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TPD Study of Mordenite-Type Zeolites for Selective Catalytic Reduction of NO by NH_3

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The effect of the adsorption of NO and NH_3 on catalytic activity has been examined by temperature-programmed desorption over a series of cation-exchanged mordenite catalysts for selective catalytic reduction (SCR) of NO by NH_3. The catalytic activity observed in a packed-bed flow reactor was well correlated with the cation content of the catalyst and its adsorption properties, making it possible to elucidate the role of metals and acidity in this reaction system. The amount of NH_3 and NO adsorbed on the catalyst surface proportionally increased with the degree of cation exchange of the catalyst, especially at the Brønsted acid site (H^+) and the metal site (Cu^{2+}). SCR activity also gradually increased with the acidity of the catalyst and/or its degree of catalyst cation exchange. Surface acidity of the mordenite catalysts appears to be a dominant factor in the high performance of the SCR reaction system. The common activation energy is observed to be about 12 kcal/mole for NaHM and CuHM catalysts, independent of their cation content on the catalyst surface. The active sties of this catalytic system are both the Brønsted acid site and the metal site. Furthermore, the reaction occurred in a Langmuir–Hinshewood manner with a dual-site catalysis mechanism. © 1996 Academic Press, Inc.

INTRODUCTION

The emission of nitrogen oxides is a global environmental issue, and selective catalytic reduction (SCR) is one of the most effective technologies for removing NO from stationary combustion sources, which are mainly utility boilers, industrial boilers, and cogeneration turbines.

Numerous catalysts, including various metals, transition metal oxides, and mixed metal oxides (1, 2), have been employed for NO reduction. Recently, acidic zeolites such as copper ion-exchanged Y zeolites (3–5), H mordenite, and Cu–H mordenite (6) have been reported to be efficient catalysts for NO reduction by NH_3, particularly for the high-temperature application of SCR technology. Not much attention, however, has been paid to the role of zeolitic material in this reaction. Nevertheless, acidity is one of the most important characteristics of the zeolite surface which may make it catalytically effective (7). Particularly in the SCR system, NH_3, which is a common probe molecule for the measurement of catalyst acidity, is one of the major reactants. It may be of interest to correlate the catalytic activity of the SCR reaction with the catalyst acidity of the catalyst.

To investigate the strength, number, and structure of acid sites on zeolite, various methods of acidity measurement can be utilized, such as titration, calorimetry, and infrared spectroscopy (8). All these methods have advantages as ways to measure the acidity, quantitatively and qualitatively. The restriction which has been frequently encountered concerns the size of the base molecule, as well as its strength. From such a viewpoint, temperature-programmed desorption (TPD) of NH_3 may be a fair method for measuring the acidity of the catalyst as well as its adsorption properties. Although this method strongly depends on the experimental conditions such as the rate of temperature increment and equilibrium conditions, which makes comparisons difficult, it is considered a good method for examining the amount and distribution of acid sites and adsorption of reactants.

The purpose of this study is to elucidate the effect of acidity and/or adsorption properties of reactants on SCR activity for a mordenite-type zeolite catalyst by the systematic investigation of the SCR activity and TPD characteristics of such catalysts by NO and NH_3. In addition, it has been observed that an unexchanged mordenite catalyst, H mordenite (HM), also exhibited substantial activity for this reaction system (6). It is of interest to determine why HM still reveals considerable NO removal activity. HM even shows higher activity than CuHM for a certain region of reaction conditions where the activity of CuHM decreases due to side reactions, particularly the NH_3 oxidation reaction. It has been generally speculated that HM strongly adsorbs NH_3 and that its adsorption is further enhanced when copper is present on the catalyst surface. In this study, this will be clarified and the role of cations on the catalyst structure will also be discussed.

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EXPERIMENTAL METHOD

Catalyst Preparation

The raw catalyst was the sodium form of mordenite (NaM) from PQ Corporation (Zeolon 900Na) in 20/30 mesh pellets. The cation-exchanged catalysts, NaHM with various sodium contents from 0.18 to 4.2 wt% and CuHM with various copper loadings up to the 4.1 wt%, were prepared by the ion-exchange method. Exchange time (5 min to 10 hr) and concentration of NH_4Cl solution (0.1 to 1 *N*) were varied to obtain a series of catalysts with different Na contents. This procedure was repeated and eventually HM with only 0.18 wt% of Na ions was prepared. CuHM catalysts with different loadings of copper were obtained from HM with a cupric nitrate solution and varying exchange time (5 min to 12 hr) and concentration (1 to 3 *N*). The degree of cation exchange was determined by atomic adsorption spectroscopy and is given next to the catalyst designation by percentage of total exchangeable cations as shown in Table 1. NaM was also examined as a base catalyst in this study.

