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The Effects of Steaming and Sodium Exchange on the Selective Catalytic Reduction of NO and NO_2 by NH_3 over HZSM-5

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We have studied the selective catalytic reduction of NO and NO_2 by NH_3 over a series of HZSM-5 catalysts that have been modified by mild steaming and by sodium exchange. We find that the activity of an HZSM-5 sample for the reduction of NO is increased following a moderate steaming. Kinetic data collected for this sample can be accurately fit using the rate expression developed for unsteamed catalysts. Mild steaming increases the rate constants for SCR and ammonia oxidation by approximately a factor of two but requires no change in the ammonia adsorption constant, suggesting that steaming increases the rate by increasing the number of active sites. We also observe that the rate of NO reduction is not strongly affected by the level of sodium exchange. Given that mild steaming is known to increase the concentration of extra-framework alumina while sodium exchange is known to primarily affect the acidity of the framework Brønsted alumina, these observations strongly support our earlier conclusion that the active site for the selective catalytic reduction of NO by ammonia over HZSM-5 is highly acidic extra-framework alumina. We also find that while the fully exchanged sample is active for the reduction of NO_2 by NH_3, the rate is strongly dependent on the number of unexchanged framework Brønsted sites, suggesting that both framework and extra-framework alumina are active for NO_2 reduction. © 2002 Elsevier Science (USA)

Key Words: **selective catalytic reduction; HZSM-5; zeolite; NO; NO_2; NO_x; acid site modification.**

INTRODUCTION

The selective catalytic reduction (SCR) of nitric oxide by ammonia is the most widely used process for the removal of NO_x from flue gas (e.g., 1). The generally accepted stoichiometry for this reaction involves the combination of equimolar amounts of NO and NH_3 in the presence of oxygen to produce nitrogen and water.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

Although a variety of materials show some catalytic activity for this reaction, catalysts based on mixtures of vanadia and titania are currently used in most commercial SCR units. There has been significant interest, however, in developing zeolite-based catalysts. Zeolites offer a number of advantages over vanadia/titania catalysts: they are active over a wider temperature range, they are more resistant to thermal excursions, and the spent catalyst can present less of a disposal problem.

Although the literature on the SCR reaction over metal-exchanged zeolite catalysts is relatively large, there have been far fewer studies on the mechanism or kinetics of this reaction over zeolites in the hydrogen form. In a previous publication (2) we have summarized the relevant literature on the kinetics of NO_x reduction by NH_3 over H-form zeolites (3–12). Literature reports of the kinetics and mechanism of the SCR reaction over zeolites have focused on H–mordenite (3–7, 11, 12) and H–ZSM-5 (8–12) catalysts. Studies have observed this reaction to be first order in NO (7, 9) or nearly so (11) and first order in oxygen (3, 11) or nearly so (9), but negative order in ammonia (9, 11). Measured activation energies have generally been observed to be near 60 kJ/mol (4, 7, 11), although lower values have also been reported (9). Interestingly, the reaction is observed to be more rapid when mixtures of NO and NO_2 are fed than when either is fed separately (3–5). The oxidation of NO to either NO^+ or NO_2 has been suggested to be rate determining (4, 5, 9, 11, 12), although not all authors are in agreement with this conclusion (10). The disproportionation of NO to give NO_2 and N_2O has also been proposed as the rate-determining step (8). Both Lewis (4) and Brønsted acid sites (12) have been suggested to be the active site for this reaction.

In two previous publications (2, 13), we have reported the results of our own kinetic studies of the reduction of NO and NO_2 by NH_3 over an HZSM-5 catalyst. We collected kinetic data over a range of temperatures and inlet NO, NH_3, and O_2 concentrations and developed a model that accurately describes the experimental results; a similar, but much less extensive, set of data was collected for NO_2 reduction. Based on these results, we reached two main

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conclusions: the rate-determining step in the reduction of NO by NH_3 over HZSM-5 is the oxidation of NO, and the active site for this reaction is highly acidic extra-framework alumina.

