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The Effect of Copper Loading on the Selective Catalytic Reduction of Nitric Oxide by Ammonia Over Cu-SSZ-13

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Abstract The effect of Cu loading on the selective catalytic reduction of NO_x by NH_3 was examined over a series of Cu ion-exchanged (20–80%) SSZ-13 zeolite catalysts. High NO reduction efficiencies (80–95%) were obtained over all catalyst samples between 250 and 500 °C, and at the gas hourly space velocity of 200,000 h^{-1}. Both NO reduction and NH_3 oxidation activities under these conditions were found to increase slightly with increasing Cu loading at low temperatures. However, NO reduction activity was suppressed with increasing Cu loadings at high temperatures (>500 °C) due to excess NH_3 oxidation. The optimum Cu ion exchange level appears to be $\sim$40–60% since higher than 80% NO reduction efficiency was obtained over 50% Cu ion-exchanged SSZ-13 up to 600 °C. The NO oxidation activity of Cu-SSZ-13 was found to be low regardless of Cu loading, although it was somewhat improved with increasing Cu ion exchange level at high temperatures. During the "fast" SCR (i.e., NO/$NO_2 = 1$), only a slight improvement in NO_x reduction activity was obtained for Cu-SSZ-13. Regardless of Cu loading, near 100% selectivity to N_2 was observed; only a very small amount of N_2O was produced even in the presence of NO_2. The apparent activation energies for NO oxidation and NO SCR were estimated to be $\sim$58 and $\sim$41 kJ/mol, respectively.

Keywords Selective catalytic reduction · Nitric oxide · Ammonia · Copper · Zeolite

1 Introduction

Lean-burn diesel engines can offer substantially higher fuel efficiency, good driving characteristics, and reduced carbon dioxide emission compared to stoichiometric gasoline engines. Since conventional three-way catalysts (TWC) are not effective in reducing nitrogen oxides (NO_x) under lean conditions, various lean NO_x catalyst technologies have been developed to date. Significant research and development efforts have been made for lean NO_x trap (LNT) catalysts that can store NO_x under lean conditions and reduce the stored NO_x under rich conditions, and selective catalytic reduction (SCR) catalysts that can selectively reduce NO_x in the presence of excess O_2 with a reducing agent (e.g., NH_3, urea, hydrocarbons).

A typical diesel emission control system using SCR also includes an oxidation catalyst (DOC) and a diesel particulate filter (DPF) in order to control the emissions of carbon monoxide, hydrocarbons (HC), and particulate matters (PM). They are placed in a specific order to achieve a desired level of emission reduction performance. Since NO_x reduction performance at low temperatures is often suppressed by slow SCR kinetics and hydrocarbon poisoning, a DOC is often used in upstream of the SCR catalyst. Because soot is often removed from DPF at high temperatures (>650 °C), high thermal stability and high-temperature NO reduction activity are both required for the SCR catalyst to remain effective for NO_x emission control [1].

SCR based on $V_2O_5/WO_3/TiO_2$ catalysts have been used commercially for stationary applications since the 1970s.

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However, zeolite-based base metal (e.g., Cu, Fe) catalysts have been developed for mobile applications because of their thermal stability and high NO_x reduction activity over a wide range of conditions. In particular, Cu^{2+} ion-exchanged ZSM-5 (Cu-ZSM-5) zeolites have been investigated most extensively for their NO decomposition and SCR activity [2]. Early development efforts were also focused on Cu-beta catalyst for its high NO_x reduction activity over a wide range of conditions [3].

Most recently, small pore zeolite-based Cu catalysts have become the subject of considerable study as they are now used commercially. Compared to Cu-ZSM-5 and Cu-beta, they have been found to be more active and selective, and less prone to deactivation by hydrocarbon inhibition or thermal degradation [4–8]. For example, following hydrothermal treatment at 800 °C for 16 h, little changes in NO_x reduction activity and physicochemical properties were observed for Cu ion-exchanged SSZ-13 (Cu-SSZ-13), a zeolite with the Chabazite (CHA) structure containing small radius (~3.8 Å) eight-membered ring pores [9]. In this paper, the effects of Cu loading on the NO_x reduction activity and selectivity over Cu-SSZ-13 were examined in order to determine the optimum ion exchange level.

