

Adsorption Studies on Cu–ZSM-5: Characterization of the Unique Properties of Ion-Exchanged Cu

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Simultaneous temperature-programmed desorption/thermogravimetric analysis (TPD–TGA) measurements of isopropylamine have been used to characterize a series of Cu(H)–ZSM-5. At the Brønsted acid sites in H–ZSM-5, isopropylamine decomposes to propene and ammonia between 575 and 650 K. The addition of Cu decreases the concentration of these Brønsted acid sites and leads to a new propene–ammonia decomposition feature between 650 and 800 K in TPD–TGA. This high-temperature feature is not observed when Cu is incorporated into a silicalite sample, implying that it is associated with Cu at the Al sites. Furthermore, the sum of Brønsted acid sites and high-temperature Cu sites is approximately constant and close to the Al content for H(Cu)–ZSM-5 series. Propene also interacts strongly with the Cu that is present at the Al sites in a stoichiometry close to 1/Cu at room temperature. Infrared measurements indicate that the Cu sites are neither Brønsted acid nor Lewis acid sites. All of the samples examined, including ion-exchanged silicalite, contained significant quantities of other Cu which do not appear to be associated with Al sites. Finally, ion exchange of Cu into a Na–ZSM-5 sample is shown to result in Brønsted acid sites, showing that protonic sites are easily incorporated into the zeolite during ion exchange, even when this is not done intentionally. The implications of these results for the characterization of Cu-exchanged zeolites are discussed. © 1993 Academic Press, Inc.

INTRODUCTION

Cu-exchanged zeolites have received considerable research attention over the past couple of years because of their ability to promote the decomposition and selective hydrocarbon reduction of nitric oxide (NO) in the presence of a large excess of oxygen (1, 2). These properties are of particular interest for automotive exhaust catalysis because the ability to convert NO_x under fuel-lean (i.e., excess oxygen) conditions will be essential for implementing lean-burn vehicles that demonstrate improved fuel economy while complying with current and forthcoming NO_x emission standards. Current automobile technology is almost exclusively based on stoichiometric air–fuel mixtures and so-called “three-way” exhaust catalysts which rely on Group VIII metals for controlling emissions of carbon monoxide, hydrocarbons, and nitrogen oxides.

These catalysts convert NO_x efficiently only in a very narrow range around the stoichiometric air–fuel mixture. Lean-burn engines will require a separate lean-NO_x catalyst in addition to, or in place of, the three-way catalyst.

Cu-exchanged zeolites are equally interesting from a scientific standpoint because they exhibit significant activities at much lower temperatures than normal supported-Cu catalysts or zeolites alone. This suggests that there must be unique chemical or physical interactions between the Cu ions and the zeolite or that the zeolite is able to stabilize a special form of Cu. Even though there have been numerous investigations on these materials, the particular form or forms of Cu which are active for the NO-removal reactions are not established. While there is evidence that the ability of Cu to cycle between the +1 and +2 oxidation states is important in the reactions involving NO

(3, 4), there are a number of experimental observations which are not fully understood. For example, definitive explanations have not been given for the following questions: In what form are the +2 ions when they exchange into high-silica zeolites for which exchange sites may be widely separated? Why does molecular oxygen enhance the activity of Cu-ZSM-5 for the selective reduction of NO? Why does the maximum activity of Cu-ZSM-5 occur at exchange levels in excess of 100%? And why do different zeolite structures vary dramatically in their effectiveness (5, 6)? Furthermore, there has been the suggestion that, in the selective reduction of NO by hydrocarbons, the acidity of the zeolite may be of equal importance to the Cu chemistry, thereby implying a type of bifunctional catalysis involving both the Cu and the acid sites in the zeolite (7).

In the present study, we attempted to address questions concerning the nature of Cu exchange in ZSM-5 by measuring the Brønsted acid site concentrations on a series of H/Cu-exchanged samples using temperature-programmed desorption (TPD) of isopropylamine. Previous studies have shown that isopropylamine is protonated by strong, Brønsted acid sites. In TPD, the protonated isopropylamine decomposes to propene and ammonia in a well-defined temperature region, between 575 and 650 K, by a reaction similar to Hofmann elimination in quaternary ammonium ions (8, 9). For high-silica zeolites in the hydrogen form, like H-ZSM-5, the number of amine molecules which decompose in TPD is equal to the Al content of the zeolite, which is also equal to the Brønsted acid site concentration (8). By examining the Brønsted acid site concentration as a function of Cu content in a series of H(Cu)-ZSM-5 samples, it is possible to obtain information on the ion-exchange process with Cu.

