., light-off) curves. Equations used to calculate reactant conversions can be found elsewhere [16].

3. Results

3.1 Steady-state reaction results

Fig. 1 compares light-off curves in standard SCR for fresh Cu- and Fe/SSZ-13 catalysts. Both NO and NH₃ conversions are plotted so that SCR selectivities can also be readily compared. For the Cu/SSZ-13 catalyst, the light-off temperature is slightly below 200 °C and over the entire temperature ranges investigated here, SCR selectivities are excellent (i.e., NO and NH₃ conversions are essentially equal at all temperatures). In contrast, Fe/SSZ-13 displays no activity below 200 °C and only becomes highly active above ~300 °C. To emphasize the difference, the temperature at 50% NO conversion (T_{50}) for Cu/SSZ-13 is ~120 °C lower than that for Fe/SSZ-13. It is generally believed that the poor SCR activity for Fe/zeolites at low temperatures is due to NH₃ inhibition [31, 32]. This point will be discussed in more detail below. It is also clear from Fig. 1 that, at 275 °C and above, SCR selectivities on Fe/SSZ-13 is ~90% in terms of NH₃ conversion; that is, ~10% NH₃ overconsumption via non-selective oxidation reaction is evident.

Figs. 2(a) and (b) present light-off curves for the HTA Fe/SSZ-13 and Cu/SSZ-13 catalysts, respectively. For both catalysts, performance becomes somewhat inferior as compared to their fresh counterparts. Again, low-temperature activity for Cu/SSZ-13 is much better than Fe/SSZ-13. However at ~400 °C, NO conversions on both catalysts become comparable. Importantly, at ~500 °C and above, catalytic performance for Fe/SSZ-13 is now clearly superior to Cu/SSZ-13. In this case, Cu/SSZ-13 substantially loses SCR selectivities due to non-selective NH₃ oxidation, yet Fe/SSZ-13 maintains good SCR selectivities.

NO and NH₃ oxidation are relevant reactions to better understand SCR kinetics. Fig. 3(a) presents NO oxidation ($\text{NO} + \frac{1}{2} \text{O}_2 = \text{NO}_2$) results on fresh catalysts. Fresh Fe/SSZ-13 shows good activity; above 400 °C, NO conversions are partially influenced by gas phase NO/NO₂ equilibrium. We have shown previously that, in the absence of moisture, this catalyst is even more active for this reaction [25]. In contrast, the fresh Cu/SSZ-13 used here is completely inert below ~350 °C (the ~2.5% NO conversions come from background gas phase reactions), and only become marginally active at temperatures above 400 °C. Interestingly, as displayed in Fig. 3(b), reactivity for Fe/SSZ-13 decreases considerably after aging, while Cu/SSZ-13 becomes much more active after aging. Above 400 °C, NO conversions on HTA Cu/SSZ-13 surpass those on HTA Fe/SSZ-13, and the difference in rates increases with increasing temperature.

NH₃ oxidation ($4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$) kinetics show some particularly interesting differences. As illustrated in Fig. 4(a), fresh Fe/SSZ-13 has no activity below ~300 °C, yet at 350 °C and above, NH₃ conversions increase rather rapidly with temperature. Presumably, as with the case for standard SCR, low temperature activity is suppressed on this catalyst due to poisoning by adsorbed NH₃. Fresh Cu/SSZ-13 displays rather complicated kinetic behavior with temperature. Notably, this catalyst has some low-temperature (≤ 300 °C) activity suggesting a lack of NH₃ inhibition as opposed to Fe/SSZ-13. Between 300 and 400 °C, the rather unusual behavior of relatively constant NH₃ oxidation rates is observed. Above 400 °C, NH₃ conversion increases with increasing temperature again; however, this catalyst is clearly less active than Fe/SSZ-13 at such high temperatures. As shown in Fig. 4(b), HTA Fe/SSZ-13 is much less active for NH₃ oxidation, where reactivity only becomes apparent at ~450 °C and above. On the other hand, HTA Cu/SSZ-13 loses low-temperature (≤ 300 °C) activity, but gains considerable high-temperature activity as compared to the fresh sample.

The different optimum operation temperature windows for Cu and Fe/zeolite catalysts evident in Figs. 1 and 2 make it a straightforward consideration to combine the two into a complex catalyst; and, in fact, this has already been practiced previously [26, 29, 30]. Using the Cu- and Fe/SSZ-13 catalysts studied here, we carried out a standard SCR reaction on a catalyst system made by mixing the HTA materials at a 1/1 ratio. As shown in Fig. 5(a), compared to the Cu/SSZ-13 catalyst alone, the low-temperature activity for this physical mixture is only slightly sacrificed yet the high-temperature selectivity appears to be improved. Importantly, the mixed catalyst gives very stable NO conversions over a wide temperature window from 200 to more than 500 °C. Moreover, as shown in Fig. 5(b), HTA Fe/SSZ-13 is particularly unselective for the formation of the undesired byproduct, N₂O, yet HTA Cu/SSZ-13 performs poorly above 400 °C in this regard. The mixed catalyst is able to significantly lower N₂O formation as compared to Cu/SSZ-13. Note especially that, at a reaction temperature of 550 °C, N₂O formation (~8 ppm) from the mixed catalyst is less than half of that by Cu/SSZ-13 (~25 ppm). Even accounting for the fact that the amount of Cu/SSZ-13 in the mixed catalyst is ½ the total used for kinetics measurements on Cu/SSZ-13 alone, the mixed catalyst is performing considerably better with respect to N₂O formation (i.e., 12.5 ppm versus 8 ppm for the mixture). This suggests that there is indeed synergy between the two components perhaps by the decomposition of some N₂O generated by Cu/SSZ-13 over the Fe/SSZ-13 component.