Catalytic Reaction and TPDs of NO and NH_3

NO reduction by NH_3 was carried out in a packed-bed flow reactor system similar to that described elsewhere (9). Typically, 1 g of 20/30 mesh size catalyst is charged in a $\frac{3}{8}$-in. aluminum tube reactor and treated at 500°C for 2 hr in air flow before the test. The diffusion effect of the catalyst employed in this study may not be significant, since its effectiveness factor was found to be above 0.9, depending upon the reaction temperature (10). The reactor temperature was controlled by two thermocouples located on the top and the bottom of the catalyst bed. A feed gas mixture containing NH_3 (500 ppm), NO (500 ppm), O_2 (5%), and N_2 (balance) was supplied through mass flow controllers (Brooks 5878). The concentration of NO was analyzed by a chemiluminescence NO–NO*x* analyzer (Thermo Electron, Model 10) calibrated by span gas of NO. Total flow rate of the reactor system was 1.9 liters/min in order to maintain 100,000 hr^{-1} of the reactor space velocity.

TPD was performed in a Pyrex flow system. About 0.5 g of sample was evacuated in a quartz tube at 500°C for 2 hr, exposed to NH_3, a probe molecule for the TPD test, at 100°C for 1 hr, and then flushed with He to remove the remainder of the adsorbate in the gas phase and the physisorbed on the catalyst surface. For NO TPD, a NO–N_2 mixture (500 ppm) was added to the catalyst sample with the same experimental procedure as that of NH_3 TPD. The carrier gas, He, was purified to remove impurities by Molecular Sieve 4A and MnO/SiO_2 traps in series. The TPD experiment was performed from 100 to 800°C with a heating rate of 10°C/min and a flow rate of He of 60 cm^3/min. Desorbed molecules were examined with a Gow-Mac thermal conductivity detector (TCD) and the outlet of the TCD was monitored with a VG Micromass quadrupole mass spectrometer (MMPC 300D).

TABLE 1

Physicochemical Properties of Ion-Exchanged Mordenite-Type Zeolite Catalysts

Catalyst	Si/Al (wt%)	Na (wt%)	Cu (wt%)	SA (m^2/g)
NaM	5.1	4.2	—	330
NaHM66	—	3.5	—	370
NaHM22	—	1.2	—	400
NaHM3(HM)	—	0.18	—	410
CuHM34	5.3	0.16	2.4	410
CuHM58	5.5	0.15	4.1	420

Note. —, no available data.

RESULTS

SCR Activity of Mordenite Catalysts

Since the objective of this work was to identify the role of acidity in SCR of NO by NH_3 and to correlate the catalytic activity with the adsorption properties obtained from TPD experiments by NO and NH_3, the SCR activity for the mordenite family catalysts listed in Table 1 was examined. The activity of NO reduction of the catalysts expressed in fractional NO conversion for a constant reactor space time is shown in Figs. 1 and 2. Unexchanged catalyst, NaM, exhibits little activity, but HM shows significant activity, and upon addition of copper to the catalyst, CuHM reveals greatly enhanced NO removal activity.

The promoting effect of copper is obvious, especially at low reaction temperature. The bell-shape activity–

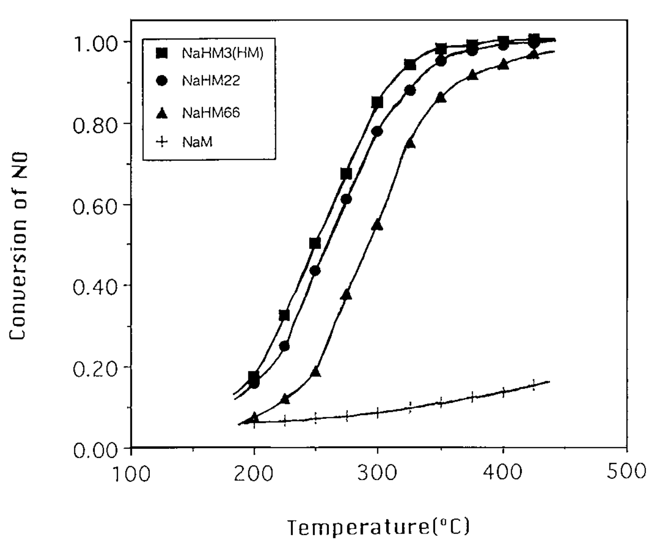

FIG. 1. Performance of NaHM catalysts for the SCR reaction (reactor space velocity = 100,000 hr^{-1}).