Our results demonstrate that Brønsted acid sites are indeed removed by ion exchange of Cu; however, less than one protonic site is removed for each Cu ion which

TABLE I
Physical Properties of Samples Used in This Study

Sample	Al content ($\mu\text{mol/g}$)		Particle size (μm)	Pore volume (cm^3/g)
	Bulk	Framework		
ZSM-5A	476	425	1-5	0.18
ZSM-5B	<5	<5	4	0.185
ZSM-5C	637	600	—	0.123

is added, even for low levels of exchange. Apparently, a fraction of the Cu is not associated with Al sites, which may help to explain the findings of some studies that Cu exists in at least two environments in Cu-ZSM-5 (10-13). In confirmation of this, we found that a significant amount of Cu could be exchanged into a silicalite sample which had essentially no Al. Second, the adsorption and reaction properties of the Cu fraction which is associated with the Al sites are significantly different from those of the second type of Cu. The Cu at Al sites interacts more strongly with both isopropylamine and propene. Third, the TPD results for isopropylamine demonstrate that Brønsted acid sites are introduced by ion exchange of Cu into Na-ZSM-5, even when there is no intentional addition of acidic species.

EXPERIMENTAL

Three different ZSM-5 samples were used in this study and some of their properties are listed in Table 1. ZSM-5A was obtained from Mobil and had been synthesized with a Si/Al ratio of 35 using a template. ZSM-5B was a silicalite sample synthesized in our laboratory using procedures described elsewhere (14), with TPA-Br (Johnson Matthey) as a template, Ludox AS-30 (DuPont) as the silica source, and NaOH as the base. ZSM-5C was obtained from Alcoa and had been synthesized without using a template. It has been reported that materials prepared without a template have a more uniform Al concentration, which could be important for these applications (15). Calcination of the samples was carried out in dry, flowing air for 2 h at 873 K.

Each sample was characterized by X-ray diffraction and appeared to be highly crystalline. Pore volumes measured by *n*-hexane uptakes were good for the template-synthesized materials, approaching the ideal values of 0.19 cm³/g, but the volume was low for the non-template-synthesized material. Bulk Al and Cu concentrations were measured with a Perkin-Elmer Model 3100 atomic absorption spectrometer using samples dissolved in specially prepared solutions manufactured by Inorganic Ventures, Inc. Comparison between the Cu contents measured in the zeolite and the amount of Cu which had been removed from solution indicated that the reported Cu contents are accurate to within $\sim 10 \mu\text{mol/g}$. Framework Al contents were estimated from TPD-TGA measurements of isopropylamine on the hydrogen form of the zeolites. (It has been shown that isopropylamine decomposes to propene and ammonia at Brønsted acid sites and that the Brønsted acid site concentration in H-ZSM-5 is equal to the framework Al content (8)).

Most samples were first ion-exchanged with 1 M (NH₄)₂SO₄ (Sigma) at 363 K and activated in dry, flowing air at 873 K for 1 h in order to place them into the hydrogen form before the addition of Cu. Cu was added by first preparing solutions of varying molarity with cupric acetate (Fisher) and deionized water (pH ~ 6.5) and then mixing 0.5 g of zeolite in 50 ml of the solution at room temperature with vigorous stirring for 1 h. For most of the samples, the zeolite was simply filtered from solution and dried; at the molarities used in our study, estimates of the amount of Cu which would be contained in the solution in the pores indicated that, for a solution concentration of 0.01 M, only 2 $\mu\text{mol/g}$ of Cu would be added to the sample as a result of not washing. However, one sample, ZSM-5A(271) which contained 271 $\mu\text{mol/g}$ of Cu, was washed three times with 100 ml of deionized water to determine whether our preparation procedure had a significant effect on the final results. Washing reduced the Cu content to 186 $\mu\text{mol/g}$,

but the measurements made on this sample showed that it was essentially indistinguishable from a sample which had been prepared with this Cu content but had not been washed. The only other pretreatment performed on these catalysts prior to adsorption involved heating the samples to 750 K in vacuum.