3.2 Temperature-programmed reaction results

Both standard and fast SCR reactions were also performed in a temperature-programmed reaction mode to study transient behaviors of the catalysts, and to specifically probe effects from NH₃ storage and ammonium nitrate/nitrite deposition. The experimental procedure is as follows: a catalyst is first treated in an O₂/N₂ flow (300 sccm, containing ~20% O₂) at 550 °C for 30 min to remove trapped carbonates and organics, and then cooled to 100 °C in the same flow. Reaction

feeds are subsequently switched on ($\equiv$ time=0) and the recording of gas outlet concentrations of various reactant and product species an on-line FTIR detector is initiated. The sample is maintained at 100 °C for 60 min, and then ramped up to 500 °C at 2 °C/min, and then immediately ramped back down to 100 °C at the same rate. Finally, the sample is maintained at 100 °C until gas outlet values become approximately equal to inlet ones. Following this, the reaction feeds are turned off, and the sample is purged with pure N₂ (300 sccm) for 60 min before a final temperature-programmed desorption (TPD) step. TPD is conducted by ramping the sample from 100 to 600 °C at 10 °C/min, and maintaining at 600 °C until desorption is complete.

Fig. 6(a) presents the temperature curve (dashed line) and NO/NO₂/N₂O/NH₃ outlet curves (solid lines) as a function of time for standard SCR carried out on a fresh Fe/SSZ-13. The horizontal dot-dashed line represents NO and NH₃ inlet concentrations (350 ppm each). Due to differences in the storage of these species on the catalyst, NO outlet values reach 350 ppm within 1 min at 100 °C, while it takes ~15 min for NH₃ to reach its inlet value of 350 ppm. During the ramping steps, NO predominately undergoes SCR reaction while NH₃ undergoes SCR reaction, non-selective oxidation reaction and storage. When NH₃ outlet concentrations surpass NO ones (e.g., during the ramping up step from 350 to ~400 °C), the “extra” NH₃ comes from desorption of NH₃ that was stored at lower temperatures. When NO outlet values surpass NH₃ (e.g., during the ramping down step from 500 to 100 °C), the extra NH₃ consumption comes from non-selective oxidation and storage. For the case where NO and NH₃ outlet values are equal (e.g., during the ramping up step from 100 to ~350 °C), NH₃ is predominately consumed by SCR and NH₃ adsorption/desorption or non-selective oxidation processes are negligible. Note also from Fig. 6(a) that NO₂ and N₂O are barely detectable during the whole process.

Fig. 6(b) presents data collected during fast SCR on a fresh Fe/SSZ-13 catalyst. Note that two dot-dashed horizontal lines are included representing NO and NO₂ inlet values (175 ppm

each), and NH_3 inlet ones (350 ppm). During the first 60 min at 100 °C, fast SCR does not proceed at appreciable rates as indicated by the nearly constant concentrations of NO that are only slightly lower than the inlet 175 ppm values. However, extensive NH_4NO_3 storage must have occurred as indicated from the low NO_2 and NH_3 outlet concentrations. Note that NO is not involved in NH_4NO_3 formation at 100 °C, as indicated by the fact that, again, its inlet and outlet concentrations are similar. The NO “spike” above the inlet of 175 ppm during the first a few minutes is due to NO formation from the NO_2 disproportionation reaction in the presence of H_2O (i.e., $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$). During the ramping up step, small amounts of N_2O are generated via NH_4NO_3 decomposition between 220 to 300 °C, a process not observed during the cooling step. Note that NO_2 concentrations have not returned to inlet values by 500 min (the program used to collect gas outlets only records data for this length of time). However even in this case, the sample was continuously held at 100 °C until NO_2 and NH_3 outlets become the same as inlets (i.e., until NH_4NO_3 storage saturates, not shown) prior to the subsequent TPD to be discussed below.

The same measurements were also conducted on HTA Fe/SSZ-13, and fresh and HTA Cu/SSZ-13. For the sake of brevity, the results are shown only in the Supplementary Information (Figs. S1-S3). As mentioned above, NO does not store during the temperature-programmed reaction steps; therefore, NO conversions can be calculated and compared at any reaction temperature based on data shown in Figs. 6 and S1-S3. Fig. S4 presents NO conversion versus temperature during steady-state and the cooling down step for the temperature-programmed standard SCR reactions on a fresh Fe/SSZ-13 catalyst. The similarity of these curves clearly demonstrates that a ramping rate of 2 °C/min is sufficiently slow such that NO can be deemed to be in a quasi-steady-state during the temperature-programmed reaction. Note that this is not the case for NH_3 and NO_2 where conversions cannot be readily calculated during temperature-

programmed reactions. N_2O , another weakly-bound molecule, is expected to desorb immediately upon formation.

