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Priority Communication

Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NO_x with NH_3

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ABSTRACT

Superior activity and selectivity of a Cu ion-exchanged SSZ-13 zeolite in the selective catalytic reduction (SCR) of NO_x with NH_3 were observed, in comparison with Cu-beta and Cu-ZSM-5 zeolites. Cu-SSZ-13 was not only more active in the NO_x SCR reaction over the entire temperature range studied (up to 550 °C), but also more selective toward nitrogen formation, resulting in significantly lower amounts of NO_x by-products (i.e., NO_2 and N_2O) than the other two zeolites. In addition, Cu-SSZ-13 demonstrated the highest activity and N_2 formation selectivity in the oxidation of NH_3. The results of this study strongly suggest that Cu-SSZ-13 is a promising candidate as a catalyst for NO_x SCR with great potential in after-treatment systems for either mobile or stationary sources.

1. Introduction

The abatement of environmentally harmful NO_x compounds (NO, NO_2, and N_2O) emitted from mobile or stationary power sources remains a challenging task for the catalysis community. In particular, conventional three-way catalysts used in the exhaust after treatment technologies of internal combustion engines prove ineffective when the engine is operated under highly oxidizing conditions (to achieve better fuel efficiency). The problem is daunting, since reduction chemistry (NO_x to N_2) has to be carried out under highly oxidizing conditions. Several approaches have been proposed for lean-NO_x abatement, each of them with its own specific sets of problems. The two technologies that seem to have clear advantages among the processes proposed are the selective catalytic reduction either with hydrocarbons (HC-SCR) or with ammonia (NH_3-SCR), and lean-NO_x traps (LNT). For the NH_3-SCR technology, transition metal (in particular Fe and Cu) ion-exchanged zeolite catalysts have shown high activity and N_2 selectivity.

The most extensive studies have been carried out on Cu^{2+} ion-exchanged ZSM-5 (Cu-ZSM-5) zeolites, first shown to exhibit high NO decomposition rates and NO_x SCR activities in the 1980s [1–7]. More recently, Cu^{2+}-exchanged beta zeolite (Cu-beta) has been shown to have excellent activity in the SCR of NO_x with NH_3, and metal-exchanged beta zeolites are generally found to have greater hydrothermal stability than similar ZSM-5 catalysts [8]. In the very recent patent literature, Cu^{2+} ion-exchanged SSZ-13 (Cu-SSZ-13) has been reported to exhibit NO_x conversions of 90–100% over a wide temperature range in the NH_3-SCR process, and its activity exceeded 80% even after extensive high-temperature hydrothermal aging [9]. The SSZ-13 zeolite has chabazite (CHA) structure with a relatively small pore radius (~3.8 Å) in an eight-membered ring [10]. The enhanced thermal stability of the Cu-SSZ-13 catalyst has been attributed to the location of copper ions within the cage; i.e., just outside the six-membered rings of the zeolite framework, as evidenced by XRD analysis [11]. Although, high catalytic activity has been reported in the patent literature for the Cu-SSZ-13 catalyst under a specific set of reaction conditions, no comparisons have been made with other, widely studied NH_3-SCR catalysts (i.e., Cu-ZSM-5 and Cu-beta) under the same reaction conditions. Here, we report on the performance of a Cu-SSZ-13 catalyst in the SCR of NO_x with NH_3, particularly focusing on the activity and N_2 selectivity in comparison with those of Cu-beta and Cu-ZSM-5. We also compare the NH_3 oxidation activities/selectivities of these catalysts under highly oxidizing conditions. Our results confirm that the activity and selectivity of the Cu-SSZ-13 catalyst for both NO_x SCR with NH_3 and NH_3 oxidation are superior to those of both Cu-beta and Cu-ZSM-5.

2. Experimental

The SSZ-13 zeolite was synthesized using the methods recently published by Fickel and Lobo [11], reported to give a material with a Si/Al_2 ratio of ~12. The structure-directing agent used in the synthesis, N,N,N-trimethyl-1-adamantanamine iodide, was synthesized using the procedure reported by Zones [10]. After synthesis,

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the SSZ-13 was calcined at 550 °C for 5 h in air before ion exchange in order to remove the zeolite framework structure-directing agent. Copper ions were exchanged into the zeolite in an aqueous ion-exchange process, using 0.1 M $Cu(NO_3)_2$ solutions; solution volumes were such that they contained twice the amount of Cu^{2+} needed for complete ion exchange. After ion exchange over 1 day at room temperature, the catalysts were filtered, thoroughly washed with distilled water, and dried overnight at 100 °C. To ensure complete ion exchange, this process was carried out a second time with an aqueous solution of Cu^{2+} of the same initial concentration. The dried catalysts were pre-calcined at 500 °C in laboratory air for 2 h before reaction tests. The CHA structure in Cu-SSZ-13 was confirmed with XRD measurement.