The TPD-TGA measurements were performed simultaneously in a system which has been described in detail elsewhere (14). Briefly, approximately 10 to 20 mg of sample was placed in the pan of a Cahn microbalance which could be evacuated to 10⁻⁷ Torr with a turbomolecular pump. A quadrupole mass spectrometer, attached to the pump, was used to monitor major cracking fragments of the products which desorbed upon heating. Typically, the sample was exposed to ~ 10 Torr of the gas of interest until the weight stopped changing. The samples were then evacuated for 1 h and the temperature was ramped, linearly, at 20 K/min while monitoring the weight and the partial pressures above the sample. All weights reported in this paper are referenced to the initial sample weight prior to adsorption, and, in all cases, the weight returned to its initial value after an adsorption-desorption cycle. Also, adsorption on each of the samples was completely reversible. TPD-TGA measurements carried out on the same sample a second time were identical, implying that the adsorption-desorption cycle had no effect on the state of Cu in the catalysts.

IR measurements were performed in a homemade cell which was evacuated with a liquid-nitrogen-trapped mechanical pump (16). The zeolite wafers were mounted on a stainless-steel mesh, which has appreciable IR transmission, supplied by Buckbee-Mears Co. IR spectra were recorded after adsorption of pyridine at room temperature, followed by evacuation at 500 K to remove physisorbed species.

RESULTS

TPD-TGA results for isopropylamine from a representative group of samples prepared

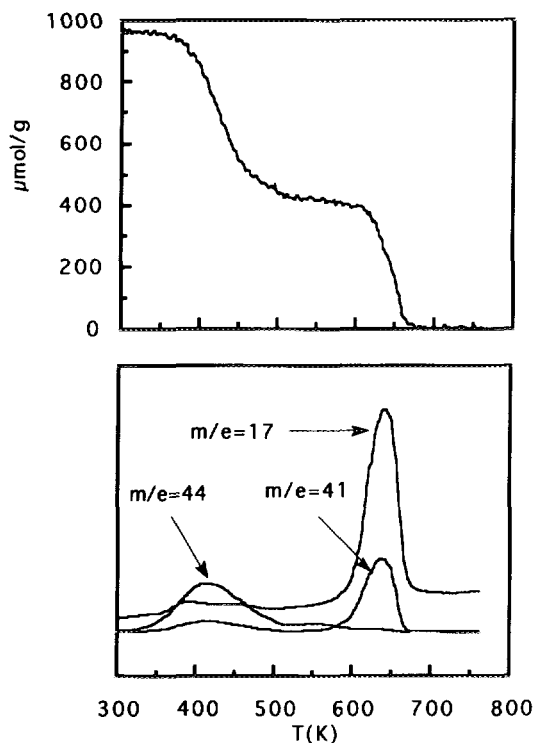


FIG. 1. TPD-TGA curves for isopropylamine from H-ZSM-5A. The mass peaks correspond to isopropylamine ($m/e = 44, 41,$ and 17), propene ($m/e = 41$), and ammonia ($m/e = 17$).

by Cu exchange into H-ZSM-5A are shown in Figs. 1 through 4. For the unexchanged H-ZSM-5A in Fig. 1, we observe two desorption features. Below 500 K, only unreacted isopropylamine ($m/e = 44, 41,$ and 17) desorbs from the sample and the amount leaving the sample in this temperature range depends on the ZSM-5 sample and the evacuation time, as discussed elsewhere (8). The second desorption event occurs between 575 and 650 K and is observed as propene ($m/e = 41$) and ammonia ($m/e = 17$). Based on previous work, this feature has been assigned to the decomposition of the isopropylammonium ion, which implies that the amine molecules associated with this feature were adsorbed at Brønsted acid sites (14). The temperature at which the alkylammonium ions decompose appears to be independent of the acid strength, implying that

the reaction is independent of the framework anion. The amount of isopropylamine which decomposes in this second feature is equal to the framework Al content of the zeolite.

Upon the addition of Cu, two new desorption features are observed, as shown in Fig. 2 for a Cu content of 271 $\mu\text{mol/g}$. First, there is a second, unreacted-isopropylamine feature between 500 and 550 K. From experiments performed on the Cu-ZSM-5B sample discussed later, it appears that this desorption event results from Cu sites which are not associated with framework Al. In addition to this unreacted peak, we observe a second decomposition peak between 650 and 800 K. This decomposition at higher temperatures appears to occur through a different mechanism from the one observed at lower temperatures. We suggest that it results from the decomposition of a Cu-