Our conclusion that NO oxidation was rate determining was based on the following observations:

- The SCR reaction was first order in NO and O_2 but negative order in NH_3, suggesting that NO and O_2 participated in the series of steps up to and including the rate-determining step but that NH_3 did not.
- Only small amounts of NO_2 were observed in the gas exiting the reactor even though the same HZSM-5 catalyst converted significant amounts of NO to NO_2 in the absence of NH_3.
- The kinetics of NO oxidation were similar to the kinetics of NO reduction and the rate constants were approximately equal.
- The reduction of NO_2 was observed to be two to three orders of magnitude faster than the reduction of NO under the same conditions.
- The kinetics of NO_2 reduction were found to be significantly different from the kinetics of NO reduction, suggesting that the primary barrier to NO conversion had been removed by feeding NO_2.

Our conclusion that the active site for NO oxidation was highly acidic extra-framework alumina was based on less-direct evidence. We observed that strong ammonia adsorption inhibited the rate of NO reduction, suggesting that ammonia was decreasing the rate by adsorbing on the active site and that the active site was therefore an acid site. Our kinetic modeling indicated that the coverage of ammonia on this site was very high, considerably higher than could be accounted for by the known strength of ammonia adsorption on framework zeolite alumina.

In order to further test our conclusions concerning the active site in the selective catalytic reduction of NO by NH_3 over zeolites, we tested the activity of catalysts modified by two methods known to alter the relative amounts of framework and extra-framework acid sites: mild steaming and sodium exchange. Mild steaming is known to increase the amount of highly acidic extra-framework alumina and, if our hypothesis concerning the active site is correct, might be expected to increase the rate of NO reduction without changing its kinetics. Sodium exchange is known to primarily affect the framework Brønsted sites and might be thought to provide some insight into the importance of these sites in the SCR reaction. The results of these studies are reported in this work.

EXPERIMENTAL

The parent catalyst used for the steaming study was a Mobil commercial preparation of HZSM-5. It was synthesized hydrothermally at approximately 100°C using an *n*-propylamine template. The Si/Al molar ratio in the synthesis mixture was 27 : 1; elemental analysis indicated that the actual Si/Al ratio in the final catalyst was roughly 22 : 1 and that the catalyst contained approximately 700 ppm sodium. The material used as the parent for the sodium exchange studies was very similar; chemical analysis suggested it to have a silicon/aluminum ratio of 22 : 1 and, as received, approximately 1500 ppm sodium. The average crystal size of both samples, as measured by TEM, was approximately 0.50 μm. Samples were carefully pretreated (2) to ensure reproducibility from run to run; we have previously observed that differences in pretreatment can lead to measurable differences in activity.

For the steaming experiments, 0.46 g of catalyst was loaded into a reactor, as described below. Kinetic experiments using various amounts of NO, ammonia, and oxygen were performed; the kinetics and kinetic constants were found to be essentially the same as those we reported previously using a different sample of the same catalyst (2). This sample, while still loaded in the open glass reactor tube, was allowed to adsorb moisture from the air for approximately 6 weeks. The tube was then remounted in the kinetics unit and 2074 ppm NH_3 in He was flowed over the catalyst at a rate of 50 cm^3/min and a temperature of 50°C for 18 min. Based on ammonia measurements at the reactor exit we calculate that approximately 75 μmol of ammonia was adsorbed. The flow was then stopped, and the sample was heated under static conditions to 400°C at a rate of 20°C/min and held at this temperature for 130 min. Because there was no gas flow during this heating, the sample was exposed to both ammonia and water vapor, due to the desorption of adsorbed ammonia and water. The sample was then treated in a flowing stream of 2% oxygen in helium for 45 min at 500°C to remove all ammonia, after which it was cooled to room temperature in flowing helium to be used for the kinetic studies described below.

The sodium-exchanged samples were prepared by the following procedure: a known amount of sodium nitrate was dissolved in distilled water and mixed with 3–4 g of HZSM-5. Approximately 10 ml of solution was used for each 1 g of catalyst. The solution and the catalyst were stirred for 30 min; in some cases the solution and catalyst were allowed to remain in contact unstirred for an additional 18 h. Following this, the liquid was decanted, the sample was washed with 20 ml of water, and the mixture was filtered. The resulting material was dried in air for 2 h at 120°C and calcined in dry air for 2 h at 400°C. In this manner samples determined by chemical analysis to contain 0.158, 0.367, and 1.27 mol of Na/mol of Al were prepared. They were compared with two additional samples: one in which a 2 M solution of ammonium nitrate was used in place of the sodium nitrate solution in the procedure described above, giving a sample containing only 0.029 mol of Na/mol of Al, and a second sample that was merely washed