Next, details on NO conversions, N_2O formation and TPD results after temperature-programmed reactions are presented. Results for fresh and HTA Fe/SSZ-13 are given in Figs. 7 and 8, with the corresponding data for Cu/SSZ-13 presented in Figs. 9 and 10.

Fig. 7(a) displays a direct comparison on NO conversions during the heating and cooling steps in standard SCR over fresh (upper panel) and HTA (lower panel) Fe/SSZ-13 catalysts. For the fresh catalyst, two interesting minor hysteresis loops are found; between 'A' and 'B', NO conversions during the cooling step are slightly higher whereas between 'B' and 'C', the reverse is evident. For the HTA sample, a single hysteresis loop is found between 'D' and 'E' where NO conversions are slightly higher during the cooling step. Fig. 7(b) plots results for fast SCR on the same two catalysts. In this case, hysteresis appears to be much more pronounced (especially for the HTA sample) as compared to standard SCR. It is also interesting to note that, (1) for the fresh catalyst, NO conversions appear to be unusually high during the onset of the heating step, likely due to NO reaction with the deposited NH_4NO_3 . (2) light-off temperatures on the HTA sample in both heating and cooling steps are substantially *lower* than those for the fresh sample. This is somewhat surprising and will be discussed in more detail along with the TPD results. Fig. 7(c) presents N_2O yield profiles during temperature-programmed fast SCR for the fresh and HTA Fe/SSZ-13 catalysts (N_2O formation during standard SCR on both samples are barely detectable so those data are not shown). For the fresh sample, significant N_2O formation occurs between ~220 to 300 °C in the heating step likely due to the decomposition of deposited NH_4NO_3 . At other temperatures for the fresh sample, as well as in the whole temperature range for the HTA sample, N_2O formation yields in the heating and cooling steps are rather similar and fairly small.

Fig. 8(a) presents TPD results following the temperature-programmed standard SCR reactions. For the fresh Fe/SSZ-13 (upper panel), no NO_x desorption is detected. NH_3 desorbs between ~ 300 to 600°C , predominately from Brønsted acid sites. H_2O displays two desorption states: (1) low-temperature desorption below $\sim 200^\circ\text{C}$ is due to trapped H_2O , for example, via hydrogen-bonding interactions; and (2) the desorption feature between ~ 300 to 500°C likely due to dehydration of Fe centers [25]. For the HTA sample, NH_3 desorption becomes substantially weaker demonstrating a marked decrease in residual Brønsted acid sites for this sample. The high-temperature H_2O desorption state is also absent suggesting a change in the nature of the Fe species during aging. Again, no NO_x species desorb from the HTA sample. Fig. 8(b) depicts TPD results after fast SCR. For the fresh sample (upper panel), extremely weak NO desorption is found at $\sim 220^\circ\text{C}$, while a single prominent NO_2 desorption state is observed at $\sim 240^\circ\text{C}$. N_2O displays two desorption states at ~ 220 and $\sim 280^\circ\text{C}$, and NH_3 appears to have weak desorption states at ~ 220 , 240 and 280°C , and a much stronger state from Brønsted acid sites at higher ($>350^\circ\text{C}$) temperatures. H_2O displays very strong desorption states at ~ 220 and 280°C , similar to N_2O . The higher-temperature H_2O desorption state, due to Fe species dehydration, is still detected, yet the low-temperature state due to trapped H_2O is now largely absent. With an online FTIR analyzer, N_2 formation during TPD is unfortunately not detectable; however, H_2O desorption between ~ 200 to 300°C should be due entirely to decomposition of deposited NH_4NO_3 , and to reactions between adsorbed NH_3 and NH_4NO_3 . Therefore, H_2O yield in this temperature window provides a good measure of NH_4NO_3 deposition prior to TPD. In this sense, it is very interesting that NH_4NO_3 deposition is much less on the HTA sample (lower panel). For the latter, the $\sim 220^\circ\text{C}$ N_2O and H_2O desorption states appear to be stronger than the $\sim 280^\circ\text{C}$ state, which is the opposite for the fresh sample.

The temperature-programmed reaction results (Figs. S2 and S3) on fresh and HTA Cu/SSZ-13 are analyzed in the same way and these results are discussed next. Fig. 9(a) presents NO conversions on fresh and HTA samples in standard SCR. Note that the HTA sample used in these experiments was aged from a different batch as opposed to the sample used for steady-state measurements and appears to be slightly more active. Yet this does not change the key findings and main conclusions. For the fresh sample (upper panel), light-off occurs below ~ 200 °C, and low-temperature hysteresis appears to be very minor where NO conversions are slightly higher during the cooling step. During the cooling step, there is a drop in NO conversions between 300 and 400 °C. This is caused by migration of Cu ion centers; phenomena that have been discussed in detail recently [23]. Note that a similar drop is not seen in this temperature range during the heating step because of complete NO conversions. For the fresh Fe/SSZ-13 (Fig. 7(a), between ‘B’ and ‘C’), NO conversions are also higher during the heating step in this temperature range. As will be shown below, the “extra” NO conversion during the heating step is due to reactivity of NH_3 stored (at lower temperatures) on Brønsted acid sites. The HTA sample (Fig. 9(a), lower panel) shows comparable activities except that NO conversions decrease with increasing temperature due to non-selective NH_3 oxidation above ~ 400 °C. Fig. 9(b) displays NO conversions during fast SCR. In the low-temperature (< 250 °C) regime, both the fresh and HTA samples show strong hysteresis, where NO conversions during the cooling step are substantially higher than during the heating step. In the high temperature regime, excellent SCR selectivity maintains up to ~ 450 °C as judged from the 100% NO conversion for the fresh catalyst. For the HTA sample, however, SCR selectivity starts to decrease at ~ 370 °C. The substantially higher activities for the HTA sample in fast SCR at low-temperatures found for Fe/SSZ-13 (Fig. 7(b)), are *not* evident for the Cu/SSZ-13 samples.