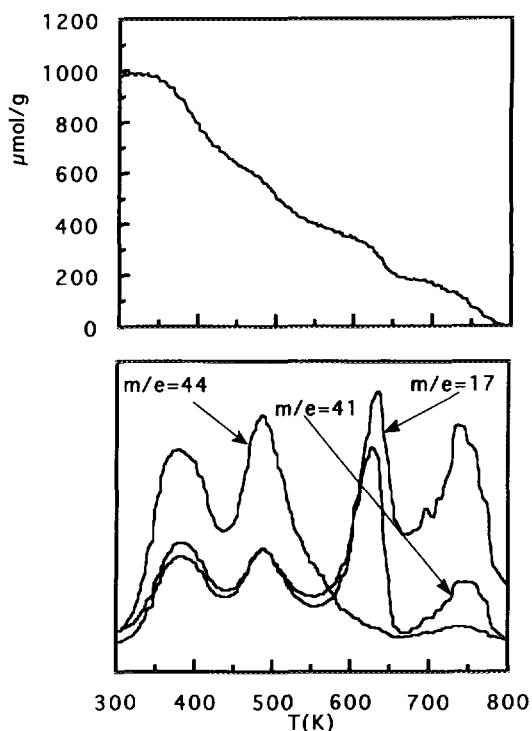


FIG. 2. TPD-TGA curves for isopropylamine from ZSM-5A(271).

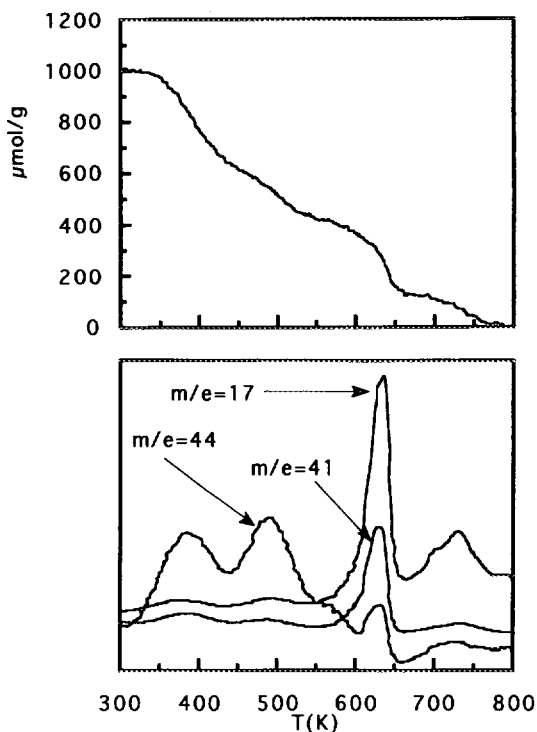


FIG. 3. TPD-TGA curves for isopropylamine from ZSM-5A(186).

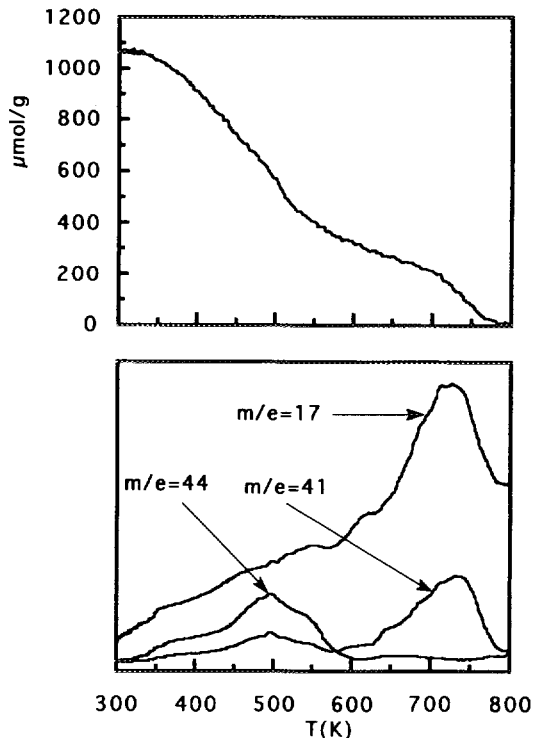


FIG. 4. TPD-TGA curves for isopropylamine from ZSM-5A(743).

alkylamine complex. The size of this second decomposition feature increases with Cu content at the expense of the reaction peak between 575 and 650 K. As discussed under Experimental, sample preparation did not alter the results. Figure 3 shows the TPD-TGA results for the same sample used in Fig. 2 after washing three times with deionized water, ZSM-5A(186). Except for a decrease in the Cu-related peaks due to the decrease in Cu content and a subsequent increase in the Brønsted acid sites, the results are very similar. Following the addition of 743 $\mu\text{mol/g}$ of Cu, the reaction peak associated with Brønsted acid sites is completely removed, leaving only the higher temperature peak, as shown in Fig. 4.