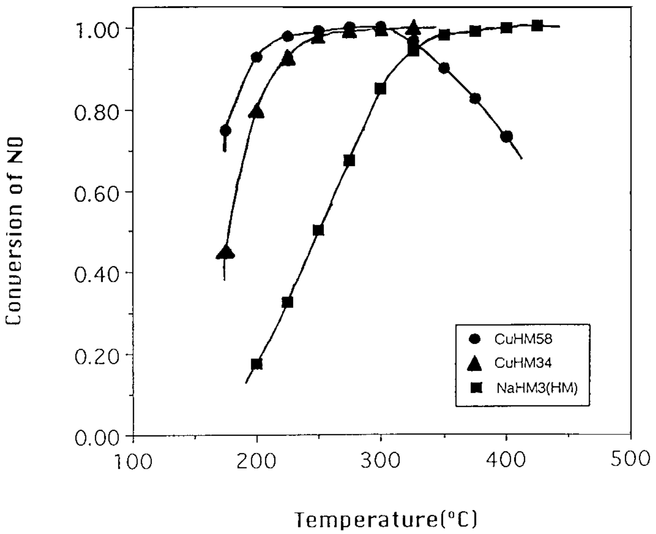

FIG. 2. Performance of CuHM catalysts for the SCR reaction (reactor space velocity = 100,000 hr^{-1}).

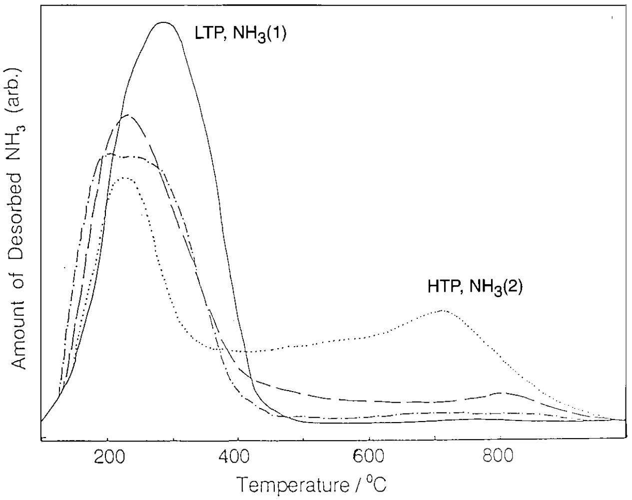

FIG. 3. NH_3 TPD spectra of NaHM catalysts. ——, NaM; – –, NaHM66; –·–, NaHM22; · · ·, NaHM3(HM).

temperature relationships for CuHM catalysts are commonly observed and have been attributed to the increased rate of the NH_3 oxidation reaction, Reactions [3] and/or [4], at a high reaction temperature more than offsetting its consumption by NO reduction, Reactions [1] and [2] (4, 11):

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad [1]$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad [2]$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad [3]$$

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O. \quad [4]$$

The catalytic activity of NaHM gradually increases as ion exchange proceeds from the Na- to H-form mordenites and that of CuHM proportionally increases with respect to the copper loadings of catalysts. As seen in Fig. 2, no maximum conversion of NO for NaHM3 catalyst was observed within the reaction temperature range from 200 to 450°C covered in this study. However, the CuHM58 catalyst produced maximum conversion at 250°C due to the NH_3 oxidation reaction, Reactions [3] and/or [4]. The maximum was shifted to lower reaction temperatures by the addition of copper to the catalyst.

NH_3 and NO TPD for Mordenite Catalysts

Typical TPD spectra of NH_3 and NO for cation-exchanged mordenite catalysts are shown in Figs. 3–6. When the TPD experiment was performed without admission of probe molecules, nothing was detected up to 800°C. When NH_3 or NO was admitted at room temperature and allowed to be desorbed, a desorption peak was observed at a temperature lower than 100°C. However, the most weakly adsorbed probe molecules are not of interest for the present study, since the weak adsorption site is believed to play no role in SCR reaction. Similar arguments can also be made for temperatures higher than 800°C.

TPD spectra of NH_3 and NO were compared to NaHM and CuHM. In Fig. 3 two distinctive desorption peaks around 230 and 720°C for NaHM catalysts with respect to their solidum content are shown. As the ion exchange of cations on the catalyst surface proceeds, the low-temperature peak (LTP) does not change systematically, while the intensity of the high-temperature peak (HTP) gradually increases. In other words, not only the degree of acidity but also its distribution are modified by the cation exchange of NaM catalysts.

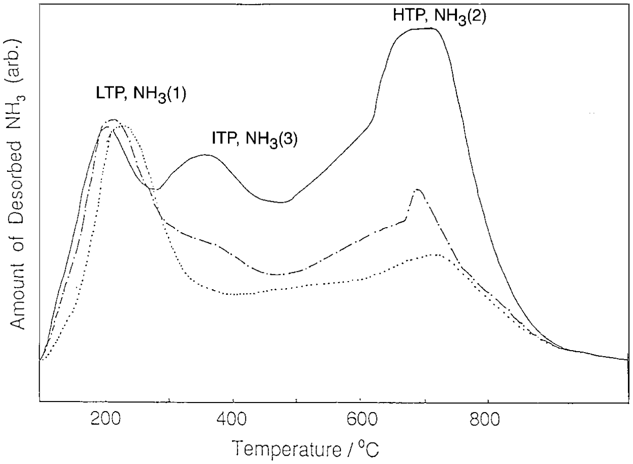

FIG. 4. NH_3 TPD spectra of CuHM catalysts. ——, CuHM58; –·–, CuHM34; · · ·, NaHM3(HM).