2 Experimental

2.1 Catalyst Preparation and Characterization

Na-SSZ-13 ($Si/Al_2 = 12$) was first prepared using the previously reported method [3, 6]. Cu-SSZ-13 catalysts were prepared by aqueous ion-exchange of Na-SSZ-13 using $Cu(NO_3)_2$ as precursor. Cu ion-exchange levels were controlled from 20 to 80% by the amount of Cu^{2+} ions in the solution and the number of ion-exchange steps. Following the ion-exchange, samples were filtered, washed, and dried at 100 °C overnight. All catalyst samples were then calcined in an oven at 500 °C for 2 h prior to evaluation and characterization. The concentrations of Cu reported here were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at Galbraith Laboratories (Knoxville, TN, USA), and the results are summarized in Table 1. Prior to analysis, all samples were dried in vacuum at 120 °C for 2 h. The % Cu ion exchange levels were then used to designate the samples (e.g., 20% IE, 80% IE, etc.).

Table 1 Elemental analysis results of the Cu ion-exchanged SSZ-13 catalysts

Sample ID	20% IE	40% IE	50% IE	60% IE	80% IE
Cu (%)	1.23	2.38	3.10	3.40	4.30
Al (%)	4.95	5.11	5.13	4.93	4.61
Si (%)	30.4	30.6	31.0	29.7	29.8
% Ion-exchange	21.1	39.5	51.3	58.6	79.2

2.2 Catalyst Activity Measurement

All reactivity experiments were conducted in a horizontal packed bed micro reactor system. 0.05 g of catalyst sample (60–80 mesh size powder) was loaded in a 3/8″ OD quartz tube, which was then placed inside an electric furnace. The catalyst temperature was monitored by a thermocouple located immediately downstream of the catalyst bed. Prior to each experiment, all samples were pre-treated in 10% O_2, 8% H_2O, and balance N_2 at 500 °C for 1 h, to remove any impurities from the atmosphere or previous testing. The reaction feed gas contained 350 ppm NO_x, 350 ppm NH_3, 14% O_2, 10% H_2O and balance N_2. All the gas lines were heated to over 100 °C to avoid condensation of water and adsorption of ammonia inside the reactor system. Different total gas flow rates were used to vary the gas hourly space velocity (GHSV) from 30,000 to 200,000 h^{-1}. Concentrations of reactants and products were measured by a Nicolet 6700 infrared (FT-IR) spectrometer equipped with a 2-meter gas cell, which was held at 60 °C and a reduced pressure of 13 kPa.

The catalysts were evaluated for their steady-state NO_x reduction and NH_3 oxidation activity. The NO_x and NH_3 conversion efficiencies were calculated based on the difference in their concentrations measured before and after the catalyst, using the following equations shown below. On the other hand, NO oxidation is defined as the conversion of NO to NO_2. Note that NO_x conversion considers NO_x reduction to N_2 only, because N_2O is an undesired byproduct.

$$\%\ NO_x\ \text{conversion} = \{(NO + NO_2)_{\text{inlet}} - (NO + NO_2 + 2 \times N_2O)_{\text{outlet}}\} / (NO + NO_2)_{\text{inlet}} \times 100$$

$$\%\ NH_3\ \text{conversion} = (NH_{3\text{inlet}} - NH_{3\text{outlet}}) / NH_{3\text{inlet}} \times 100$$

$$\%\ NO\ \text{oxidation} = (NO_{2\text{outlet}} - NO_{2\text{inlet}}) / NO_{\text{inlet}} \times 100$$

3 Results and Discussion

3.1 Effect of Space Velocity

The steady-state NO reduction ("standard" SCR) activity of 80% Cu ion-exchanged SSZ-13 (designated as 80% IE) was examined using the feed gas containing 350 ppm NO, 350 ppm NH_3, 14% O_2 and 10% H_2O at the GHSV of 30,000 to 200,000 h^{-1} between 150 and 550 °C. As shown in Fig. 1, NO reduction activity increased with increasing temperature, reaching 80–90% at 250 °C. Overall, very

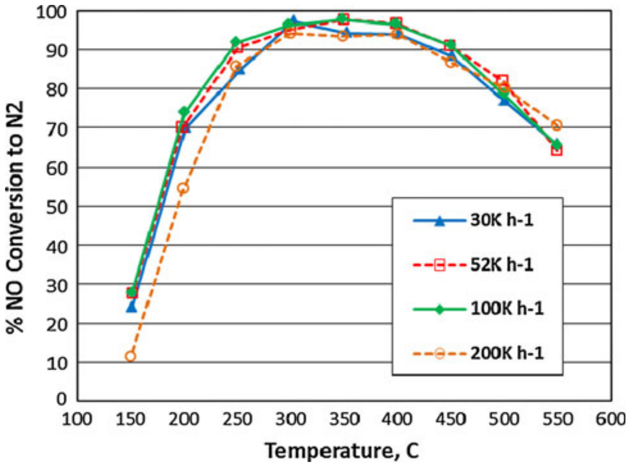

Fig. 1 Effect of gas hourly space velocity on NO conversion to N_2. Reaction feed: 350 ppm NO, 350 ppm NH_3, 14% O_2, 10% H_2O and balance N_2