Confirmation that the second reaction feature for isopropylamine is not the result of Brønsted acid sites is shown in Fig. 5, which gives the infrared spectra obtained on the

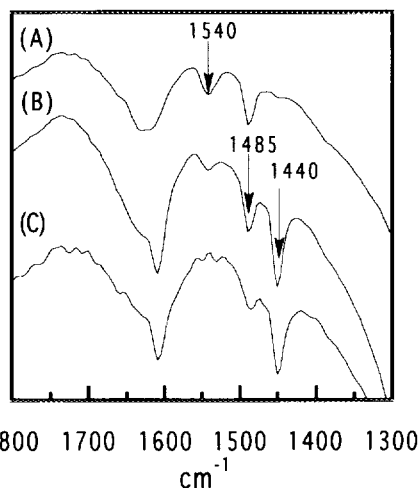


FIG. 5. IR spectra for pyridine adsorption on (A) H-ZSM-5A, (B) ZSM-5A(271), and (C) ZSM-5A(743).

same three samples shown in Figs. 1, 2, and 4 following adsorption of pyridine. On H-ZSM-5, pyridine is protonated to the pyridinium ion, as demonstrated by peaks at 1485 and 1540 cm^{-1} (17). Because heating to 500 K in vacuum removes most of the pyridine which is not associated with framework Al sites, there is only a small peak at 1450 cm^{-1} which would be associated with nonprotonated pyridine. On ZSM-5(743), which exhibited only the high-temperature reaction peak above 650 K for isopropylamine TPD, there is essentially no pyridinium ion formed. The two vibrational peaks for pyridine are observed at 1450 and 1485 cm^{-1} , which are close to the same values obtained for physical adsorption of pyridine, and there is no evidence of a peak at 1540 cm^{-1} . Samples with intermediate Cu contents exhibited both types of pyridine, as shown in Fig. 5 for ZSM-5A(271). While there must be relatively strong interactions between the pyridine and the Cu sites for pyridine to remain in the sample to 500 K, the IR spectra show that the pyridine is not protonated but may have a slight Lewis acid-like interaction (23), since strong, Lewis acid sites normally shift the two vibrational bands upward in frequency (17).

In order to quantify how Cu exchanges for

the protonic sites, we used the TPD-TGA results for isopropylamine to estimate the quantities of products which desorbed in the two reaction features which have been assigned to Brønsted acid sites and Cu sites. These numbers are listed in Table 2 and plotted in Fig. 6 for each of the ZSM-5A samples studied. While there is some uncertainty in the absolute numbers due to overlap between the two desorption features, several trends are apparent. First, the addition of Cu decreases the concentration of Brønsted acid sites and increases the concentration of Cu sites in a regular manner. Moreover, the sum of the site concentrations for the two types of sites is almost constant for the entire series. While there is a decrease in this sum at higher Cu concentrations, this could be due to an increased sample mass or possibly due to blocking of some sites by the Cu. This observation that Brønsted acid sites are removed at the same rate that the second, high-temperature reaction feature appears is further indication that the high-temperature reaction feature is due to ion-exchanged Cu at Al sites. Of additional interest, the bulk Cu concentration is greater than the concentration of sites which have been assigned to Cu exchange by a significant amount, even

TABLE 2
Site Concentrations for Samples with Varying Cu Contents

Sample	Molarity of Cu-acetate solution	Cu content ($\mu\text{mol/g}$)	$[\text{H}^+]$ ($\mu\text{mol/g}$)	Cu sites ($\mu\text{mol/g}$)
H-ZSM-5A	—	0	425	0
ZSM-5A(91)	0.001	91	370	55
ZSM-5A(145)	0.002	145	335	90
ZSM-5A(164)	0.003	164	300	100
ZSM-5A(186) ^a	0.010	186	300	120
ZSM-5A(193)	0.004	193	255	125
ZSM-5A(214)	0.005	214	270	155
ZSM-5A(271)	0.010	271	195	180
ZSM-5A(743)	0.10	743	0	350
ZSM-5B(115)	0.010	115	0	0
ZSM-5C(432) ^b	0.010	432	100	100

^a ZSM-5A(186) was washed in deionized water three times.

^b ZSM-5C(432) was prepared by ion exchange of the Na-ZSM-5C.