TABLE 1

Analysis Results for Exchanged Samples

Sample	Treatment	Al (wt%)	Si (wt%)	Na (ppm)	Na/Al (mol/mol)	Acidic Al content[a] (μmol/g)
EX-3	2.10 M $NaNO_3$, 18 h	1.76	39.0	19,100	1.274	0
EX-2	0.19 M $NaNO_3$, 18 h	1.79	40.0	5600	0.367	412
EX-4	0.03 M $NaNO_3$, 30 min	1.78	39.9	2390	0.158	548
EX-5	Distilled water, 30 min	1.80	39.6	1580	0.103	584
EX-8	2.03 M NH_4NO_3, 18 h	1.65	40.9	403	0.029	632

[a] Acidic Al content calculated as total Al/g × (1-Na/Al). Al content normalized to constant total Al concentration in all samples.

with distilled water, dried, and calcined, giving a material containing 0.103 mol of Na/mol of Al. Some properties of these samples are summarized in Table 1.

One FeZSM-5 catalyst was used to compare the behavior of a metal-exchanged zeolite catalyst to that of the HZSM-5 catalysts that were the focus of this work. The parent material used for this catalyst was the same as that used for the steaming and sodium-exchange studies. It was prepared by the incipient wetness impregnation of the HZSM-5 powder using an aqueous solution of ferrous acetate. The resulting catalyst slurry was thoroughly mixed at room temperature and dried in air overnight at 100°C in a rotary evaporator. The resulting impregnated and dried solid was then calcined in air at 600°C for 10 h to produce the final catalyst. The final iron loading was determined to be 2.5% by elemental analysis.

Kinetic data were collected using the same reactor system described in our earlier studies (2, 13). A plug flow reactor operated in a downflow configuration was used; a bypass loop allowed the measurement of feed concentrations. Catalyst was loaded into a 3.49 mm inner diameter quartz tube reactor and held in place with quartz wool. For the NO reduction experiments, approximately 0.46 g of catalyst, sized to 20/40 mesh, was loaded and a total flow rate of 500 cm^3/min was used, giving a space velocity of approximately 36,000 h^{-1}. Due to the significantly higher rate of NO_2 conversion, the space velocity for experiments using NO_2 was increased by using less catalyst and, in some cases, a higher gas flow rate. Some 0.019–0.038 g of 20/40 mesh catalyst was mixed with approximately 0.10 g of HiSil, also sized to 20/40 mesh, giving a total bed volume of approximately 0.4 cm^3 and a space velocity on zeolite of 630,000–1,750,000 h^{-1}.

Oxygen, nitric oxide or nitrogen dioxide, and ammonia in balance helium, supplied from gas cylinders, were metered using mass flow controllers and mixed with helium to give the desired inlet concentrations. Trace amounts (2–15 ppm) of nitrogen were present in the feed mixture. The NO_2 contained a small amount of NO (NO_2/NO ratio of approximately 63.) The total flow was set to either 500 or 1000 sccm. Standard inlet conditions were 500 ppm NO or NO_2, 500 ppm NH_3, and 1% O_2; variations of these concentrations were used to study the reaction kinetics. The catalyst activity was measured at temperatures between 300 and 500°C.

Effluent gas samples were recorded every 5 min. The catalyst was left on stream at each set of conditions for 90 min when the total flow rate was 1000 sccm and 3 h when the flow rate was 500 sccm; this was a sufficient length of time for the catalyst to reach steady state in all cases. An MTI 200 Gas Chromatograph was used to determine O_2, N_2, and N_2O concentrations; calibrations were made using cylinders of known concentration supplied by Matheson. Two Siemens NDIR analyzers were used to measure NO and NH_3 levels. NO_2 concentrations were estimated from an overall mass balance.