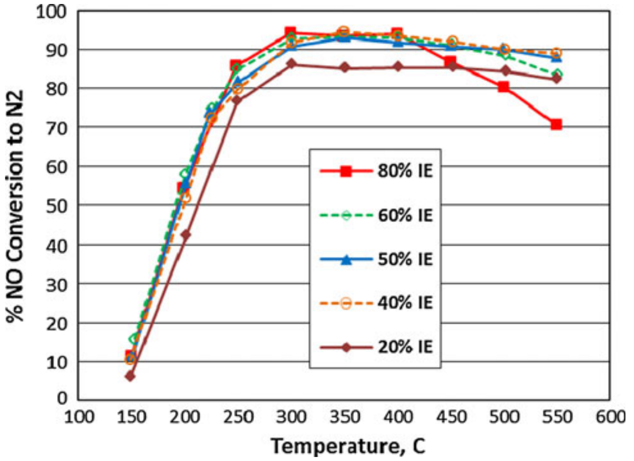

Fig. 2 Effect of Cu ion-exchange level on NO reduction to N_2. Reaction condition: 350 ppm NO, 350 ppm NH_3, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

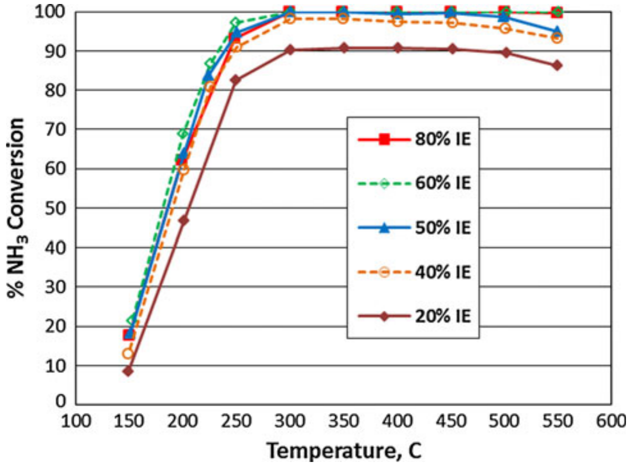

Fig. 3 Effect of Cu ion-exchange level on NH_3 conversion. Reaction condition: 350 ppm NO, 350 ppm NH_3, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

high NO reduction efficiencies (80–95%) were obtained between 250 and 500 °C under all conditions, even at a space velocity of 200,000 h^{-1}. At temperatures higher than 400 °C, NO reduction activity was limited by the availability of NH_3 reductant, because the non-selective NH_3 oxidation by O_2 becomes significant at these temperatures. Near 100% selectivity to N_2 for NO reduction was achieved, because less than 5 ppm N_2O was produced throughout the experiments. These results are consistent with our previous findings and literature data that showed high NO reduction activity and selectivity over Cu-SSZ-13 compared to other Cu/zeolite catalysts [4, 6, 9].

3.2 Effect of Cu Loading on NO Reduction by NH_3

The effect of Cu loading on selective catalytic reduction of NO by NH_3 (“standard” SCR) was examined over 20–80% Cu ion-exchanged samples at 200,000 h^{-1}. As Cu loading was increased from 20 to 80% ion-exchange level, NO reduction and NH_3 oxidation activities were slightly improved at low temperatures (shown in Figs. 2, 3). Initially, NO reduction activity increased with increasing temperature, reaching 80–90% at 250 °C, before decreasing at high temperatures (>450 °C). Overall, very high NO reduction efficiencies (80–95%) were obtained at all Cu loading levels between 250 and 500 °C. As mentioned earlier, high-temperature NO reduction activity becomes suppressed by the lack of NH_3, which is caused by the NH_3 oxidation by O_2 to NO and N_2. It appears that this non-selective NH_3 oxidation, which deprives the SCR catalyst of NH_3 reductant, is enhanced with increasing Cu loading, because high NO reduction activity was maintained up to 550 °C at lower Cu loading levels (less than 60% ion-exchange level). Regardless of Cu loading level, near 100% selectivity to N_2 for NO reduction was achieved, because less than 5 ppm N_2O was produced throughout these experiments.

During the NO reduction by NH_3 in excess O_2, NO reduction and NH_3 oxidation activities are closely related, because SCR catalysts promote the selective reaction of NH_3 with NO instead of O_2. For example, when the NO reduction and NH_3 oxidation activities are compared over 20–80% Cu ion-exchanged SSZ-13 at 150–250 °C, NO reduction activity is shown to increase linearly with NH_3 oxidation activity regardless of Cu loading levels (Fig. 4).