Fig. 9(c) presents N_2O formation during standard SCR in the temperature-programmed reaction measurements on the fresh and HTA Cu/SSZ-13 catalysts. For the fresh catalyst, N_2O formation is barely detectable (upper panel) while for the HTA sample, N_2O formation above $\sim 150^\circ\text{C}$ is clearly evident especially at high ($> 450^\circ\text{C}$) temperatures, and a local maximum is found at $\sim 250^\circ\text{C}$. The N_2O formation profiles completely overlap during the heating and cooling steps. Note again that N_2O formation is barely detectable for both fresh and HTA Fe/SSZ-13 samples in standard SCR, in contrast to the case just presented for HTA Cu/SSZ-13. Fig. 9(d) displays the more complex N_2O formation behavior during fast SCR reactions. N_2O formation, via decomposition of deposited NH_4NO_3 ($\sim 250\text{--}350^\circ\text{C}$), is only evident during the heating step and, for both samples, the yields are similar. Quasi steady-state N_2O formation yields on the HTA sample, on the other hand, appear to be higher than those for the fresh sample at all temperatures.

Fig. 10(a) depicts TPD results following temperature-programmed standard SCR reactions. For both fresh (upper panel) and HTA (lower panel) samples, no NO_x desorption is observed. On the fresh sample, NH_3 desorbs in two states: a lower-temperature state centered at $\sim 350^\circ\text{C}$ due to NH_3 desorption from Lewis acid sites (the majority of which are Cu sites), and a high-temperature peak centered at $\sim 480^\circ\text{C}$ is due to NH_3 desorption from Brønsted acid sites. Interestingly, high-temperature NH_3 desorption from the HTA sample is essentially eliminated while a concurrent enhancement in low-temperature NH_3 desorption is evident. For H_2O desorption, both samples display a low-temperature state below $\sim 200^\circ\text{C}$ due to desorption of relatively weakly bound H_2O . Both samples also present a weaker desorption state at $\sim 300^\circ\text{C}$. The origin for this state will be discussed below. Fig. 10(b) presents TPD results after fast SCR. Similar to Fe/SSZ-13 catalysts (Fig. 8(b)), multiple NO_x desorption states are observed. NO and NO_2 primarily desorb at $\sim 220^\circ\text{C}$, and N_2O desorbs at ~ 220 , 280 and 310°C . For the fresh

sample, the ~ 280 °C state appears to be the strongest. In contrast for the HTA sample, this latter peak becomes less resolved and the ~ 310 °C state dominates. It is also interesting to note that the 310 °C peak is absent for the Fe/SSZ-13 samples. The lineshapes for the H_2O profiles obtained from fresh and HTA Cu/SSZ-13 are similar to those for N_2O . As mentioned earlier, H_2O desorption provides a good measure of NH_4NO_3 deposition. The difference in the amounts of NH_4NO_3 deposited on the fresh and HTA samples prior to TPD seem rather marginal. This contrasts with case for the Fe/SSZ-13 catalysts (Fig. 8(b)), where much less NH_4NO_3 deposition is found on the HTA sample.

Although SSZ-13 in the H form only has limited activities in standard SCR, it indeed displays considerable reactivity for fast SCR. For this reason, we also carried out temperature-programmed fast SCR reactions on the parent H/SSZ-13. Fig. 11(a) presents gas outlet concentrations for various reactant and product gases as a function of time, where data are collected in the same way as those shown in Fig. 6(b). Judged from NO and NH_3 outlet concentrations, it is quite clear that H/SSZ-13 indeed displays considerable reactivity for fast SCR; however, it is less active than any of the Cu and Fe loaded samples. Another apparent difference is significant N_2O generation between 200 and 300 °C that is observed during both ramp up and ramp down portions of the experiment. Primarily, the N_2O released from H/SSZ-13 in this temperature window is likely due to NH_4NO_3 decomposition. Especially for the cooling step, this N_2O production is not seen on any of the Cu and Fe loaded samples, demonstrating that in the presence of Cu and Fe cationic species, deposited NH_4NO_3 can undergo other reactions during the ramping steps as will be discussed in more detail below. Also note that between ~ 400 and 500 °C, NO_2 outlet concentrations resemble a mirror image of NO ones demonstrating some NO_2 conversion to NO. Because of the high temperatures at which this occurs, it is likely a consequence of thermodynamics rather than catalytic kinetics. Fig. 11(b) presents NO

conversions as a function of temperature during the heating and cooling steps. Some extra NO conversion is found at the onset of the heating step, similar to that found for fresh Fe/SSZ-13 (Fig. 7(b), upper panel). Between ~200 to 400 °C, “normal” hysteresis is observed where NO conversions are slightly higher during the cooling step. Above ~400 °C, the nominal NO conversions decrease that, as just mentioned, may be a consequence of the thermodynamic equilibrium for NO and NO₂. Fig. 11(c) plots the TPD results obtained after reaction. NO desorption is barely detectable, while small amounts of NO₂ desorb at ~230 °C. N₂O and H₂O desorb in two states at ~220 and 280 °C. Note that for each of these two states, the H₂O signal intensity is roughly two times that of N₂O. Finally, NH₃ predominately desorbs from Brønsted acid sites with slightly higher yields than those from Fe and Cu loaded fresh samples.