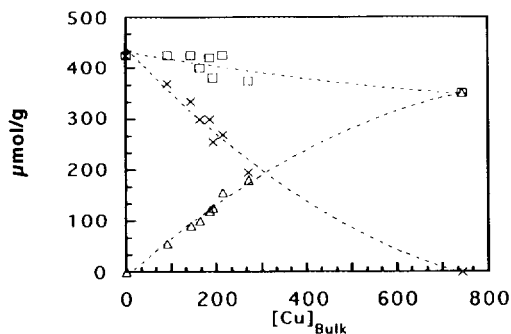


FIG. 6. Plot of site concentrations for the ZSM-5A series of samples as a function of Cu content. The sites counted were Brønsted acid sites (\times), Cu sites which decompose the amine between 650 and 800 K (Δ), and the sum of the two (\square).

at low Cu contents. Therefore, some Cu must be present at other types of sites which are not associated with framework Al in the zeolite structure.

In order to examine this other form of Cu, we measured isopropylamine adsorption on a Cu-exchanged, silicalite sample, ZSM-5B. Using the same procedure employed for the ZSM-5A samples, we found that the resulting Cu coverage on the silicate sample was less than that for H-ZSM-5 but significant. The TPD-TGA results on this sample are shown in Fig. 7 and are significantly different from those measured on the Cu-exchanged, ZSM-5A samples. The TPD-TGA curves again show an unreacted feature between 500 and 600 K on the Cu-ZSM-5B, but there is no high-temperature reaction feature above 650 K like that measured on all of the H(Cu)-ZSM-5A samples. Comparison of Fig. 7 to Figs. 2-4 suggests that the unreacted feature between 500 and 600 K on all the samples is due to Cu which is not associated with framework Al, while the reaction feature at higher temperatures must be associated with Cu at Al sites. It also indicates that the Cu ions which are present at Al sites have adsorption properties significantly different from those of the other Cu in the zeolites.

Further indication of these differences be-

tween the Cu species comes from the fact that propene interacts strongly with the Cu present at Al sites, but does not interact with the other Cu. This is shown in Fig. 8, which gives the TPD-TGA curves for propene on ZSM-5A(743). Exposure to 15 Torr of propene at room temperature, followed by evacuation, resulted in a propene coverage of $\sim 400 \mu\text{mol/g}$, which is slightly more than one molecule per framework Al in the material. The propene on ZSM-5A(743) desorbed completely in several peaks between 400 and 650 K. The results for propene adsorption on Cu-ZSM-5B, for which Cu is not associated with Al sites, were very different from those shown in Fig. 8. For this sample, a similar adsorption-evacuation procedure gave no measurable uptake of propene. This suggests that propene interacts strongly only with the Cu which is associated with the Al sites. Furthermore,

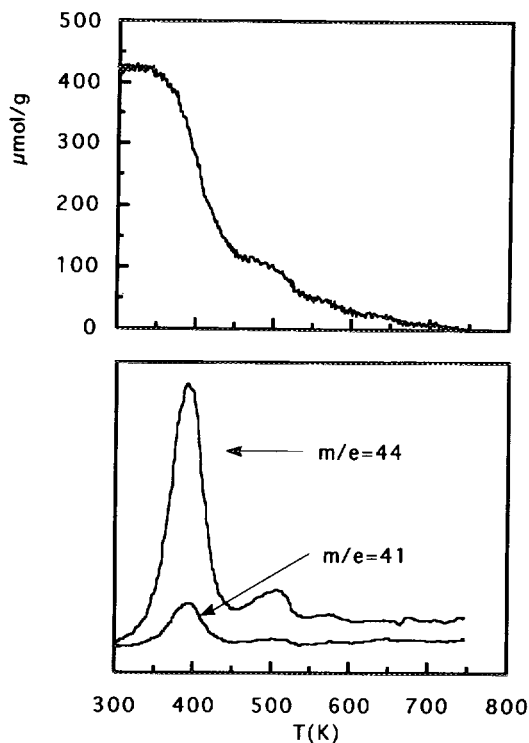


FIG. 7. TPD-TGA curves for isopropylamine from Cu-ZSM-5B.