As discussed earlier, non-selective NH_3 oxidation by O_2 becomes dominant with increasing temperature, not only depriving the SCR catalyst of the NH_3 reductant, but also producing additional NO to reduce. For this reason, when Cu loading in zeolite-based catalysts is increased to improve the low-temperature NO reduction activity,

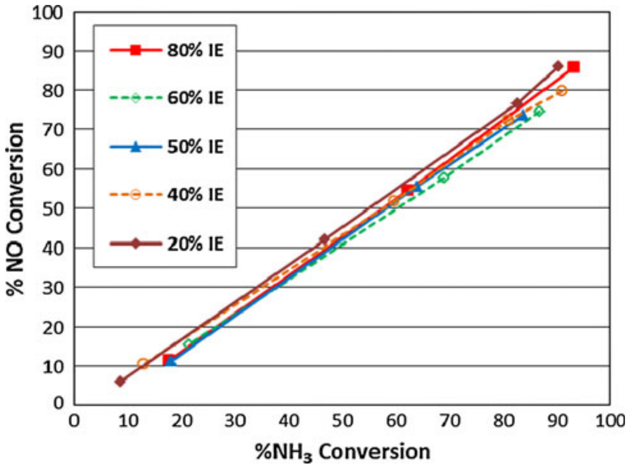

Fig. 4 Comparison between NO conversion and NH_3 conversion. Reaction condition: 350 ppm NO, 350 ppm NH_3, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

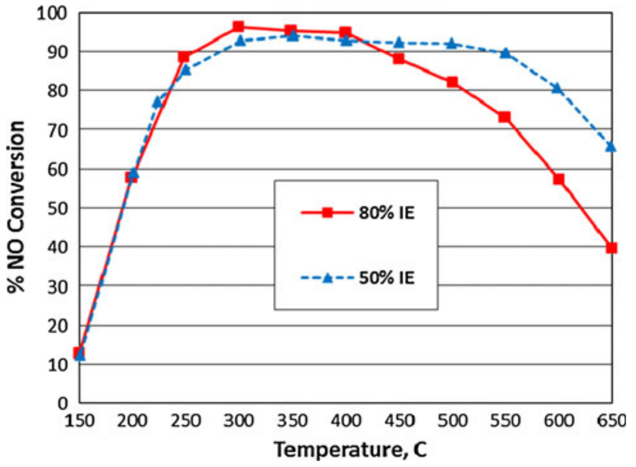

Fig. 5 Effect of Cu loading on NO reduction at high temperatures. Reaction condition: 350 ppm NO, 350 ppm NH_3, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

high-temperature NO reduction activity is often suppressed [10]. In particular, CuO particles can readily form in other types of Cu/zeolite catalysts at high Cu loadings or after aging, and these particles tend to oxidize NH_3 instead of reducing NO_x with NH_3 [9].

As noted above, high NO reduction activity over Cu-SSZ-13 was maintained up to 550 °C at lower Cu loading levels, as shown in Fig. 2. Since there was no effect of space velocity on high-temperature NO reduction activity (shown in Fig. 1), it appears that high-temperature non-selective NH_3 oxidation over Cu-SSZ-13 may be a function of Cu loading only. Thus, 50 and 80% ion-exchanged Cu-SSZ-13 catalysts (i.e., 50 vs. 80% IE) were further examined for high-temperature NO reduction activity up to 650 °C, which is a temperature that the SCR catalyst typically encounters during the diesel particulate filter (DPF) regeneration. As shown in Fig. 5, over 80% NO reduction activity was obtained up to 600 °C for the 50% IE sample, while significantly reduced NO reduction activity was obtained over the 80% IE sample. This clearly demonstrates that the high-temperature NO reduction activity of Cu-SSZ-13 can be further improved by controlling Cu loading. Considering the overall NO reduction activity between 150 and 650 °C, it appears that the optimum Cu ion-exchange level should be ~40–60% for Cu-SSZ-13 catalysts.

3.3 Effect of Cu Loading on NO Oxidation

The selective catalytic reduction of NO by NH_3 consists of several parallel and consecutive reaction steps, such as NH_3 adsorption and oxidation, NO oxidation and reduction, etc. It is well known that SCR reaction kinetics can be improved in the presence of equimolar amounts of NO and NO_2 in the feed gas, often referred to as "fast" SCR or NO/NO_2-SCR. NO oxidation activity typically increases with increasing temperature until it is limited by thermodynamic equilibrium, typically at temperatures higher than 450 °C. Previous research has suggested that NO oxidation may be the rate-determining step during the "standard" NO-SCR reaction [11, 12]. Thus, the effect of Cu loading on NO oxidation over Cu-SSZ-13 was examined for 20–80% Cu ion-exchange levels at 200,000 h^{-1}. As shown in Fig. 6, NO oxidation over Cu-SSZ-13 was found to be quite low regardless of Cu loading, although it was slightly improved with increasing Cu content at high temperatures. This apparent lack of NO oxidation activity despite very high NO reduction activity over Cu-SSZ-13 suggests that NO oxidation may not be an essential reaction step for NO reduction over this catalyst.