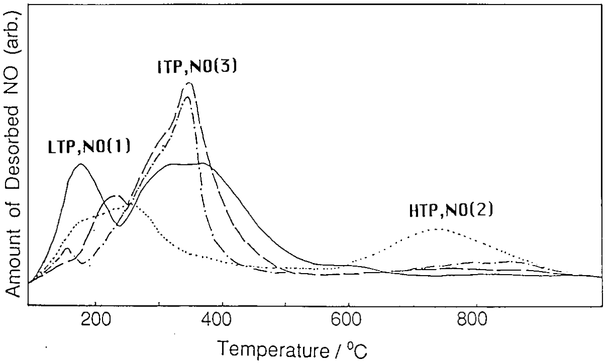

FIG. 5. NO TPD spectra of NaHM catalysts. ——, NaM; – –, NaHM66; – · –, NaHM22; · · ·, NaHM3(HM).

In Fig. 4, TPD spectra of NH_3 over CuHM catalysts with various loadings of copper show three desorption peaks around 220, 360, and 700°C. Compared with those of the HM catalysts, the intensity of the first peak at around 220°C is almost invariable; the intermediate-temperature peak (ITP) at 360°C, which was not found for NaHM and HM catalysts, presents a substantial increase in its intensity; and the third peak at around 700°C dramatically increased, all with respect to the copper loadings of catalysts. This may explain why the maximum conversion of NO was shifted to lower reaction temperatures as the copper content of the catalyst increased. The more copper contained on the catalyst surface, the more NH_3 adsorbed on the surface. It should be noted that copper also exhibits a strong capability of oxidizing NH_3 to NO and/or N_2 as a catalyst (12).

Figure 5 shows the TPD spectra of NO for the series of NaHM catalysts with three desorption peaks similar to TPD spectra of NH_3 for CuHM catalysts. Upon addition of copper ions to the catalysts, the lower temperature peaks increased in their intensities. Particularly, ITP appeared at 350°C to be somewhat shifted to a higher temperature with a higher intensity, and HTP did not change appreciably, as shown in Fig. 6. It should be noted that state of copper on the CuHM catalyst is mainly Cu(II), as revealed by ESR and X-ray absorption studies (13).

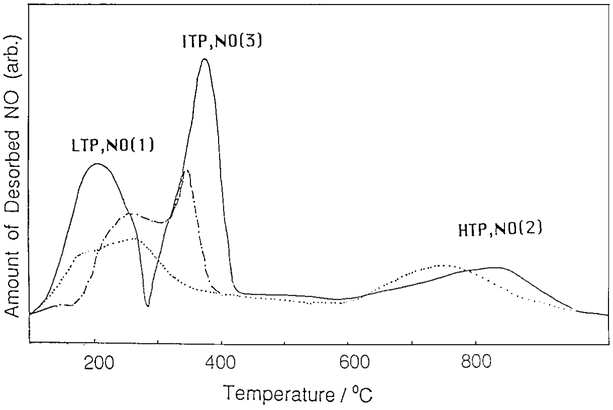

FIG. 6. NO TPD spectra of CuHM catalysts. ——, CuHM58; – · –, CuHM34; · · ·, NaHM3(HM).

DISCUSSION

Role of Catalyst Acidity for SCR Reaction

NH_3 is a common probe molecule for TPD measurement of the acidity of catalysts, including zeolites, since it can be easily stabilized on the acid site and penetrate into pores due to its strong basicity and size. Another advantage of NH_3 as a probe molecule, mentioned above, is that it is one of the major reactants in the SCR reaction. Therefore, NH_3 TPD will provide information on catalyst acidity, including the number of acid sites and the distribution of acid strength as well as the adsorption property of reactants, simultaneously.

For the interpretation of TPD spectra by NO and NH_3, it must be noted that in the course of the TPD test, the catalyst samples were always heated to a temperature considerably above the calcination temperatures and some of the TPD peak temperatures were occasionally higher than the calcination temperatures. But no TPD spectra were detected over the catalyst without the adsorption of NO and NH_3.

In Fig. 3, the intensity of HTP strongly depends on the degree of H^+ ion-exchange levels of NaM catalysts. The HTP area is considered to be the number of strong Brønsted acid sites, since NaM has no protons but HM contains protons by the ion exchange of Na^+ to H^+. The nature of HTP has already been discussed on the basis of IR results (14–16). As shown in Fig. 1, the catalytic activity of the NaHM catalyst is also a strong function of the degree of H ion exchange. Figure 7 presents the effect of the number of strong acid sites (Brønsted acid sites) on SCR activity. It should be noted that the present study may be quite specific for the analysis of catalytic data and acidity at a lower reaction temperature where NH_3 oxidation is not yet important. High-temperature data were not analyzed, since they are much more complicated due to the strong involvement of the NH_3 oxidation reaction with the NO reduction reaction.