For comparison purposes, Cu^{2+}-exchanged ZSM-5 and beta zeolites were prepared from commercially available zeolites (ZSM-5 (CBV-3024, $Si/Al_2 = 30$) and beta (CP-814C, $Si/Al_2 = 38$), both from Zeolyst International Co.), using the same ion-exchange and calcination procedures applied to the preparation of the Cu-SSZ-13 sample, except for varying the Cu^{2+} concentration of the solution to match the Si/Al_2 ratios of the particular zeolite.

The NO_x SCR activities were measured in a flow-through powder reactor system using gas mixtures containing 350 ppm NO, 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2. The total flow rate was held at 300 sccm over the 120–130 mg catalyst powder samples (SV ~ 30,000 h^{-1}). The temperature was varied from 550 to 160 °C in approximately 50 °C steps, as measured by a small type K thermocouple inserted directly into the center of the catalyst powder bed. The NH_3 oxidation reaction was carried out under similar reaction conditions in the absence of NO in the gas mixture. The reactant and product gas mixtures (NO, NO_2, N_2O, and NH_3) were analyzed using FTIR spectroscopy (Nicolet Magma 760 with OMNIC Series software) in a heated, 2-m path-length gas cell. Our reported NO_x conversions (%) are defined as $\{NO_{inlet} - (NO + NO_2 + 2 * N_2O)_{outlet}/NO_{inlet}\} * 100$.

3. Results and discussion

NO_x conversions as a function of reaction temperatures between 150 and 550 °C are shown in Fig. 1 over the three Cu–zeolites studied. Both Cu-ZSM-5 and Cu-SSZ-13 catalysts exhibit maximum conversion (>95%) at temperatures somewhat above 250 °C, while the maximum conversion over Cu-beta in the same temperature range is slightly lower (90%). Note that the Cu-SSZ-13 catalyst maintains its high conversion (>90%) up to 500 °C, while the NO_x conversion of Cu-ZSM-5 begins to decline above 300 °C. Even at 550 °C, the highest temperature of this study, Cu-SSZ-13 exhibits a respectably high conversion of 83%. The order of activity of these catalysts in the high-temperature region (350–550 °C) is as follows: Cu-SSZ-13 > Cu-ZSM-5 > Cu-beta.

In addition to NO_x conversion, significant differences in product selectivity were observed for the three zeolite catalysts studied. Fig. 2 displays the amounts of by-products NO_2 (a) and N_2O (b) formed in the SCR reaction. At reaction temperatures above 300 °C, Cu-ZSM-5 and Cu-beta produce significant amounts of NO_2, and at 500 °C the amounts of NO_2 produced over these two catalysts are 30 and 25 ppm, respectively, much higher than the <10 ppm measured over the Cu-SSZ-13. N_2O formation profiles as a function of reaction temperature, shown in Fig. 2b, also exhibit large differences among the three Cu ion-exchanged zeolite catalysts. The N_2O level over the Cu-SSZ-13 is very low (<5 ppm) over the entire temperature range studied, while the Cu-beta catalyst shows a double maxima in N_2O concentrations at low and high

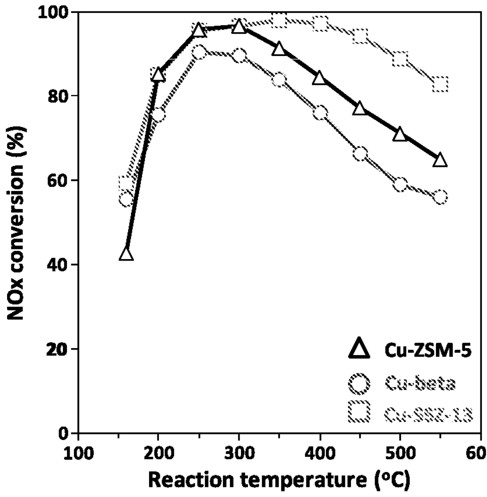

Fig. 1. NO_x conversion profiles for Cu-SSZ-13 (squares), Cu-beta (circles), and Cu-ZSM-5 (triangles) at various temperatures in a gas mixture containing 350 ppm NO, 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2.