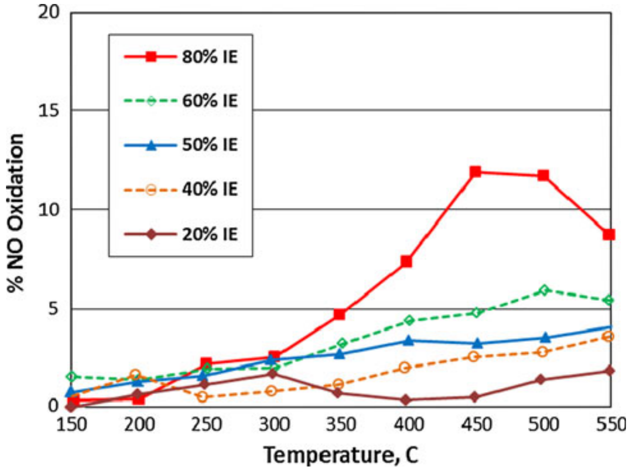

Fig. 6 Effect of Cu loading on NO oxidation. Reaction condition: 350 ppm NO, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

3.4 Effect of Cu Loading on “fast” NO/NO_2-SCR

As mentioned earlier, it is well known that NO_x reduction efficiency can be improved in the presence of equimolar amounts of NO and NO_2 in the feed (thus, known as “fast” SCR). However, as shown in Figs. 2 and 6, very high NO reduction efficiencies were obtained despite very low NO oxidation activity over Cu-SSZ-13. In fact, our previous study has shown only a slight improvement in NO_x reduction over Cu-SSZ-13 [9]. Thus, considering the lack of NO oxidation activity and relatively high NO reduction activity, the “fast” SCR activity was further examined using the 20% Cu ion-exchanged sample (20% IE) and 80% Cu sample (80%). For the 80% IE sample, little difference in NO_x reduction activity was observed under “standard” (Fig. 2) and “fast” (Fig. 7) SCR conditions, which is consistent with our previous study. On the other hand, NO_x reduction activity during “fast” SCR (Fig. 7) over the 20% IE sample was improved at all temperatures compared to “standard” SCR (Fig. 2), reaching over 90% NO_x reduction from 250 °C up to 550 °C. The higher NO_x reduction efficiency over the 20% IE sample was also accompanied by 100% NH_3 conversion efficiency (not shown). Under the “standard” SCR conditions, less than 100% NH_3 conversion efficiency was obtained over the 20% IE sample (shown in Fig. 3). Thus, this slight improvement in NO_x reduction activity over the 20% IE sample was obtained because NH_3 could be fully reacted with NO_x under “fast” SCR kinetics.

During NH_3-SCR over Cu/zeolite catalysts, N_2O formation has been proposed to proceed via a reaction mechanism that involves the formation and decomposition of NH_4NO_3:

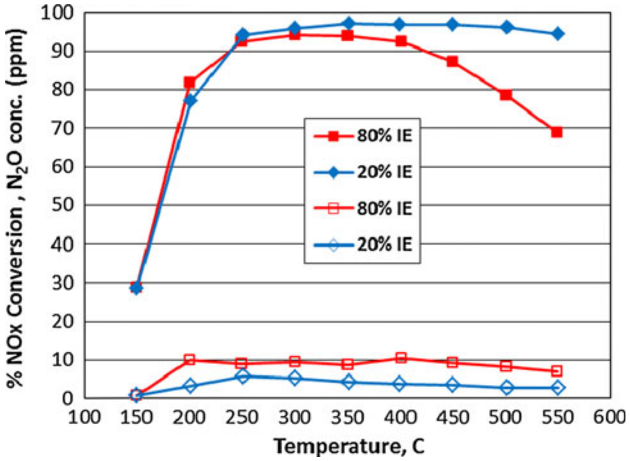

Fig. 7 Effect of Cu loading on NO/NO_2-SCR and N_2O formation. Reaction condition: 175 ppm NO, 175 ppm NO_2, 350 ppm NH_3, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}. *Closed symbols* % NO_x conversion. *Open symbols* N_2O concentration