The first-order rate constant of the NO reduction reaction observed within the range of the low reaction temperature NH_3 oxidation is not yet important was employed as a measure of SCR activity at a given temperature. The first-order kinetics of this reaction system for describing NO removal activity of the catalyst at lower reaction temperature has already been extensively discussed and reported (6, 9, 10). The constants were calculated by experimentally observed NO conversion data with the reactor space time, the inverse of the reactor space time represented by the ratio of feed gas flow rate to the reactor volume occupied by the catalyst. The bulk density of the catalyst is 0.83.

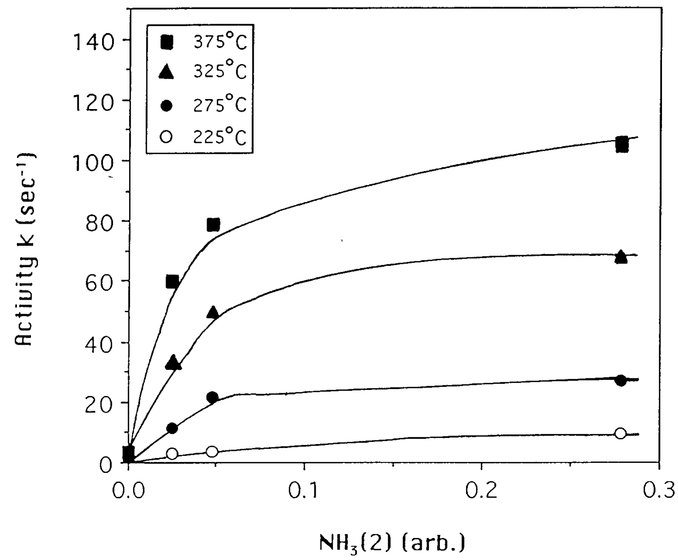

FIG. 7. Dependence of SCR activity on the amount of NH_3 adsorbed onto the strong site (2) of NaHM catalysts.

The amount of catalyst acidity is described by the amount of NH_3 desorbed based upon the areas of high-temperature TPD peaks represented by $NH_3(2)$ in Fig. 3. The total amount of adsorbed NH_3 useful for the SCR reaction on the catalyst surface observed by TPD increases at first with decreasing Na content of the catalyst. The catalytic activity of NO reduction, however, nearly levels off at 0.18 wt% of Na content for the NaHM3 catalyst shown in Fig. 7. This suggests that Brønsted acid sites are essential for the SCR reaction. It is also the reason that the HM catalyst without cations on the catalyst surface shows substantial activity for this reaction system.

On the other hand, the LTP has not been completely analyzed, and the identification seems to be still a matter of controversy. In this case, the LTP represented by weak acid sites or weakly adsorbed NH_3 was considered to have an insignificant role in this reaction system, since all of the weakly adsorbed NH_3 may not exist on the catalyst surface at the reaction temperatures covered in the present study. In addition, the NaM catalyst revealing a strong LTP shown in Fig. 3 exhibits a negligible NO removal activity over the range of the reaction temperatures.

A similar trend is observed for NO TPD as shown in Fig. 5. Also, the LTP was believed to play a small role in the SCR reaction based on the same reasoning as for NH_3 TPD in the NaHM catalyst. Again, we attempted to correlate the catalytic activity and the amount of NO adsorbed on the catalyst surface calculated from the results of NO TPD. In Fig. 8 the activities of the NaHM catalysts with respect to reaction temperatures are described as a function of the amount of NO adsorbed on the catalyst surface. The SCR activity of the NaHM catalyst strongly depends on the amount of NO(2) strongly adsorbed on its surface. However, the total amount of adsorbed NO decreased with the degree of proton exchange on the NaHM catalyst, probably because the acidic probe gas, NO, favors a basic catalyst, NaM compared with NaHM catalysts.

Role of Copper in SCR Reaction

H mordenite itself exhibits significant activity for NO reduction by NH_3. It is observed that the activity of HM is attributed mainly to its Brønsted acid sites. When copper is added to HM by ion exchange, the activity of NO reduction is dramatically enhanced. The reasons for this promoting effect by copper are not well understood.

TPD experiments of NO and NH_3, two primary reactants of the SCR reaction, will provide evidence of the role of the copper ion in this reaction system. Exchanging some of the Na ions in the NaM catalyst for protons, we found that the HTP observed in NH_3 TPD was well correlated with NO reduction activity, as shown in Fig. 7. Note that all of the weakly adsorbed NH_3 may not stay on the catalyst surface during the reaction. The addition of copper to the catalyst further increases the intensity of the HTP and creates the new ITP which may also be responsible for the SCR reaction as depicted in Fig. 9. Note that the low-temperature activity of CuHM and NaHM catalysts at around 200°C may be due to the acid sites of the ITP and HTP, which were not observed for the NaM catalyst as shown in Figs. 3 and 4.

