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# NOTE

# A Comparison of Adsorption and Reaction Properties in Cu-ZSM-5 and Cu-Y

Copper-exchanged zeolites have been studied extensively because of their ability to catalyze $NO_x$ reduction reactions in the presence of oxygen; however, the specific nature of the interaction between Cu and a zeolite is not completely understood (1–3). It is clear that ion exchange of Cu with lattice Al sites plays an important role since copper dispersed on nonzeolitic supports or materials incapable of ion exchange (silicalite) is not as active for de-$NO_x$ reactions as Cu-ZSM-5 even when the rates are normalized for Cu content (4). In addition, different zeolite structures have been reported to have markedly different catalytic activities, further suggesting a site-specific interaction for Cu at the exchange sites. For example, the temperature at which the rate for NO decomposition becomes significant is almost 100 K lower on Cu-ZSM-5 than it is on Cu-Y, even with Y samples containing twice as much copper by weight as their ZSM-5 counterparts (1). Because of the dramatic differences between Cu-Y and Cu-ZSM-5, a comparison of these two materials is of great interest since it may help identify the species most active in the catalysis of de-$NO_x$ reactions.

In this Note, we set out to answer two specific questions. First, does the Si/Al ratio of the zeolite have a pronounced effect on the activity of a Cu-exchanged zeolite? A review of the literature indicates that experiments carried out comparing activities of Cu-Y to those of Cu-ZSM-5 have always used a high Al content (as synthesized) Y zeolite (1, 4). Since isolation of the Cu sites may be essential for obtaining high catalytic activities, we examined a Y zeolite with a Si/Al ratio comparable to that found in ZSM-5 in order to determine whether the differences between Cu-ZSM-5 and Cu-Y catalysts are actually due to Al content. Second, can one quantify the number of copper atoms actually balancing framework charges in Cu-Y zeolites? A recent study of Cu exchange in H-ZSM-5 revealed a one-for-one substitution of Cu for Brønsted-acid sites and the formation of distinct adsorption sites for isopropylamine (6). This technique allows for a quantitative measure of those copper atoms which are actually balancing framework charges as opposed to other copper species which may reside on or in the zeolite. Therefore, we examined a series of Cu-Y catalysts to determine whether similar conclusions could be reached for faujasites and whether the same unique adsorption sites associated with Cu-balancing framework charges in ZSM-5 could be observed in Cu-Y.

To compare catalytic activities, we used $N_2O$ decomposition as a test reaction. While this is not the reaction of primary interest for most applications, separate works by Armor and co-workers and Iwamoto have shown that this may be a good test reaction since the relative activities of Cu-ZSM-5 and Cu-Y are similar for NO and $N_2O$ decomposition (1, 5). For our purposes, $N_2O$ decomposition is simpler to measure and does not require examination of a range of reactant pressures. To examine the exchange process for Cu, we have taken the approach used in a previous study of Cu-ZSM-5 in which the removal of Brønsted-acid sites by the replacement of the protons with Cu allows the extent of exchange to be inferred, along with an examination for unique catalytic sites (6). A particularly useful technique for probing Brønsted-acid site concentrations and finding unique adsorption sites associated with ion-exchanged Cu is temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) of isopropylamine (7–9).

In comparing our results to those of others, it is important to note that, after exchange with Cu-acetate, all samples in this work were washed, dried under ambient conditions, and heated ($10^{-3}$ Torr in the IR cell, $10^{-7}$ Torr in the TPD–TGA apparatus, dry helium flow at 7000 GHSV in the $N_2O$ flow reactor) to 750 K before each experiment. The physical properties of the zeolites used are listed in Table 1 and the results for Cu exchange are summarized in Table 2. Each sample was Cu-exchanged in the form in which it is listed in Table 1. The numbers in parentheses following each of the faujasite samples in the text refer to the bulk $Si/Al_2$ ratio of the sample.