$$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O$$

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Even in the absence of NO_2 in the feed, NH_4NO_3 can also be formed by the reaction between adsorbed NH_3 and surface nitrate species (NO_3^-) formed by the oxidation of NO on the catalyst [12]. However, when NH_3-SCR over various Cu/zeolites was compared, very little N_2O was produced over Cu-SSZ-13 even in the presence of NO_2 (also shown in Fig. 7), whereas large amounts of N_2O were formed over Cu-ZSM-5, Cu-beta, and Cu-Y under the same conditions [6, 9]. The lack of NO oxidation activity and very limited N_2O formation shown in this study suggest that the reaction mechanism proposed for NH_3-SCR over Cu/zeolites, in particular, may need to be reevaluated for Cu-SSZ-13. Because very little N_2O formation was seen over other small pore zeolite-based Cu catalysts, such as Cu-SAPO-34 and Cu/Nu-3 [6], it is possible that the observed high selectivity to N_2 and the role of NO_2 in SCR mechanism may be related to the zeolite structure/type.

3.5 Apparent Activation Energies for Reduction and Oxidation of NO

Overall NH_3-SCR chemistry is well established, and various reaction pathways have been identified for $V_2O_5/WO_3/TiO_2$, Cu/zeolite, and Fe/zeolite catalysts. NO and NO_2 react with NH_3 in the presence of O_2 at different rates, and the fastest reaction rate is obtained in the presence of equimolar mixture of NO and NO_2 (thus, called “fast” SCR). More details about the NH_3-SCR reaction mechanism and kinetics can be found elsewhere [12, 13] and beyond the scope of this paper.

The active sites in Cu/zeolite catalysts include acid sites and Cu species of various oxidation states and coordination. For example, CuO or Cu-aluminate-like species can readily form in many Cu/zeolite catalysts at high Cu loading, especially after aging [9]. However, Cu species in Cu-SSZ-13 were found to exist only as isolated Cu ions even after hydrothermal treatment at 800 °C for 16 h [9]. More recently, it has been reported that four-fold coordinated Cu^{2+} species were found to predominate in Cu-SSZ-13 as evidenced by in situ X-ray absorption spectroscopy (XAS) and density functional theory (DFT) calculation [14]. Since isolated Cu^{2+} ions would be the only active site over the Cu-SSZ-13 catalysts used in this study, it may be possible to estimate the rate parameters for Cu-SSZ-13 based on Cu ion amount for a given catalyst volume and flow rate. Thus, the apparent activation energy for the reduction of NO by NH_3 over Cu-SSZ-13 was estimated here using the data obtained at 150–250 °C at 200,000 h^{-1} (shown in Fig. 2), where conversions are less than 90%.

Previous studies have shown that the NO reduction by NH_3 over zeolite-based base metal catalysts (e.g., Cu-ZSM-5, Cu-MOR, Fe-ZSM-5) is approximately first-order with respect to NO, zero or negative-order for NH_3, and about half-order for O_2 [13, 14]. Thus, it is reasonable to expect the same reaction order for NH_3-SCR reaction over Cu-SSZ-13, and the rate for NO reduction can be expressed as the following:

$$r_{\mathrm{NO}} = -k[\mathrm{NO}][\mathrm{O}_2]^{0.5},$$

where k is the rate constant.

Because the amount of oxygen is in excess at 10%, the above equation can be re-written as pseudo first-order rate expression, and the apparent rate constant can be estimated based on the extent of NO conversion only:

$r_{\mathrm{NO}} = -k_{\mathrm{a}}[\mathrm{NO}]$, where k_{a} is the apparent rate constant, $\ln([\mathrm{NO}]_{\mathrm{out}}/[\mathrm{NO}]_{\mathrm{in}}) = -k_{\mathrm{a}}t$, where t is the residence time.

Since the amount of Cu was varied while the catalyst volume and flow rate were fixed, the residence time based on Cu content was used in this exercise. As shown in Fig. 8, linear plots were obtained for the NO conversion against residence time. This linearity suggests that the NO reduction at 150–250 °C is first-order with respect to NO over Cu-SSZ-13, as expected. Based on the rate constants from these plots, an Arrhenius plot of the logarithm of rate constant versus inverse temperature was obtained (shown in Fig. 9). From the slope of the plot, an apparent activation energy of ~41.2 kJ/mol can be estimated for the NO reduction by NH_3 ("standard" SCR) over Cu-SSZ-13, which is in line with the values obtained for various zeolite-based SCR catalysts (e.g., 29–89 kJ/mol) [14–17].