When NO_2 was fed, some measurable conversion of NO_2 and NH_3 to N_2 was observed even when the gas flow bypassed the catalyst. We believe that this conversion is due to the homogeneous reaction of NO_2 and ammonia in the heated lines leading to the ammonia analyzer. Simple bypass tests showed that this background conversion is approximately first order in NO and half order in NH_3; these results were used to correct the amount of N_2 formed over the catalyst during kinetic testing. This correction was small, typically only 1–10% of the N_2 formation rate over the catalyst. The HiSil used to dilute the zeolite bed was also tested for NO, NO_2, and NH_3 conversion activity; its contribution to the observed conversion was found to be negligible.

When NO was fed, conversions typically varied from 5 to 25%. However, when NO_2 was fed conversions were often much higher, ranging from 25% to more than 80% in some experiments. In both cases, the measured rates were corrected for nondifferential conversions using the kinetic equations developed in our previous work (2, 13). These corrections were small and, we believe, accurate for the NO reduction experiments. For the runs where NO_2 was fed and the conversion was high, however, the rates must be considered somewhat approximate. In addition, for catalyst EX-2 the measured rate of NO_2 reduction at 350 and 400°C increased significantly as the space velocity was increased, suggesting that the reaction is being limited by bulk mass transfer. For this sample it is likely that the true kinetic rates, i.e., the rates measured under conditions where mass transfer was not important, would be somewhat higher than we observed.

RESULTS AND DISCUSSION

Effect of Steaming on SCR Activity

Figure 1 shows the effect that the mild steaming treatment described above had on the activity of the HZSM-5 sample; rates were measured with inlet concentrations of 500 ppm NO, 500 ppm NH$_3$, and 1% O$_2$ at temperatures ranging from 300 to 500°C. At every temperature the activity of the catalyst was increased by steaming; the rate enhancement varied from approximately 2.25 times at 300°C to 1.6 times at 500°C. The measured apparent activation energy of the catalyst decreased slightly after steaming, from 52 (±2) kJ/mol to 47 (±4) kJ/mol (95% confidence limits.)

Figure 2 shows the effect of the steaming treatment on the kinetics of NO reduction. The rate was observed to be first order in NO concentration and negative order in ammonia both before and after steaming. The kinetic data were fit to the rate equation developed in our earlier work (2):

$$r_{N_2} = \frac{k_{SCR}[NO][O_2]}{1 + K_a[NH_3]} + \frac{k_{ox}K_a[NH_3]}{1 + K_a[NH_3]} + k_O[NO].$$

The rate constants for the SCR reaction, k_{scr}, and for ammonia oxidation, k_{ox}, as well as the ammonia adsorption constant, K_a, were estimated by fitting the data for the steamed catalyst; k_O was assumed to be the same as for the unsteamed catalyst (2), since data were collected only at one oxygen concentration. The excellent agreement of the fits (Fig. 2, solid lines) to the data show that the model accurately describes the observed rate data.

The values of the constants used to obtain the fits in Fig. 2 are presented in Table 2, where they are compared to those reported previously for the unsteamed catalyst (2). From this table we see that the SCR and ammonia oxidation rate constants, k_{scr} and k_{ox}, have nearly doubled, while the ammonia adsorption constant, K_a, remains almost unchanged. Error analysis indicates that the increase in the SCR rate constant is significant at the 95% level; the increase in the ammonia oxidation rate constant is significant only at the 70% level. The observation that the same kinetic model fits the data very well suggests that steaming does not change the mechanism of the reactions, but rather increases the number of active sites. Because the rate constants for