Although SCR activity does increase with acidity, the relationship is not linearly proportional. The activity of NO reduction for CuHM catalysts increases with their NH_3 adsorption capacity including Brønsted acidity determined by TPD. In fact, the SCR activity of a copper ion-exchanged

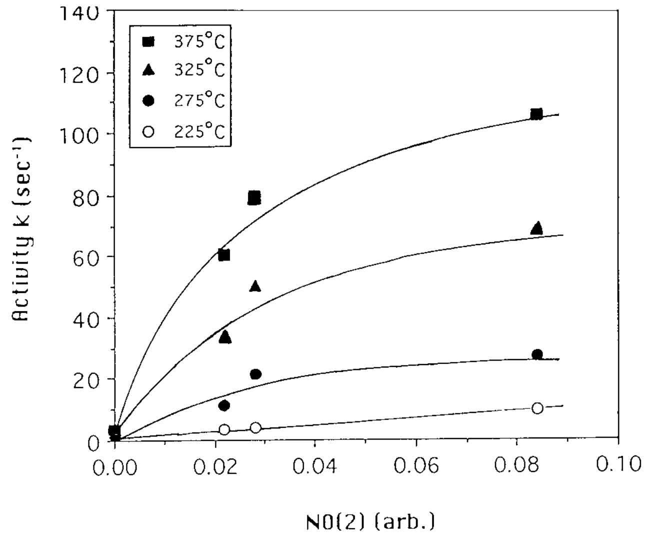

FIG. 8. Dependence of SCR activity on the amount of NO adsorbed onto the strong site (2) of NaHM catalysts.

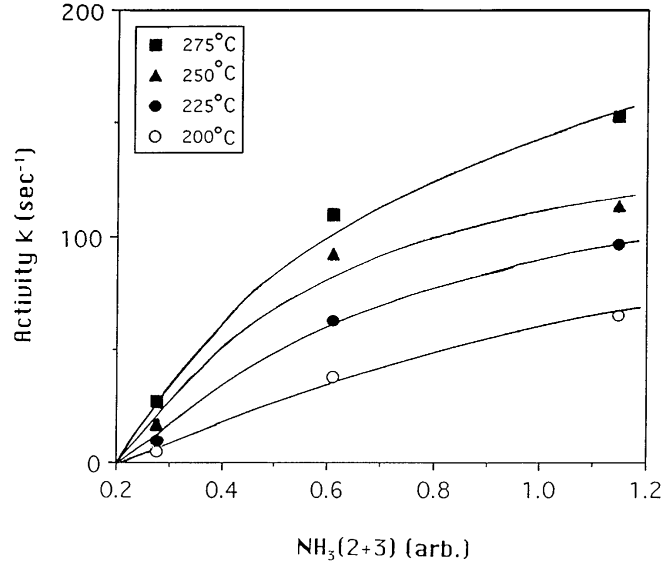

FIG. 9. Dependence of SCR activity on the amount of NH_3 adsorbed onto the strong and intermediate site (2 + 3) of CuHM catalysts.

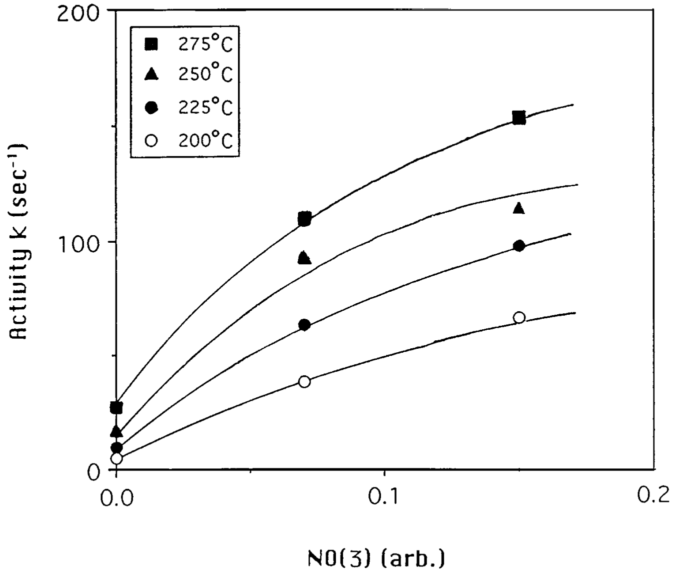

FIG. 10. Dependence of SCR activity on the amount of NO adsorbed onto the intermediate site (3) of CuHM catalysts.

catalyst is far greater than that of an unexchanged catalyst. NO reduction activity significantly depends on the amount of the exchanged cations on the catalyst surface. This indicates that the total amount of NH_3 adsorbed on the catalyst surface is a crucial feature for the SCR activity of the catalysts.