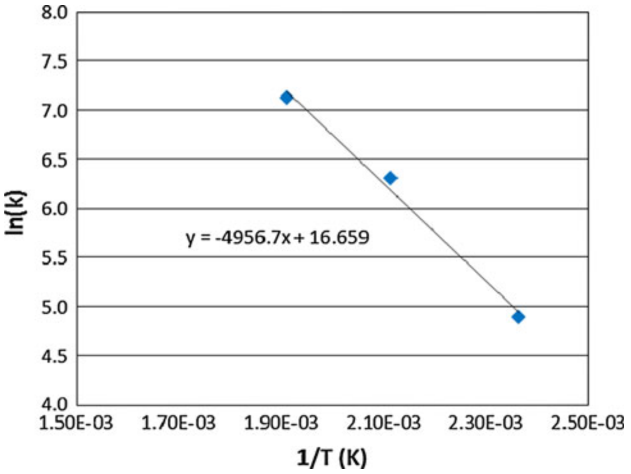

Fig. 9 Arrhenius plot of rate constant (k) for NO reduction versus inverse temperature. Reaction condition: 350 ppm NO, 350 ppm NH_3, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

In addition, the apparent activation energy for NO oxidation over Cu-SSZ-13 was also estimated based on the Cu content using the data obtained at 300–400 °C at 200,000 h^{-1} (shown in Fig. 6). Since less than 10% NO oxidation was obtained under the conditions used in this study, differential kinetics could be ensured for this reaction. Previous studies have also shown that the NO oxidation over zeolite-based base metal catalysts is approximately first-order with respect to NO and about half-order for O_2 [12, 13, 15]. Thus, same reaction orders were assumed for Cu-SSZ-13, and the same rate expression was used for NO oxidation.

Using the same approach described earlier, apparent rate constants can be estimated based on the extent of NO conversion and Cu amount. As shown in Fig. 10, linearity indicates that the NO oxidation at 300–400 °C is also first-order with respect to NO over Cu-SSZ-13 like other SCR catalysts. Using the rate constants estimated from these plots, an Arrhenius plot of the logarithm of rate constant

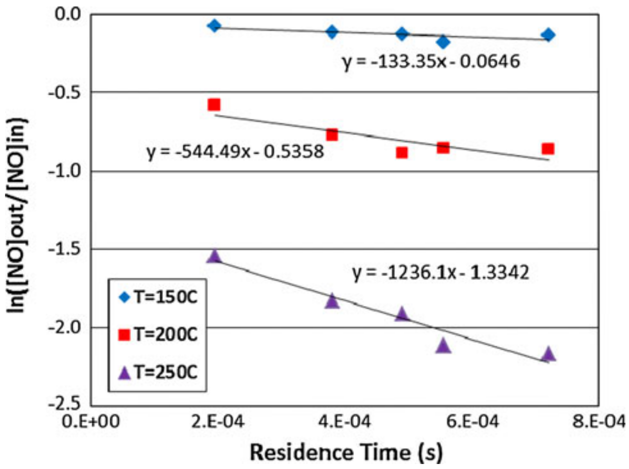

Fig. 8 First order plots for NO reduction versus residence time. Reaction condition: 350 ppm NO, 350 ppm NH_3, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

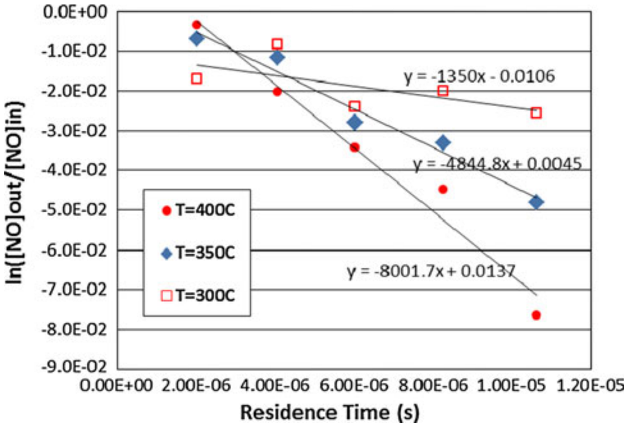

Fig. 10 First order plots for NO oxidation versus residence time. Reaction condition: 350 ppm NO, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

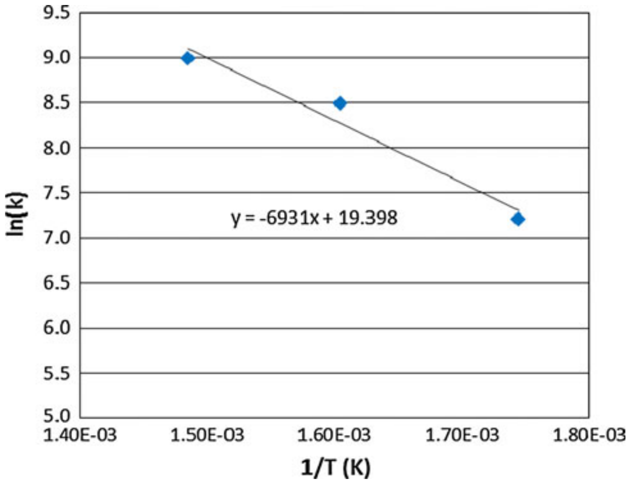

Fig. 11 Arrhenius plot of rate constant (*k*) for NO oxidation versus inverse temperature. Reaction condition: 350 ppm NO, 14% O_2, 10% H_2O, balance N_2 at 200,000 h^{-1}