4. Discussion

4.1. Reactions involved in SCR, NO/NH₃ oxidation and TPD

Chemistry involved in NH₃-SCR is rather complicated. Not only are the elementary reaction steps, especially the ones that are rate-limiting, not fully understood, even the global pathways are complex enough that an extensive reaction network is generally required for a detailed description [33]. In the present study, global reactions involved are qualitatively described below, mainly to serve as the basis for discussions of the similarities and differences between Cu- and Fe/SSZ-13 catalysts.

NH₃-SCR reactions, depending on NO/NO_x ratios, are generally classified as standard, fast, and NO₂-SCR, with global pathways listed in equations 1-3, respectively:

Among the three pathways, the NO₂-SCR is the least well-documented. Grossale et al. [27, 34] applied transient reaction analysis to understand this reaction on a commercial Fe/zeolite, and proposed a mechanism where surface nitrates are first formed by NO₂ disproportionation, followed by their catalytic reduction to nitrogen by ammonia:

Note that because of the much higher thermal stabilities of NH₄NO₃ as compared to NH₄NO₂, reaction (6) can be further divided to reactions (7) and (8):

Although standard and fast SCR are very selective, numerous studies have realized the correlation between NO₂-SCR and N₂O formation; and literature has documented very well that ammonium nitrate can decompose to generate N₂O:

In this sense, N₂O formation might be regarded as a “fingerprint” for NO₂-SCR. Moreover, in the presence of a standard SCR feed, Tronconi and coworkers [35, 36] have discovered a so-called “enhanced SCR” pathway important even at relatively low temperatures (e.g., 200 °C) on Fe/zeolites:

This “enhanced SCR” may be a result of another important reaction involving NH₄NO₃, that being its reduction by NO:

Other critical reactions, that are closely related with NH₃-SCR, are the oxidations of NO and NH₃. Cu- and Fe/zeolites catalyze these reactions rather selectively, and their reaction pathways are likely to be as complex as NH₃-SCR. On Cu- and Fe/zeolite catalysts, NO is selectively oxidized to NO₂:

Possible minor side reactions include NO decomposition to N₂ and O₂, and nitrate formation due, as discussed above, to NO₂ disproportionation. NH₃ is typically selectively oxidized to N₂ by Cu- and Fe/zeolite catalysts:

For this reaction, side reactions include NH₃ oxidation to NO, NO₂ or N₂O. These are typically very minor and only occur at relatively high temperatures (≥ 400 °C).

Reactions involved in TPD comprise two categories: deposition processes occurring prior to TPD, and decomposition reactions during TPD. For standard SCR, as shown in Figs. 8(a) and 10(a), only NH₃ and H₂O desorption is detected (N₂ desorption cannot be monitored), suggesting that deposition of large amounts of NH₄NO₃ prior to TPD does not occur. For the Cu/SSZ-13 catalysts, however, H₂O evolution at ~300 °C does suggest small amounts of NH₄NO₃ deposition, which, during the subsequent temperature ramping, decompose according to equation (8). For fast SCR, maintaining the samples at 100 °C indeed allows large quantities of NH₄NO₃ deposition according to reactions (4) and (7). As shown in Fig. 11(c), TPD after temperature-programmed fast SCR on H/SSZ-13 is quite readily understood. The majority of N₂O and H₂O desorb between 200 and 300 °C and the N₂O yield is approximately 50% of that for H₂O demonstrating reaction (9) is the main decomposition pathway for deposited NH₄NO₃ on H/SSZ-13. Note, however, small amounts of NO₂ also desorb in this temperature window perhaps suggesting another minor decomposition pathway for NH₄NO₃, notably:

This pathway can be observed when a reaction occurs for NH_4NO_3 molecules associated with Brønsted acid sites (e.g., $-\text{Si}-\text{O}(\text{H})-\text{Al}-$). As evidenced by the higher NO_2 levels in TPD shown in Figs. 8(b) and 10(b), this pathway appears to be more important for Cu- and Fe/SSZ-13 catalysts than on H/SSZ-13. Also from Figs. 8(b) and 10(b), H_2O yields are greater than 2 times the N_2O yields, especially for the fresh and HTA Fe/SSZ-13 catalysts. This indicates that some H_2O must also be generated from reactions other than reaction (9). Due to the lack of NO storage, it appears likely that reaction (8), instead of reaction (10), is responsible for the formation of “extra” H_2O during TPD. However, N_2O evolution during the ramping steps (see, e.g., Figs. 7(c) and 9(d)) is substantially less than during TPD suggesting that, in the presence of SCR reactants, deposited NH_4NO_3 primarily undergoes reactions (8) and (10) instead of decomposition (i.e., reaction (9)).