A similar observation was also made for NO TPD, shown in Fig. 6. Again, only the HTP of NO was found to be responsible for the NO reduction activity of NaHM catalysts. Upon addition of copper to HM catalysts, the ITP, NO(3), strongly appears without any change in the intensity of the HTP, NO(2), which is also observed for the HM catalyst. As shown in Fig. 10, the intensity of this new peak, ITP, was also well correlated with the activity of CuHM catalysts as a function of the catalyst copper content.

When copper ions are exchanged on the HM catalyst, they are expected to take the positions previously occupied by two protons. Hence, up to 60% of the protons on the HM (NaHM3) catalyst are replaced by copper ions, which are more effective in adsorbing NO and NH_3 molecules on the catalyst surface than Na and/or H^+. Indeed, copper ion can accommodate four NH_3 molecules by the formation of Cu–NH_3 complexes under the reaction condition of the SCR system (13).

The relationship between the activation energies of the catalysts employed in this work and the amount of NO and NH_3 adsorbed on the catalyst surfaces has also been investigated. The activation energy of ion-exchanged mordenite catalysts for the SCR reaction is independent of the copper and hydrogen ion-exchange level of the catalysts as shown in Figs. 11 and 12. However, the frequency factors of the Arrhenius equation, probably indicating the number of active reaction sites on the catalyst surface, vary with respect to the catalyst sodium and copper content. They are directly or inversely proportional to the copper and sodium content of the catalysts, respectively. The activation energy of the NaM catalyst is different from those of the NaHM at CuHM catalysts. This reveals that the high activity of an ion-exchanged catalyst is simply due to the amount of NO and NH_3 adsorbed on the catalyst surface, reflecting the role of cations, which enhance the adsorption capacity of NO and NH_3 on the catalyst surface for this reaction system. The common activation energy for ion-

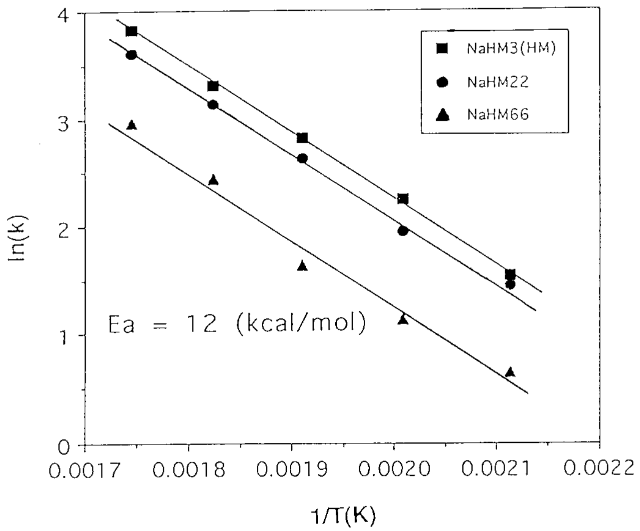

FIG. 11. Temperature dependence of first-order rate constants for NaHM catalysts.

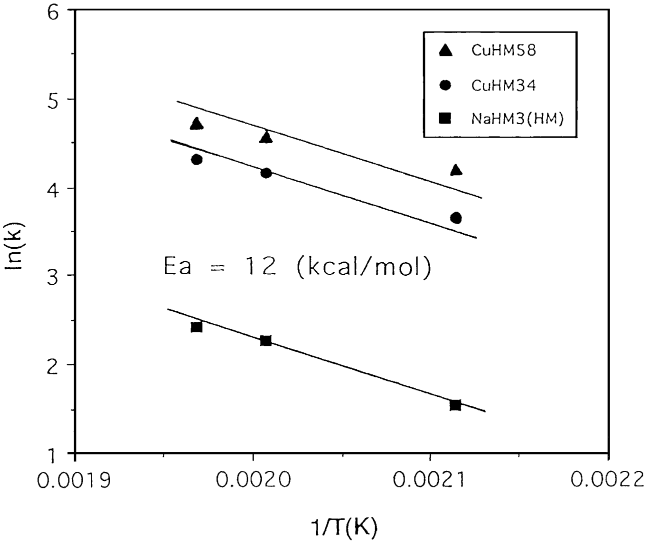

FIG. 12. Temperature dependence of first-order rate constants for CuHM catalysts.

exchanged mordenite catalysts indicates that the number of active reaction sites on the catalyst surface is gradually increased as the ion exchange proceeds. Note that the frequency factor of the Arrhenius equation may represent the number of reaction sites on the catalyst surface. All of these observations are quite consistent with those of the previous investigation (6) and even with those for a deactivated catalyst (17).