versus inverse temperature was obtained as shown in Fig. 11. The apparent activation energy of ~57.6 kJ/mol for NO oxidation over Cu-SSZ-13 can be estimated from this plot, and it is somewhat higher than those obtained previously for other zeolite-based SCR catalysts (e.g., 24–48 kJ/mol) [13, 15–17].

4 Conclusions

In this work, the effect of Cu loading on the selective catalytic reduction of NO_x by NH_3 was examined over Cu ion-exchanged SSZ-13 catalysts in the 20–80% ion-exchange level. High NO reduction efficiencies (80–95%) were obtained over all catalyst samples between 250 and 500 °C, and at the space velocity of 200,000 h^{-1}. Both NO reduction and NH_3 oxidation activities were found to increase slightly with increasing Cu loading at low temperatures. However, NO reduction activity was suppressed with increasing Cu loadings at high temperatures (>500 °C) because of non-selective NH_3 oxidation by O_2, which deprived Cu-SSZ-13 of the NH_3 reductant for NO reduction. More than 80% NO reduction efficiency was obtained over 50% Cu ion-exchanged Cu-SSZ-13 up to 600 °C, which suggested that optimum Cu ion exchange level appears to be ~40–60% for Cu-SSZ-13. NO oxidation over Cu-SSZ-13 was found to be quite low regardless of Cu loading, although it was enhanced slightly with increasing Cu ion-exchange level at high temperatures. During the "fast" NO/NO_2-SCR, only a slight improvement in NO_x reduction activity was obtained, and very small amounts of N_2O were produced. The lack of NO oxidation activity and very limited N_2O formation shown in this study suggest that the reaction mechanism proposed for NO_x reduction by NH_3 over Cu/zeolites may need to be reevaluated for Cu-SSZ-13. The apparent activation energies for NO oxidation and NO SCR over Cu-SSZ-13 were estimated to be ~58 and ~41 kJ/mol, respectively.

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References

1. Lee JH, Paratore MJ, Brown DB (2009) SAE Int J Fuels Lubr 1:96
2. Iwamoto M, Furukawa H, Mine Y, Uemura F, Mikuriya S, Kagawa S (1986) J Chem Soc Chem Commun 11:1272
3. Peden CHF, Kwak JH, Kim DH, Lee JH, Cavataio G, Cheng Y, Jen HW, Lambert C (2011) Catal Today (accepted)
4. Kwak JH, Tonkyn RG, Kim DH, Szanyi J, Peden CHF (2010) J Catal 275:187
5. Bull I, Xue WM, Burk P, Boorse RS, Jaglowski WM, Koermer GS, Moini A, Patchett JA, Dettling JC, Caudle MT (2009) US Patent 7:610
6. Andersen PJ, Casci J, Chen HY, Collier K, Fedeyko JM, Foo R, Rajaram R (2011) The 22nd North American Catalysis Society Meeting (no publication yet)
7. Fickel DW, Lobo RF (2010) J Phys Chem C 114:1633
8. Fickel DW, D'Addio E, Lauterbach JA, Lobo RF (2011) Appl Catal B 102:441
9. Kwak JH, Tran D, Burton SD, Szanyi J, Lee JH, Peden CHF (2011) J Catal (accepted)
10. Park JH, Park HJ, Baik JH, Nam IS, Shin CH, Lee JH, Cho BK, Oh SH (2006) J Catal 240:47
11. Eng J, Bartholomew CH (1997) J Catal 171:14
12. Colombo M, Nova I, Tronconi E (2010) Catal Today 151:223
13. Metkar PS, Salazar N, Muncrief R, Balakotaiah V, Harold MP (2011) Appl Catal B 104:110
14. McEwen JS, Anggara T, Schneider WF, Kispersky VF, Miller JT, Delgass WN, Ribeiro FH, Catal Today (submitted)
15. Sjovall H, Blint RJ, Olsson L (2009) Appl Catal B 92:138
16. Wang TJ, Baek SW, Kwon HJ, Kim YJ, Nam IS, Cha MS, Yeo GK (2011) Ind Eng Chem Res 50:2850
17. Pant A, Schmieg SJ (2011) Ind Eng Chem Res 50:5490