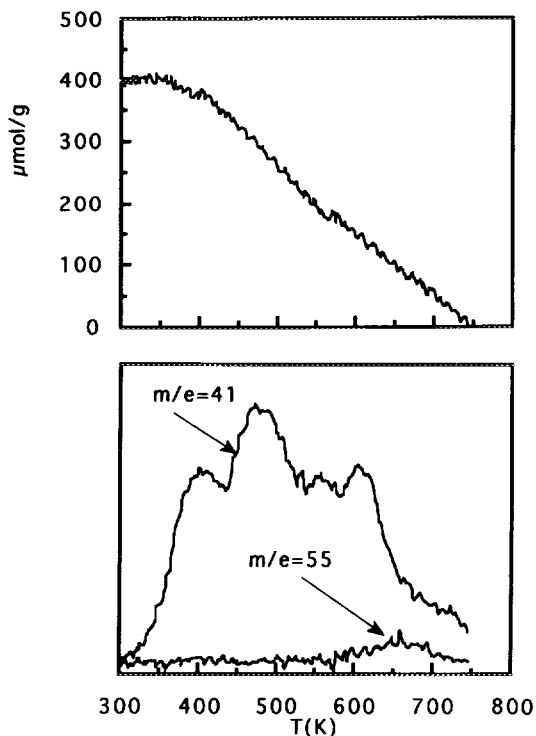


FIG. 8. TPD-TGA curves for propene adsorption on ZSM-5A(743).

the stoichiometry of adsorption is very close to 1/Cu at these sites.

The TPD-TGA curves for ZSM-5A(743) also indicate that almost all of the propene desorbed unreacted. Only a small amount of oligomer products was formed, as evidenced by the small peak at $m/e = 55$. This is very different from what happens when propene adsorbs on Brønsted acid sites in H-ZSM-5. In that case, propene oligomerizes at room temperature and desorbs as a wide range of oligomer cracking products, beginning at ~ 400 K (18). This oligomerization and cracking is also observed on the Cu-containing samples which still have Brønsted acid sites.

Finally, we examined the exchange of Cu into a Na-ZSM-5 in order to determine whether our earlier results were dependent on the presence of protons in the zeolite. Na-ZSM-5C was obtained in the Na form

and, initially, contained no Brønsted acid sites according to isopropylamine desorption measurements. Isopropylamine desorbed completely as unreacted isopropylamine, with no reaction to propene and ammonia at higher temperatures. However, the isopropylamine desorption curves obtained after ion exchange with 0.01 M cupric acetate show clear evidence for both Brønsted acid and ion-exchanged Cu sites, as shown in Fig. 9. The sum of these two types of sites does not equal the total ion-exchange capacity of the sample, which probably indicates that the sample still contains significant quantities of Na, but it is clear that protonic sites are also formed in the sample during the addition of the Cu. It has been suggested that these protonic sites could be very important during the selective reduction of NO by hydrocarbons (7). Even if they are not directly responsible for the

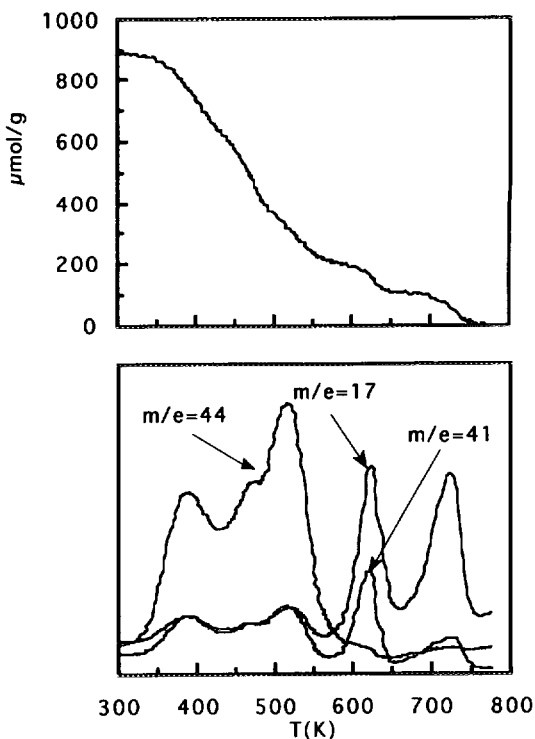


FIG. 9. TPD-TGA curves for isopropylamine from ZSM-5C(432).

catalytic activity, they may be necessary for forming olefinic species which could then interact with Cu.

DISCUSSION

Our results give a clear indication that Cu which has been ion-exchanged at the Al sites in ZSM-5 is significantly different from other forms of Cu. The Cu ions associated with Al sites interact strongly with both propene and isopropylamine and are probably responsible for the catalytic activity in Cu-ZSM-5. The fact that they can be observed so clearly with isopropylamine desorption suggests that TPD-TGA may be a very useful method for characterizing the effect of different preparation conditions and deactivation processes.