4.2. Comparison between reactivity of Cu and Fe active sites

In the introduction section, literature findings for comparative SCR activities between Cu- and Fe/zeolites are summarized [26-30]: (1) Fe/zeolites display strong NH_3 inhibition effects at low temperatures; (2) Cu/zeolites are much less sensitive to NO_2/NO_x ratios of the reactant feed; and (3) Fe/zeolites are typically less selective in N_2O formation, especially at NO_2/NO_x ratios ≤ 0.5 . In the present study, all of these findings are reproduced on our Cu- and Fe/SSZ-13 catalysts. For example, SCR reaction data shown in Fig. 1 are readily explained by NH_3 inhibition of Fe/SSZ-13. This inhibition effect can be understood in two ways: (1) NH_3 binds with Fe centers strongly at low temperatures thereby preventing NO_x coordination with Fe; or (2) Fe ions are ‘trapped’ in the +2 oxidation state (Fe(II)) due to reduction by NH_3 such that Fe(III)/Fe(II) redox cannot proceed for NO oxidation at low temperatures. The fact that fast SCR proceeds on Fe/zeolites at rather low temperatures strongly suggests that explanation (2) is more

likely. As to the insensitivity of NO_2/NO_x ratios for SCR rates on Cu/zeolites, Fig. 9 provides a good example to demonstrate that “fast” SCR does not proceed any faster than standard SCR on Cu/SSZ-13. Furthermore, due to NH_4NO_3 inhibition (which will be discussed below), fast SCR can even proceed slower than standard SCR. Although not fully understood yet, these results do strongly suggest that standard SCR proceeds via a mechanism distinct from fast SCR; specifically, NO_2 does not necessarily have to be involved as a reaction intermediate in a standard SCR mechanism [18, 37-39]. Comparative N_2O formation during SCR on Cu- and Fe/zeolites is also an interesting and important subject that will be taken up below.

For the fresh Cu- and Fe/SSZ-13 samples, the key catalytic sites are extra-framework cationic species. However, complexity with respect to the active species is evident when the fresh samples are hydrothermally aged. A key feature for hydrothermal aging is dealumination and the consequent Cu/Fe ion migration from the now missing zeolitic ion exchange sites. To better understand comparative dealumination during aging, Fig 12 presents ^{27}Al NMR of the fresh and HTA Cu- and Fe/SSZ-13 samples. Details on NMR data collection can be found elsewhere [22]. By comparing normalized framework Al (Al_f) signal intensities, both HTA samples dealuminate substantially, and HTA Fe/SSZ-13 dealuminates even more severely. The NMR results are fully consistent with the NH_3 -TPD data shown in Figs. 8 and 10. In particular from NH_3 -TPD, HTA Fe/SSZ-13 loses most of the NH_3 chemisorption capacity while HTA Cu/SSZ-13 mainly weakens this capacity. Significantly, these results also indicate that tetrahedral Al sites from Fe/SSZ-13 do not convert to extra-framework Lewis acid sites after aging while they apparently do for aged Cu/SSZ-13. In our recent study, CO/NO titration FTIR results suggest FeAlO_x formation in aged Fe/SSZ-13 [25]. This explains, in part, the lack of Lewis acidity in aged Fe/SSZ-13.

It is not clear why HTA Fe/SSZ-13 dealuminates more than Cu/SSZ-13 at identical aging conditions. One plausible explanation is that Fe(III) can adopt tetrahedral coordination and get into the zeolite framework to replace Al, while this is not expected for Cu(II). However, there is not yet strong evidence to prove that this is occurring even for Fe. In any case, a portion of $\text{Fe}^{3+}/\text{Cu}^{2+}$ ions will have to migrate from charge-balancing cationic sites upon dealumination. In HTA Fe/SSZ-13, CO/NO titration FTIR suggests FeAlO_x and FeO_x formation [25]; while for HTA Cu/SSZ-13, CuO_x formation is expected. Because of the need to activate O_2 , it is generally agreed that only Cu/Fe ion dimers or clusters catalyze NO and NH_3 oxidation reactions [23, 40, 41]. For Cu/Fe oxide clusters, one expects that their activity decreases with increasing cluster size due to decreased surface site exposure. As shown in Figs. 3 and 4, Fe/SSZ-13 markedly loses oxidation activity upon aging. From the discussion immediately above, this can be rationalized by the depletion of active Fe ion dimers during aging. Note that Branderberger et al. [42] also found a decrease in NH_3 oxidation reactivity upon hydrothermal aging of Fe/ZSM-5. On the other hand, Cu/SSZ-13 gains NO oxidation activity (Fig. 3), loses low-temperature ($\leq 300\text{ }^\circ\text{C}$) but gains high-temperature NH_3 oxidation activity (Fig. 4) upon aging. This, in general, can be rationalized by the formation of CuO_x clusters during aging, which are highly active for oxidation reactions. Note, however, that NH_3 oxidation kinetics shown in Fig. 4 are quite complex and may be better understood by invoking a temperature-dependent transition of active centers [23]. Finally for standard SCR, steady-state kinetics illustrated in Figs. 1 and 2 clearly show how NH_3 oxidation activities affect high-temperature SCR selectivities, explaining why Cu/SSZ-13 loses high-temperature SCR selectivities upon aging while Fe/SSZ-13 becomes more selective at high-temperatures after hydrothermal aging.