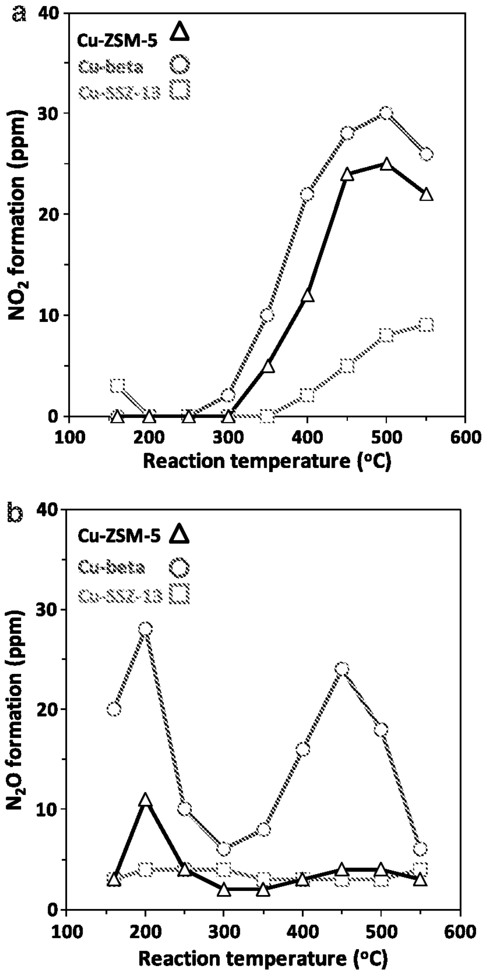

Fig. 2. NO_2 (a) and N_2O (b) formation profiles during NH_3 SCR on Cu-SSZ-13 (squares), Cu-beta (circles), and Cu-ZSM-5 (triangles) at various temperatures in a gas mixture containing 350 ppm NO, 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2.

temperatures; i.e., 27 ppm at 200 °C and 24 ppm at 450 °C, respectively. The Cu-ZSM-5 catalyst produced a similar N_2O formation profile to Cu-beta, but the amounts of N_2O formed were much smaller. These N_2O formation profiles are likely related to the reaction mechanisms of the NO_x reduction reactions. For example, our results demonstrate that reaction intermediates (e.g., NO_x–NH_3 adsorbed complexes) on Cu-SSZ-13 take a more selective reaction route toward the production of N_2 than do the complexes on the Cu-beta and Cu-ZSM-5 catalysts.

The differences in activity and selectivity of the three zeolites studied may be related to fundamental differences in the known structures of these zeolites, i.e., the pore sizes and locations of the copper ions. The order of high-temperature NH_3 SCR reactivity discussed earlier is the inverse of the order in pore size, i.e., SSZ-13 having the smallest pores (~4 Å, 8-membered ring) being the most active, ZSM-5 with medium size pore opening (~5.5 Å, 10-membered ring) having medium activity, and beta with the largest pores (~7 Å and ~5.5 Å, 12-membered ring) having the lowest activity and N_2 selectivity. For these three catalysts, the smaller size pores seem to be preferred for the desirable reaction pathways; however, detailed mechanistic studies need to be conducted to substantiate the correlation between pore size and activity/selectivity. In summary, both the activity and selectivity of NO_x SCR with NH_3 for Cu-SSZ-13 are superior to those of Cu-ZSM-5 and Cu-beta over the entire temperature range studied (up to 550 °C).

The differences observed in the ammonia SCR reactivities and N_2 formation selectivities for the three catalysts studied may also be related (at least in part) to their abilities to oxidize ammonia. Therefore, we performed NH_3 oxidation reactions over the three different Cu–zeolite catalysts in the absence of NO and the results are presented in Fig. 3. Ammonia conversions (Fig. 3a) reveal that the light-off temperature for NH_3 oxidation is the lowest for Cu-SSZ-13, indicating its superior intrinsic NH_3 oxidation ability. For this catalyst, the NH_3 oxidation reaction lights off at around 200 °C and reaches a conversion level of more than 90% at ~300 °C. The NH_3 conversion profiles for Cu-beta and Cu-ZSM-5 are shifted to higher temperatures by ~50 and ~100 °C, respectively, relative to that of Cu-SSZ-13.