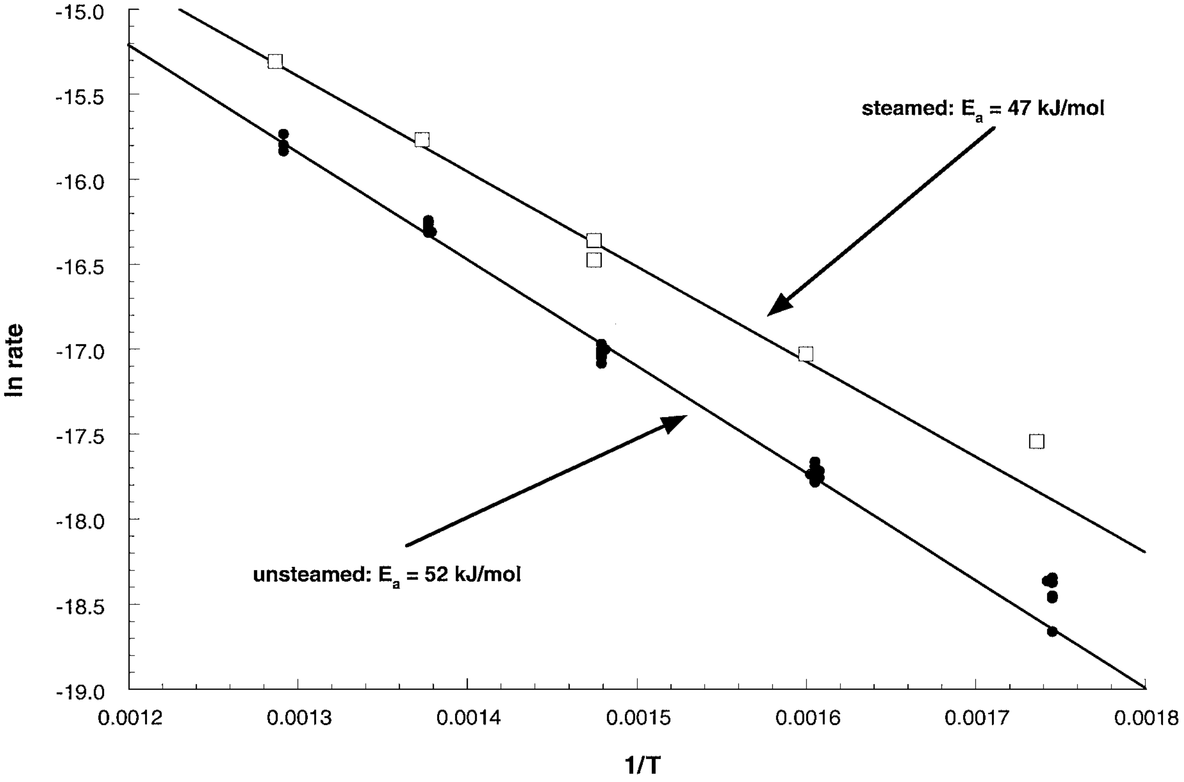

FIG. 1. The effect of steaming on NO reduction activity. Inlet conditions: 500 ppm NO; 500 ppm NH$_3$; 1% O$_2$; GHSV = 36,000 h^{-1}.