The Cu associated with the Al sites is almost certainly associated with catalytic activity in these materials. The fact that the sum of Brønsted acid sites and amine-decomposing Cu sites in the isopropylamine TPD-TGA measurements was approximately constant, independent of Cu content, implies that this Cu has been ion-exchanged for the protons, with a stoichiometry of one Cu per proton. This observation would tend to imply that the Cu associated with Al sites exists in a +1 oxidation state or that the ion is in the form of a complex (e.g., $[\text{Cu}^{+2}(\text{OH}^{-})]^{+1}$) if its oxidation state is +2. In either case, the results help explain why the catalytic activity of Cu-exchanged zeolites continues to increase with exchange levels well above 100%. (For example, 700 $\mu\text{mol/g}$ of Cu nominally corresponds to almost 330% exchange for a sample with 425 $\mu\text{mol/g}$ of exchange sites.) If the Cu is indeed in the +1 oxidation state, it seems likely that this reduction occurs upon heating in vacuum prior to adsorption. This is consistent with reports of a decrease in the ESR signal upon annealing in vacuum (21). It should be noted that simple annealing has been reported to leave a significant fraction of the Cu in the +2 state. It is possible that the Cu which is less easily reduced is not present at Al sites.

Stabilization of the Cu^{+1} in high-silica zeolites has been suggested to be responsible for the unusual catalytic properties of these materials and may help to explain some of our adsorption results (1). The strong interaction of propene with the Cu at the Al sites would be consistent with Cu^{+1} chemistry, since one might expect Cu^{+1} to be capable of interacting with the π orbitals of the olefin more easily than Cu^{+2} . However, one should expect Cu^{+2} to interact more strongly with amines than Cu^{+1} due to its stronger Lewis acidity. Clearly, additional spectroscopic studies, coupled with adsorption studies, are necessary to identify the species which we have observed in our experiments.

A considerable fraction of the Cu present in our samples was not associated with framework Al sites *even at low exchange levels*, a fact which complicates spectroscopic characterization. There are a number of possibilities for explaining the location of this second type of Cu. The first possibility is that Cu may be ion-exchanged at defect sites. For example, it has been reported that Na can be ion-exchanged into a pure silicalite and that this exchange appears to be due to the presence of "nested silanols" at vacancy defects (19). If this occurs with Cu, the amount of Cu which is not present at Al sites will depend on the particular sample being studied, since defect concentrations can be altered by synthesis and pretreatment conditions for ZSM-5 (20). Alternatively, polymeric chains or other stable forms of Cu oxide may form in the zeolite pores (24, 25). Independent of the Cu state, knowledge about how much of this kind of Cu is present in a particular sample is very important during spectroscopic studies, since both types of Cu will be probed. For example, ESR studies which have reported the presence of Cu in two different environments will be sampling this second type of Cu in addition to the Cu which is present at the Al sites (10-13).

In retrospect, the observation that Brønsted acid sites are formed during ion

exchange of Na-ZSM-5 is not surprising. It has been observed that fairly high Na concentrations must be used to obtain a Na-ZSM-5 sample with no protonic sites (22), and it is probable that there is an equilibrium between protons in the water and Na cations. When the sample is washed with deionized water, the Na content of the wash water will be low in comparison to the proton concentration and the resulting samples could contain significant Brønsted acidity. As pointed out earlier, Brønsted acidity could be important for the selective reduction of NO.

However, the observation that ion-exchanged Cu can interact strongly with propene may indicate that Brønsted acid sites are not necessary for the selective reduction reactions. It has been shown by a number of groups that NO adsorbs readily on ion-exchanged Cu sites (1, 21). The present study confirms that olefins also adsorb on the same Cu sites. This raises the possibility that both NO and olefin will reside on a single Cu site and that reaction could occur on this site. Since our work has shown that the olefin complexes which form on the ion-exchanged Cu sites are highly stable, it may even be possible to observe these reactions in transient experiments. This will be explored in future work in our laboratories.

There is obviously still much to be learned from these very interesting catalysts and the processes they catalyze. Our results suggest that TPD-TGA measurements with isopropylamine and other probe molecules can be a very useful method for characterizing these systems. We believe that further work on adsorption of reactive molecules could help answer many of the questions which remain about these materials.

SUMMARY

Our results demonstrate that the Cu associated with the Al sites in a ZSM-5 zeolite have significantly different adsorption properties for isopropylamine and propene than other forms of Cu. This suggests that TPD-TGA measurements with isopro-

pylamine are useful for characterizing the nature of Cu exchange and provide clues to the reasons for the unique catalytic properties of these materials.

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