The concentrations of NO_x ($NO + NO_2 + N_2O$) in the reaction effluent, which are regarded as by-products during NH_3 oxidation to N_2, are plotted in Fig. 3b. The Cu-beta catalyst produced relatively higher levels of these by-products, with a maximum of about 55 ppm at 350 °C, while the Cu-ZSM-5 catalyst produced significant amounts of by-products at 550 °C. The relative lack of NO_x formation during ammonia oxidation on the Cu-SSZ-13 catalyst implies that most of the NH_3 is converted to N_2 over a wide temperature range for this catalyst. The near absence of further oxidization to N_2O, NO, or NO_2, as was the case for the Cu-beta and Cu-ZSM-5 catalysts, suggests again that the environment within the Cu-SSZ-13 catalyst may provide optimum conditions for selective conversion of reaction intermediates to N_2.

According to the results of previous studies, noble metal catalysts, including Pt [12], have been found to be very active in ammonia oxidation, but rather non-selective to N_2 formation, while transition metal oxides such as MnO_2 and CuO [13] have higher N_2 selectivity, but require significantly higher temperatures. Cu-SSZ-13, on the other hand, can meet the two important requirements: excellent NH_3 oxidation activity and N_2 selectivity over a wide temperature range. Thus, for example, the use of Cu-SSZ-13 as an NH_3 oxidation catalyst at the downstream end of a NO_x SCR with NH_3 unit might provide flexibility for controlling the dose of urea introduced before the SCR catalyst, since any excess of NH_3 can perhaps be removed more easily over the catalyst bed.

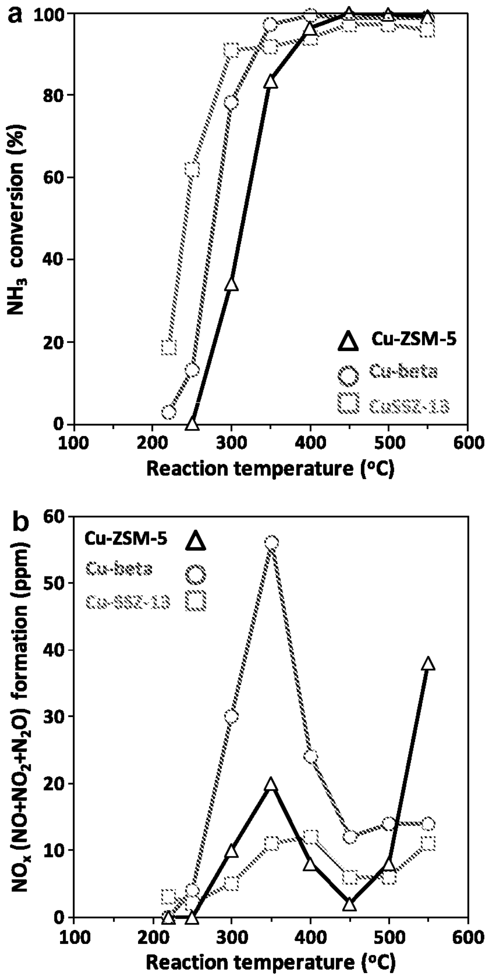

Fig. 3. (a) NH_3 conversion profiles and (b) NO_x product distributions during the NH_3 oxidation reaction on Cu-SSZ-13 (squares), Cu-beta (circles), and Cu-ZSM-5 (triangles) at various temperatures in a gas mixture containing 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2.

4. Conclusions

Under the same reaction conditions for NO_x SCR with NH_3, Cu-SSZ-13 demonstrates superior activity and N_2 formation selectivity in comparison with Cu-beta and Cu-ZSM-5 zeolites. We find that Cu-SSZ-13 is more active for NO_x conversion over the entire temperature range studied (160–550 °C). Moreover, the Cu-SSZ-13 is also more selective toward the formation of N_2, producing lower amounts of undesired by-products such as NO_2 and N_2O. Our results also demonstrate that Cu-SSZ-13 has superior performance for NH_3 oxidation (lower light-off temperature) than Cu-beta and Cu-ZSM-5 zeolites, while also producing significantly lower amounts of (over-oxidized) NO_x species. These results suggest that Cu-SSZ-13 is an excellent candidate catalyst for use in practical NH_3 SCR of NO_x and/or NH_3 oxidation applications (the after-treatment systems of various mobile or stationary sources). Detailed mechanistic studies are currently under way in our laboratory to understand the origin of the different activities and selectivities observed for these three catalysts in both the NO_x SCR and NH_3 oxidation reactions.

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