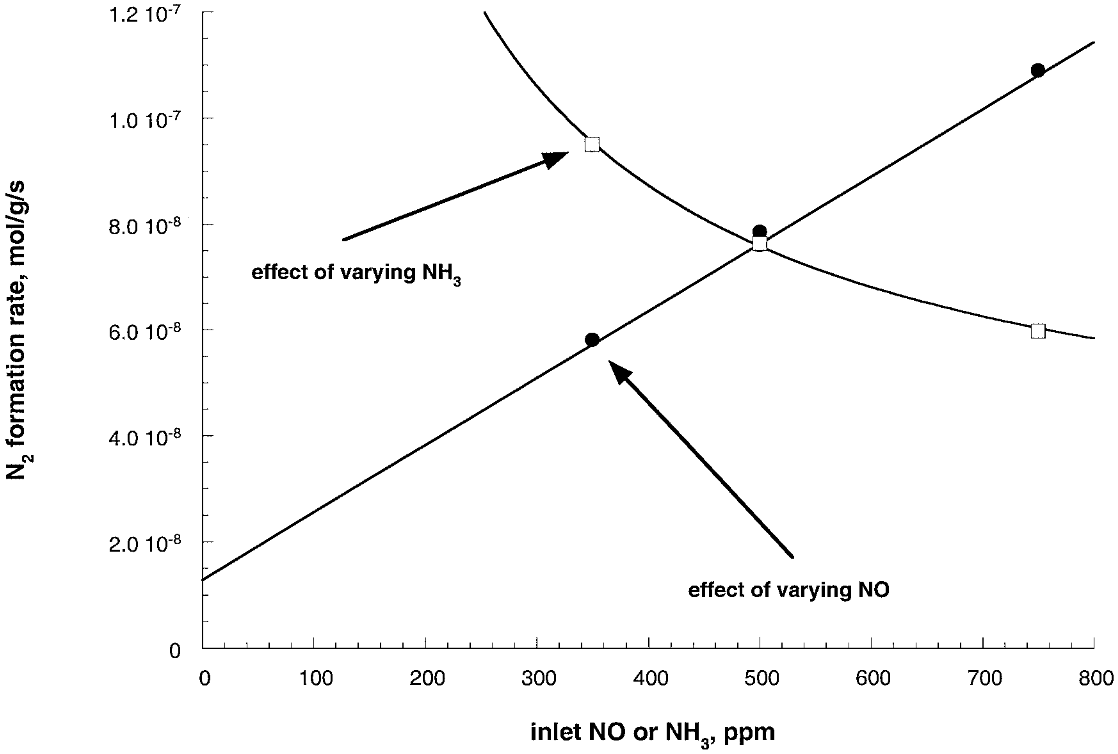

FIG. 2. The kinetics of NO reduction over steamed HZSM-5. Experimental data (points) fit using kinetic model (solid lines). Solid circles show effects of varying NO (NH_3 held constant at 500 ppm) and open squares show effects of varying NH_3 (NO held constant at 500 ppm). Inlet $O_2 = 1\%$; GHSV = 36,000 h^{-1}.

ammonia oxidation and the SCR reaction increase by approximately the same amount, it would also seem reasonable to suggest that both occur on the same active site.

It is well-known from the literature (e.g., 15–20) that mild steaming increases the number of strongly acidic extra-framework alumina sites in a variety of zeolites, including HZSM-5. The observation that steaming also increases the number of active sites for the SCR reaction suggests that extra-framework alumina is in fact the active site for this reaction. This suggestion is in agreement with our earlier work (2), where we proposed that the active site for the SCR reaction over HZSM-5 was extra-framework alumina based on the extent of ammonia inhibition of the reaction.

TABLE 2

Changes in Kinetic Fitting Parameters due to Steaming[a]

Constant	Units	Unsteamed	Steamed	% change
k_{scr}	$cm^6/mol/g/s \times 10^{-7}$	9.85	19.5 (13.2–42)	98%
K_a	$cm^3/mol \times 10^{-8}$	5.36	4.75 (2.5–14.1)	−11%
k_{ox}	$mol/g/s \times 10^9$	8.11	14.1 (2.8–23.7)	74%
k_O	$cm^3/g/s$	0.558	0.558[b]	—

[a] $T = 400°C$; 95% confidence intervals (14) shown in parentheses.
[b] This parameter was not varied in the data fitting.

Effect of Sodium Exchange on NO Reduction

Table 3 shows the effect of sodium exchange on the rate of NO reduction. At 350°C there is no effect of sodium exchange; the rate of N_2 formation over the completely exchanged sample is the same as the rate over the low-sodium sample prepared by exchange with ammonium nitrate. At 400°C the activity of all the samples is the same within experimental error with the exception of the fully exchanged sample, which is about 25% less active. Only at 450°C do we see a consistent trend of declining activity with increasing

TABLE 3

Effect of Na Exchange Level on Activity for NO Reduction[a]

Sample	Free Al content (μmol/g)	SCR rate (mol/g/s × 10^8) 350°C	400°C	450°C	E_a[b] (kJ/mol)
EX-3	0	2.81	3.98	4.65	19 (±6)
EX-2	412	2.87	5.39	9.03	43 (±6)
EX-4	548	2.90	5.28	9.35	44 (±6)
EX-5	584	2.63	4.91	9.35	47 (±6)
EX-8	632	2.76	5.41	10.5	50 (±6)

[a] Inlet conditions: 500 ppm NH_3 and NO; 1% O_2. GHSV = 36,000 h^{-1}.
[b] 95% confidence intervals shown in parentheses.

sodium level. Even at this temperature, however, the rate is not proportional to the amount of unexchanged alumina; sample EX-2 has 35% less unexchanged aluminum than sample EX-8, but its NO reduction activity is only 15% less. Likewise, sample EX-3, which has little or no unexchanged aluminum, still retains 45% of the activity of the low-sodium samples.

It is known (e.g., 21) that while the framework Brønsted alumina sites are easily exchanged with sodium, the extra-framework alumina is not. If framework alumina was the active site for the reduction of NO, we would expect to see a linear relationship between sodium content and SCR activity. Instead, we see almost no effect of sodium level at lower temperatures and only a weak effect at higher temperatures. We view this data as very strong supporting evidence that extra-framework alumina is the active site for the reduction of NO by NH_3 over HZSM-5.