The TPD–TGA curves for isopropylamine in purely acidic H-ZSM-5 zeolites have been discussed elsewhere (7–9). Two desorption events are observed. Unreacted isopropylamine desorbs below ~450 K, while molecules associated with the Brønsted-acid sites desorb as propene and ammonia between 575 and 650 K. The number of molecules of isopropylamine which decompose is equal to the framework aluminum content of the zeolite (7–9). The TPD–TGA curves for Cu-exchanged ZSM-5

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TABLE 1

Physical Properties of Samples Used in This Study

| Zeolite | Al content ($\mu$mol/g) Bulk | Framework | [H+][a] ($\mu$mol/g) | Pore volume[b] (cm$^3$/g) |
|---|---|---|---|---|
| ZSM-5A | 480 | 425 | 425 | 0.180 |
| ZSM-5B | <5 | <5 | <5 | 0.185 |
| Na-Y(5) | 4400 | 4200[c] | <5 | 0.321 |
| H-Y(60) | 550 | 300[c] | 160 | 0.315 |
| NH4-Y(8) | 4300 | 2300[c] | 800 | 0.321 |

[a] The amine molecules desorbing between 575 and 650 K in isopropylamine TPD–TGA.

[b] Results were determined for ZSM-5 samples by hexane at 14.5 Torr and 298 K and for Y sample using $O_2$ at $P/P_0 = 0.4$ and 77 K.

[c] Determined from the lattice parameters in X-ray diffraction, using correlations given in Sohn *et al.* (16).

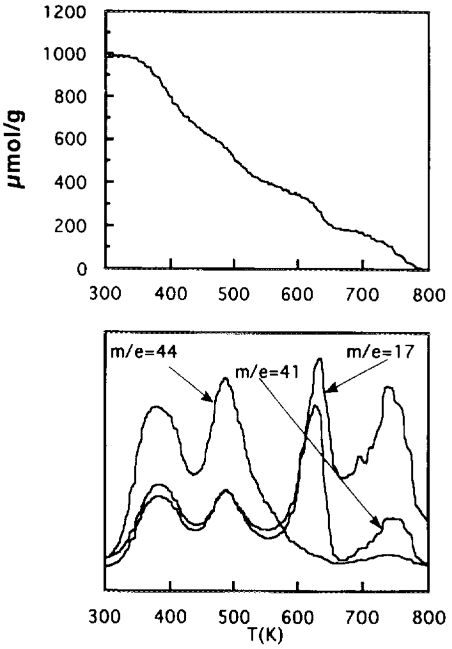

FIG. 1. TPD–TGA curves for isopropylamine from H(Cu)-ZSM-5A with 270 $\mu$mol/g of Cu. The mass peaks correspond to isopropylamine (*m/e* = 44, 41, and 17), propene (*m/e* = 41), and ammonia (*m/e* = 17) (6).

have also been discussed elsewhere (6). A typical result of isopropylamine on a H-ZSM-5A, after exchange with 270 $\mu$mol/g of Cu, is shown in Fig. 1. The Brønsted-acid site feature between 575 and 650 K (confirmed with pyridine IR) is still present, although to a lesser extent, along with the physisorbed species below 450 K. In addition to these, however, there are two desorption features on the Cu-containing sample, including (i) an unreacted isopropylamine (*m/e* = 44, 41, and 17) peak between 450 and 550 K and (ii) a feature which is clearly reaction products (*m/e* = 41 and 17) above 650 K (17). Since Cu-impregnated silicalite gives an unreacted isopropylamine peak between 450 and 550 K, this feature was assigned to Cu not associated with ion-exchange sites. The Cu present at the Al sites is associated with the decomposition feature at high temperatures. Evidence from this comes from the following observations: (i) The Brønsted-acid site density, determined by the amount of amine decomposing between 575 and 650 K, decreases with Cu content and (ii) the sum of the molecules in the two decomposition features was equal to the Al content of the sample for a wide range of Cu contents.

TABLE 2

Site Concentrations for Samples with Varying Cu Content

| Sample | Molarity of Cu-acetate solution | Cu content ($\mu$mol/g) | [H+][a] ($\mu$mol/g) | [Cu][b] ($\mu$mol/g) |
|---|---|---|---|---|
| ZSM-5A | 0.01 | 270 | 195 | 180 |
| ZSM-5A | 0.10 | 743 | <20 | 350 |
| ZSM-5B | 0.01 | 115 | <5 | 0 |
| Na-Y(5) | 0.01 | 1200 | 700 | 0 |
| Na-Y(5) | 0.10 | 1720 | 800 | 0 |
| H-Y(60) | 0.01 | 230 | 140 | <20 |
| H-Y(60) | 0.10 | 630 | 150 | 0 |
| NH4-Y(8) | 0.01 | 670 | 770 | 0 |
| NH4-Y(8) | 0.10 | 990 | 750 | 0 |

[a] The amine molecules desorbing between 575 and 650 K in isopropylamine TPD–TGA.