4.3. Hysteresis and roles of NH_4NO_3 in temperature-programmed reactions

In temperature-programmed standard SCR, “normal” weak hysteresis in NO conversion is found (Figs. 7(a) and 9(a)) where NO conversions are slightly higher during the cooling step. This can be explained by a weak “NH₃ inhibition” effect; in essence, at the same reaction temperature in the regime where such hysteresis is found, the only difference expected between the heating and cooling steps are small variations in the amounts of stored NH₃. During the heating step, higher NH₃ concentrations on Cu/Fe centers could cause Cu/Fe centers to be more reduced and, thus, slightly less active. An exception to this “normal” hysteresis occurs in the temperature window where stored NH₃ starts to be desorbed from Brønsted acid sites (e.g., region from “b” to “c” in Fig. 7(a)). In this case, stored NH₃ molecules themselves become reactive causing transient higher NO conversions in the heating step.

The much more pronounced hysteresis found during fast SCR (Figs. 7(b) and 9(b)) comes from “NH₄NO₃ inhibition”, and arguments from a redox mechanism perspective given above no longer apply. For example, in an operando X-ray absorption spectroscopy (XAS) study by Kispersky et al. [10], the authors found that Cu in Cu/SSZ-13 permanently stays as Cu(II) under fast SCR conditions. The strongest evidence for “NH₄NO₃ inhibition” comes from a comparison in NO conversions between fresh and HTA Fe/SSZ-13 (Fig. 7(b)), and the TPD results following reaction (Fig. 8(b)). Interestingly, HTA Fe/SSZ-13 shows substantially enhanced low-temperature performance relative to fresh Fe/SSZ-13 due to much reduced NH₄NO₃ inhibition. For the fresh and HTA Cu/SSZ-13 samples (Fig. 9(b)), difference in low-temperature fast SCR performance between fresh and aged catalysts is much less dramatic as compared to the Fe/SSZ-13 samples. Indeed, TPD data shown in Fig. 10(b) indicates that the amounts of NH₄NO₃ deposition are rather similar for fresh and HTA Cu/SSZ-13. This is consistent with the fact that HTA Cu/SSZ-13 dealuminates much less than HTA Fe/SSZ-13 (Fig. 12). These findings are important in elucidating the NH₄NO₃ deposition mechanism shown in equation (7).

Based on the fact that acidity (Lewis and Brønsted alike) apparently promotes NH_4NO_3 deposition, the following reactions seem likely to be involved:

From the temperature programmed fast SCR reaction results, it is also important to note the difficulty of conducting low-temperature steady-state fast SCR measurements with Chabazite based catalysts. For example from Fig. 9(b), depending on whether the catalyst is relatively clean or has an NH_4NO_3 deposit, NO conversions can change from nearly 100% to as low as ~30% at a reaction temperature of 200 °C. This indicates that at temperatures where net NH_4NO_3 deposition exists, a steady-state is difficult to reach. This is the primary reason why fast-SCR kinetics are only conducted in a temperature-programmed mode here.

4.4. Application potentials for Fe/SSZ-13

At temperatures for normal diesel engine on-road operations (i.e., 200 to 300 °C), Cu/SSZ-13 provides much better performance than Fe/SSZ-13. Therefore Fe/SSZ-13 alone is insufficient as a good SCR catalyst for transportation needs. However, as displayed in Fig. 5, the combination of the two catalysts (in the form of a physical mixture here) indeed provides more stable performance and reduced N_2O formation at high temperatures. High-temperature N_2O generation by aged Cu/SSZ-13 is mainly due to non-selective NH_3 oxidation:

The possibility for N_2O reduction by Fe/SSZ-13, on the other hand, can be understood from the following N_2O -SCR pathway:

Results shown in Fig. 5(b) indicate that Fe/SSZ-13 is a much better catalyst than Cu/SSZ-13 in catalyzing this latter high-temperature reaction. The synergy for the mixed catalyst in this regard, therefore, is that some N₂O generated by Cu/SSZ-13 is consumed by Fe/SSZ-13.

The combination of Cu and Fe/zeolites as a concept has existed for several years and very detailed work, for example, the mass ratio and positioning in a layered coating for the two catalysts, has been carried out previously [26, 29, 30]. Several advantages for a combined catalyst are envisioned: (1) performance at transient high-temperature conditions, e.g., during combustion of trapped particulate matter; (2) for conditions when the NO₂ content in the feed is elevated; and (3) in the presence of sulfur poisoning. Overall, for this working concept, Fe/SSZ-13 can certainly be considered as one component because of its excellent hydrothermal stability, and especially its low selectivity for N₂O formation [25].

5. Conclusions

(1) For standard SCR, both fresh and aged Cu/SSZ-13 catalysts show much better low-temperature performance than Fe/SSZ-13 catalysts, which can be explained by an increased sensitivity to NH₃-inhibition by Fe/SSZ-13. The nature of this inhibition may be related to Fe(III) reduction to Fe(II) by NH₃.