Proposed SCR Reaction Mechanism for the CuHM Catalyst

In the case of other catalysts for the SCR reaction such as V_2O_5/Al_2O_3, $/SiO_2$, or $/TiO_2$, the Eley–Rideal mechanism, assuming the surface reaction step between adsorbed NH_3 and bulk NO as a rate-determining step, has been proposed to describe the observed kinetics (18–20). However, for the mordenite catalysts employed in this study, the traditional Langmuir–Hinshelwood mechanism, assuming a surface reaction between adsorbed NH_3 and NO on the catalyst surface, appears to be appropriate, since both NO and NH_3 were found to be adsorbed on the catalyst surface, and the amounts of both molecules adsorbed are responsible for the SCR activity of the mordenite-type catalyst. The reaction kinetics can be easily understood by comparison of the desorption temperatures and peak areas of these species presenting their adsorption capacities. On the basis of these NO and NH_3 TPD results for the adsorption of reactants with first-order kinetics at a low reaction temperature, it can be proposed that the NO–NH_3 reaction occurs between adsorbed NO and NH_3 molecules on two different reaction sites, metal and acid, which can be represented by the dual site catalysis mechanism as follows.

Adsorption:

$$\mathrm{NO} + \mathrm{s1} \underset{k'_{\mathrm{NO}}}{\overset{k_{\mathrm{NO}}}{\Longleftrightarrow}} \mathrm{NO\text{–}s1} \qquad [4]$$

$$\mathrm{NH_3} + \mathrm{s2} \underset{k'_{\mathrm{NH_3}}}{\overset{k_{\mathrm{NH_3}}}{\Longleftrightarrow}} \mathrm{NH_3\text{–}s2} \qquad [5]$$

Surface reaction:

$$\mathrm{NO\text{–}s1} + \mathrm{NH_3\text{–}s2} + \left(\tfrac{1}{4}\right)\mathrm{O_2} \xrightarrow{k_s} \mathrm{N_2} + \left(\tfrac{3}{2}\right)\mathrm{H_2O} + \mathrm{s1} + \mathrm{s2}. \qquad [6]$$

The reaction mechanism assumed in the present study is quite consistent with the results from TPD of NH_3 and NO. As shown in Figs. 4 and 6, NH_3 and NO may adsorb on to two different reaction sites on the surface of CuHM catalysts; ITP and HTP for NH_3 adsorption and ITP for NO adsorption are mainly responsible for the SCR activity with bulk O_2 described in Reactions [2] and [6] (4). Since the oxygen concentration remains essentially constant due to its typical concentration in the present study (5%), its contribution to the kinetic equation can be barely distinguished. Therefore, the following rate equation can be derived based upon Hougen–Watson formalism,

$$-r_{\mathrm{NO}} = \frac{k_s K_{\mathrm{NO}} K_{\mathrm{NH_3}} P_{\mathrm{NO}} P_{\mathrm{NH_3}}}{(1 + K_{\mathrm{NO}} P_{\mathrm{NO}})(1 + K_{\mathrm{NH_3}} P_{\mathrm{NH_3}})}, \qquad [7]$$

where s1 and s2 are reaction sites, k_i and k'_i are the rate constants for adsorption and desorption, k_S is the surface reaction rate constant, P_{NO} and P_{NH_3} are the partial pressures of NO and NH_3, and K_{NO} and K_{NH_3} are the adsorption equilibrium constants, respectively. Equation [7] can be easily reduced to the first-order kinetics with respect to the partial pressure of NO for the CuHM catalyst if $K_{NO}P_{NO} \ll 1$ and $K_{NH_3}P_{NH_3} \gg 1$. It is quite true that the adsorption of NH_3 is much stronger than that of any other components involved in this reaction system based upon the results from the TPD experiment:

$$-r_{\mathrm{NO}} \approx kP_{\mathrm{NO}}. \qquad [8]$$

The first-order reaction for the SCR system is the most common reaction kinetics observed for the SCR reaction system. The rate constant, k in Eq. [8] for the first order kinetics was already employed in this study as a measure of catalytic activity to correlate with the catalyst acidity and its adsorption capacity of NO and NH_3. Again, it has already been observed for CuHM (6, 9, 10) and V_2O_5/Al_2O_3 (10) catalysts at low reaction temperatures.

CONCLUSION

The catalytic activity of the mordenite-type zeolite catalyst for SCR of NO by NH_3 was significantly improved by the addition of Brønsted acid sites and copper ion sites to the NaM catalyst. Brønsted acid sites increase the amount of NH_3 adsorbed on the catalyst surface. Moreover, copper ions on the CuHM catalyst provide additional adsorption sites for NO and NH_3 for high performance NO reduction. Both the SCR activity and the adsorption capacities for NO and NH_3, including Brønsted acidity as measured by TPD increase with increasing proton and copper content of the catalyst. The active reaction sites for the SCR reaction are both Brønsted acid sties and copper ion sites. The common activation energy for this reaction system was observed regardless of the degree of ion exchange on the catalyst surface. Furthermore, the SCR reaction occurred in a Langmuir–Hinshelwood manner on the ion-exchanged mordenite-type zeolite catalysts with a dual-site catalysis mechanism involving two different reaction sites on the catalyst surface.

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