[b] Reported as the total amount of isopropylamine desorbing between 650 and 775 K.

Isopropylamine TPD–TGA results for H-Y(8) and H-Y(60), as well as for Na-Y(5) after varying degrees of exchange with $H^+$, have also been reported in previous publications (10–12). On Na-Y(5), all of the amine molecules desorb intact below 550 K. On H-Y(8) and H(Na)-Y(5) samples, the results are very similar to those obtained in H-ZSM-5 in that one observes unreacted amine desorbing below 550 K, with decomposition to propene and ammonia between 575 and 650 K. The major difference between the results for H-ZSM-5 and the H-Y catalysts is that the stoichiometry of the decomposition feature is less than one molecule per Al site in the faujasites. From infrared measurements, it was shown that reaction of the amine is associated with the high-frequency hydroxyl band centered at 3640 cm$^{-1}$, while molecules associated with the low-frequency band at 3560 cm$^{-1}$ do not cause react amine molecules in TPD. It appears, therefore, that only a fraction of the Al in H-Y zeolites results in Brønsted-acid sites.

To demonstrate what happens when Cu is exchanged into faujasites, it is interesting to look at the TPD–TGA

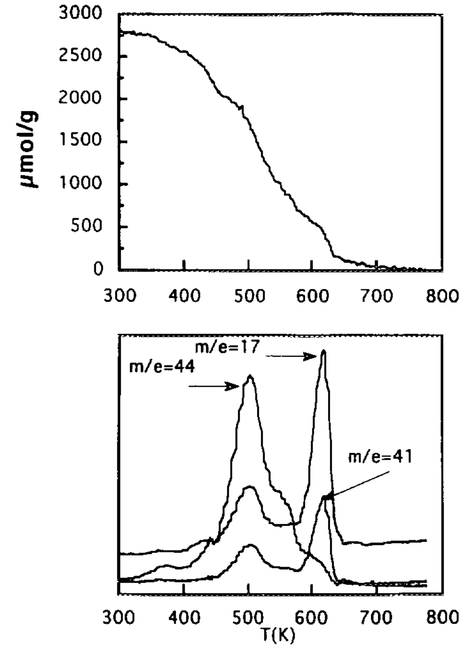

FIG. 2. TPD–TGA curves for isopropylamine from Na-H-Y(5) with 1720 μmol/g of Cu.

curves obtained following the exchange of 1720 μmol/g of Cu into Na-Y(5), as shown in Fig. 2. These results are virtually identical to what is obtained after ammonium-ion exchange in Na-Y(5) (12), with the exception of a larger amount of unreacted amine desorbing between 450 and 550 K on the Cu sample. Based on previous work with Cu-silicalite, we have assigned this feature to isopropylamine desorbing from Cu that is not interacting with exchange sites. Even after high levels of Cu exchange, the primary change in the TPD–TGA results is the generation of significant amounts of Brønsted sites. This is in agreement with results by Hall *et al.* (13) in which they inferred that Brønsted sites were present in a Cu-exchanged Na-Y sample after observing Brønsted-acid-catalyzed products during their measurements. It is interesting to note that Cu exchange in Na-ZSM-5 also produced Brønsted acidity; however, a significant number of Cu sites were produced with isopropylamine reaction above 650 K in TPD.

Of equal interest is what is *not* observed in Fig. 2. Unlike the results of Cu-ZSM-5, there is no high-temperature decomposition feature above 650 K which can be assigned to Cu balancing the framework Al. Since it is known that exchange of Cu for Na cations must occur initially (TPD–TGA results in which Na-Y was "exchanged" using only deionized water did not exhibit Brønsted sites), we believe there are three possibilites which might explain our results. First, the Cu ions may migrate into the sodalite cages and be inaccessible to adsorbate molecules. Second, the site geometry may result in a different coordination of the Cu ions which would create different adsorption and reaction properties of the probe molecule. (Some ESR evidence for this has been presented by others (14).) Third, the high concentration of Al sites in the lattice compared to that present in high silica zeolites like H-ZSM-5 may allow formation of Cu oxide and prevent formation of isolated Cu sites. We eliminate from these possibilities any change in the lattice itself (steaming) because of the excellent agreement between the Brønsted-acid site density of excessively Cu-exchanged and ammonium-exchanged samples of Na-Y(5).