It is not clear why the relative activity of the sodium-exchanged samples changes as the temperature is increased, with the samples containing the most sodium showing somewhat less activity than the low-sodium samples at the higher temperatures. This effect also manifests itself in the apparent activation energies for the five samples; Table 3 shows that the measured activation energies decline as the sodium content increases, although the relationship is not linear. Several explanations are possible for this behavior. It is possible that at reaction temperatures of 400°C and above the sodium moves in the zeolite to some extent and blocks a certain number of the extra-framework acid sites. In agreement with this hypothesis, the activity of sample EX-3, which was essentially fully exchanged, decreased with time on stream to a much greater extent than any other sample; at 400°C its activity declined 16% across the course of 13 h, while no other sample showed more than a 7% deactivation under similar conditions. A second possibility is that the sodium may partially block the zeolite channels, hindering access of the reactants. If so, such an effect would be expected to be more pronounced at higher temperature, where the rate is higher, and for samples containing higher sodium levels. Such an effect might be especially severe for the fully exchanged sample, since it contains approximately 25% excess sodium. Finally, the possibility must be considered that the framework Brønsted sites take part in the reaction to some extent at the higher temperatures. If so, it would be expected that the activity of all the samples would be the same at low temperature while the highly exchanged samples would not show as high an activity at 450°C. However, we do not believe that this hypothesis is consistent with the strong inhibition of the rate due to ammonia that we observe at 450°C (2). In any case, it is clear from the data that the framework aluminum contributes little to the rate at 400°C and below, where the sodium level is observed to have little or no effect on the NO reduction rate.

TABLE 4

Effect of Na Exchange Level on Activity for NO_2 Reduction[a]

Sample	Free Al content (μmol/g)	GHSV (h^{-1})	$N_2 + N_2O$ formation rate (mol/g/s $\times 10^6$) 300°C	350°C	400°C
EX-3	0	1,750,000	1.20	1.02	0.88
EX-2	412	1,250,000	4.15[b]	13.8	19.4
EX-8	632	850,000	5.45	—	—

[a] Inlet conditions: 500 ppm NH_3 and NO_2; 1% O_2.
[b] GHSV = 630,000 h^{-1}.

Effect of Sodium Exchange on NO_2 Reduction

Table 4 shows the effect of sodium exchange on the rate of NO_2 conversion to N_2 and N_2O. As observed in our earlier work on NO_2 reduction over ZSM-5 (13), the rate of NO_2 conversion is several hundred times faster than the rate of NO reduction. Somewhat to our surprise, the rate of NO_2 reduction is strongly affected by the level of sodium exchange and hence the concentration of free framework Brønsted sites, unlike the rate of NO reduction, which was not greatly affected by the sodium level. The data in Table 4 show that at 300°C there is an almost linear relationship between the calculated amount of free aluminum and the NO_2 conversion rate. At 400°C sample EX-2 was more than 20 times more active than sample EX-3, which was fully exchanged. This suggests that the reduction of NO_2 occurs readily on the framework acid sites in HZSM-5. From the fact that the fully exchanged sample retains a measurable level of activity as well as the observation that the effect of sodium exchange increases with temperature, it can be concluded that both the extra-framework and the framework acid sites can catalyze NO_2 reduction. However, in the low-sodium sample the relative number of framework sites is so much larger relative to the concentration of extra-framework aluminum that the activity of the former dominates. At 350 and 400°C sample EX-2 showed evidence of bulk mass transfer limitations while sample EX-3 did not, suggesting that the difference between the low-sodium and high-sodium samples is in fact even greater than measured. It is also worth noting that even in the fully exchanged sample the rate of NO_2 reduction was 20–35 times faster than the rate of NO reduction.

The conclusion that both framework and extra-framework aluminum species can reduce NO_2 is in agreement with our previously reported data on the effect of inlet NH_3 concentration on the rate of NO_2 reduction (13). Adsorption constants estimated from this data were of the same order of magnitude as those given in the literature for ammonia adsorption on framework aluminum in HZSM-5 (22).