(2) During hydrothermal aging, both catalysts undergo dealumination but Fe/SSZ-13 dealuminates more severely. One plausible explanation for maintenance of the zeolite in this case is that Fe can replace framework Al.

(3) For aged catalysts, Cu/SSZ-13 gains oxidation activity due to formation of CuO_x. However, Fe/SSZ-13 loses oxidation activity even though formation of FeO_x clusters and FeAlO_x species also occurs. Because of such differences, aged Cu/SSZ-13 loses, while Fe/SSZ-13 maintains high-temperature SCR selectivities. As such, a physical mixture of aged catalysts provides stable

SCR performance in a wide temperature range, and is also able to decrease N₂O formation at high reaction temperatures. This suggests that Fe/SSZ-13 can be used as a cocatalyst for Cu/SSZ-13 for transportation applications.

(4) During temperature-programmed SCR reactions, weak hysteresis is found during standard SCR due to NH₃ inhibition. In this case, NO conversions during the cooling step are slightly higher than during the heating step except in the temperature window where NH₃ molecules are released by Brønsted acid sites. For fast SCR, hysteresis caused by NH₄NO₃ inhibition is much more significant. NH₄NO₃ deposition is considerably enhanced by Brønsted and Lewis acidity of the catalysts. NH₄NO₃ inhibition also makes low-temperature steady-state fast SCR reaction measurements challenging.

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Figure Captions

Figure 1 NO/NH₃ conversions as a function of temperature during standard SCR for the fresh Cu- and Fe/SSZ-13 samples. Reactant feed contains 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹.

Figure 2 NO/NH₃ conversions as a function of temperature during standard SCR for the HTA (a) Fe/SSZ-13, and (b) Cu/SSZ-13 samples. Reactant feed contains 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹.

Figure 3 NO conversions as a function of temperature during NO oxidation for the (a) fresh, and (b) HTA Cu- and Fe/SSZ-13 samples. Reactant feed contains 350 ppm NO, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹.

Figure 4 NH₃ conversions as a function of temperature during NH₃ oxidation for the (a) fresh, and (b) HTA Cu- and Fe/SSZ-13 samples. Reactant feed contains 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹.

Figure 5 (a) NO conversions as a function of temperature during standard SCR for the HTA Cu/SSZ-13, Fe/SSZ-13 and mixed (1/1) samples. Reactant feed contains 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹. (b) N₂O yields as a function of temperature during the reaction on the three catalysts.

Figure 6 (a) Temperature and gas outlet concentrations as a function of time during temperature-programmed standard SCR for a fresh Fe/SSZ-13 catalyst. Reactant feed contains 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹. (b) Temperature and gas outlet concentrations as a function of time during temperature-programmed fast SCR on a fresh Fe/SSZ-13 catalyst. Reactant feed contains 175 ppm NO, 175 ppm NO₂, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹.

Figure 7 NO conversions as a function of temperature during temperature-programmed (a) standard SCR, and (b) fast SCR for fresh (upper panel) and HTA (lower panel) Fe/SSZ-13 samples. NO conversions are calculated using data from Figs. 6 and S1. (c) N₂O yields as a function of temperature during fast SCR for fresh (upper panel) and HTA (lower panel) Fe/SSZ-13 samples.

Figure 8 Temperature-programmed desorption profiles for fresh (upper panel) and HTA (lower panel) Fe/SSZ-13 samples after (a) standard SCR and (b) fast SCR reactions.

Figure 9 NO conversions as a function of temperature during temperature-programmed (a) standard SCR, and (b) fast SCR for fresh (upper panel) and HTA (lower panel) Cu/SSZ-13 samples. NO conversions are calculated using data from Figs. S2 and S3. N₂O yields as a function of temperature for fresh (upper panel) and HTA (lower panel) Cu/SSZ-13 samples during temperature-programmed (c) standard SCR, and (d) fast SCR.

Figure 10 Temperature-programmed desorption profiles for fresh (upper panel) and HTA (lower panel) Cu/SSZ-13 samples after (a) standard SCR and (b) fast SCR reactions.

Figure 11 (a) Temperature and gas outlet concentrations as a function of time during temperature-programmed fast SCR for an H/SSZ-13 catalyst. Reactant feed contains 175 ppm NO, 175 ppm NO₂, 350 ppm NH₃, 14% O₂, 2.5% H₂O balanced with N₂ at a GHSV of 200,000 h⁻¹. (b) NO conversions as a function of temperature calculated using data from (a). (c) Temperature-programmed desorption profiles obtained after reaction.

Figure 12 (a) Solid state ²⁷Al-NMR spectra for the fresh and HTA Fe/SSZ-13 samples. The bottom spectra are catalyst mass and scan number normalized for direct comparison. The upper spectrum is a magnified view for the HTA sample in order to provide more details. (b) Solid state ²⁷Al-NMR spectra of the fresh and HTA Cu/SSZ-13 samples. The spectra are catalyst mass and scan number normalized.

Gao, et. al., Figure 1

Gao, et. al., Figure 2

(a)

(b)

(a)

(b)

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(a)

(b)

(c)

(a)

(b)

(c)

(d)

(a)

(b)

(c)

Graphical abstract