In order to determine if the third possibility is a valid explanation of our results, we examined Cu exchange in high-silica faujasites, H-Y(8) and H-Y(60). The TPD–TGA curves for H-Y(8) and H-Y(60) have been reported previously and exhibit identical to those of H-Na-Y(5), shown in Fig. 2 (9). Copper exchange in H-Y(8) did not decrease the Brønsted-acid site density measured in TPD–TGA. The only change was that additional unreacted isopropylamine desorbed from the sample between 450 and 550 K, similar to that following Cu exchange in Na-Y(5). For very high Cu exchange levels in H-Y(60), there is residual weight loss above 650 K in the TPD–TGA of isopropylamine; however, the amount is small and the change in Brønsted-acid site concentration is minimal. Although inaccessibility of isopropylamine to small cavities in the Y zeolite may prevent some sites from being counted, it is important to note that: (i) we have confirmed that the same Brønsted site density for the H-Y(60) sample is observed for isopropylamine, pyridine, and *ammonia* (15) and (ii) no changes in the Brønsted-acid density of H-Y(60) were observed even after exchange with 230 μmol/g of Cu, a value approaching that of its framework Al content of 300 μmol/g.

To relate the TPD–TGA results to catalytic activities, $N_2O$ decomposition rates were measured on selected samples. The results are displayed in Fig. 3. For comparison to other published data where a comparison is valid, we note that a conversion of 50% in Fig. 3 implies a specific rate of $7.4 \times 10^{-2}$ μmol/g/s. All of the rates were highly reproducible and there were no observable changes in the catalysts with time. As expected, the activities of H-ZSM-5A, without Cu, and ZSM-5B, with 115 μmol/g of Cu but no framework Al, were very low. Even at 720 K, these two samples gave only 20% conversion of $N_2O$. By contrast, the H(Cu)-ZSM-5A sample, which had 270 μmol/g of Cu and 180 μmol/g of the Cu sites which cause decomposition of isopropylamine in TPD–TGA, was the most active catalyst studied (5). A conversion of 50% of the $N_2O$ was achieved at temperatures of ~650 K on this sample. While the (Cu)-H-Y samples did exhibit activity, significantly higher temperatures (80 K) were

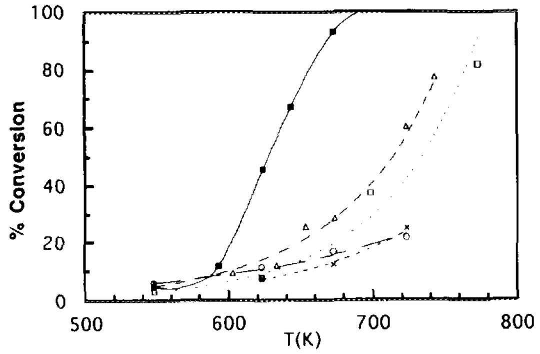

FIG. 3. Steady-state conversions for $N_2O$ decomposition as a function of temperature, using 1000 ppm of $N_2O$ in He GHSV = 7000. (○) H-ZSM-5A; (■) ZSM-5A with 270 μmol/g of Cu; (×) ZSM-5B with 115 μmol/g of Cu; (△) H-Y(60) with 630 μmol/g of Cu; and (□) NH4-Y(8) with 990 μmol/g of Cu.

required to achieve similar conversions to that of the Cu-ZSM-5 zeolite. Since this was true for the Cu-Y(60) which had a $Si/Al_2$ ratio comparable to that of H-ZSM-5, one must conclude that structure and not $Si/Al_2$ ratio plays the dominant role in the differences observed between the two zeolites.

In this Note, we have demonstrated that the results for Cu-Y are very different from Cu-ZSM-5, even when samples having comparable Si/Al ratios and Cu contents are compared. Based on adsorption results, it appears that ion-exchanged Cu does not remain at the tetrahedral Al sites after heating under vacuum to 750 K, but rather is replaced by a proton which results in Brønsted acidity. We suggest that it is this instability of exchanged Cu in Y zeolites that is responsible for the dramatic differences in catalytic activity between Cu-ZSM-5 and Cu-Y. While we do not have a firm explanation why this complex is unstable in Y zeolites, it may be that the more open structure of Y zeolites and the lack of five-membered-ring pockets which are present in ZSM-5 allow the Cu to migrate more easily in the Y structure. This obviously needs to be investigated in detail.

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