Although the strong correlation between sodium level and activity for NO_2 reduction suggests that both framework and extra-framework aluminum are active for this reaction, it does not necessarily follow that framework aluminum participates in the reduction of NO via the oxidation of NO to NO_2 on an extra-framework site followed by the desorption of NO_2 and its subsequent reduction on a framework aluminum site. Because of the high activity of the extra-framework sites for NO_2 reduction, it is possible that little or no NO_2 desorbs from the extra-framework sites before it is converted to N_2, especially at lower temperatures, where NO oxidation and desorption are slower. At 400°C and above, however, where small amounts of NO_2 are observed in the effluent during NO reduction, it is probable that some of the NO_2 is indeed reduced to N_2 over the framework Brønsted sites. This may explain the decrease in NO reduction rate observed at 400°C and above for the fully exchanged sample; in this sample, there are no framework acid sites available to reduce NO_2 and the rate may, as a consequence, be decreased.

Comparison of HZSM-5 and FeZSM-5 Catalysts

We have also made limited measurements of the effects of modifying our HZSM-5 catalysts by impregnation of the parent material with ferric acetate to a final Fe concentration of approximately 2.5 wt%. A large number of reports attest to the fact that the addition of iron (e.g., 5, 23–25) and other transition metals (e.g., 5, 26–32) to zeolites significantly increases their activity for NO reduction. The results of our measurements are shown in Table 5, which shows the activity of the HZSM-5 and FeZSM-5 catalysts for the reduction of NO and NO_2 by NH_3. As we previously reported (13), under these conditions the rate of reduction of NO_2 by HZSM-5 is almost three orders of magnitude faster than the rate of NO reduction. In contrast, the FeZSM-5 catalyst shows only a fivefold increase in activity when NO is replaced with NO_2 in the feed. Although the FeZSM-5 catalyst is two orders of magnitude more active than the HZSM-5 catalyst for NO reduction, it is actually less active for NO_2 conversion. Given that we have shown considerable evidence that the rate-determining step for the reduction of NO over HZSM-5 is the oxidation of NO to NO_2, it is tempting to speculate that the iron-exchanged catalyst is so active for NO reduction because the iron cations catalyze the oxidation of NO much more efficiently than extra-framework aluminum can.

TABLE 5

Comparison of HZSM-5 and FeZSM-5 Catalysts for NO and NO_2 Reduction

	Rate of reduction (mol/g/s $\times 10^8$)	
Sample	NO	NO_2
HZSM-5	2.3	2000
FeZSM-5	240	1250

Note. $T = 350^\circ$C, 500 ppm inlet NH_3, 500 ppm inlet NO or NO_2, 1% inlet O_2. GHSV for HZSM-5, 36,000 h^{-1} (NO) and 1,750,000 h^{-1} (NO_2); GHSV for FeZSM-5, 415,000 h^{-1} (NO) and 835,000 h^{-1} (NO_2).

SUMMARY

We have previously proposed (2, 13) that highly acidic extra-framework aluminum is the active site for the reduction of nitric oxide by ammonia on HZSM-5. In order to provide more direct evidence for this hypothesis, we have treated samples by mild steaming and by sodium exchange, two procedures that are known to change the relative amounts of framework and extra-framework acidity of ZSM-5.

We find that a mild steaming of an HZSM-5 catalyst increases its activity for the reduction of NO by NH_3. A slight decrease in apparent activation energy is observed, from 52 to 47 kJ/mol. The kinetic data collected for the steamed catalyst can be fit using the kinetic equation previously developed for unsteamed samples. Mild steaming increases the rate constants for SCR and ammonia oxidation by approximately a factor of two but does not change the ammonia adsorption constant, suggesting that steaming increases the rate by increasing the number of active sites. Because mild steaming is known to increase the amount of highly acidic extra-framework aluminum, these results provide support for our hypothesis that such sites are the active sites for NO reduction in H-form zeolites.

By exchange with sodium nitrate and ammonium nitrate, we have prepared a series of ZSM-5 catalysts containing varying amounts of sodium. It is known that framework Brønsted acid sites are easily exchanged with sodium while extra-framework acid sites are not. We find that the activity of these samples for NO reduction is only weakly dependent on the sodium level, suggesting that the framework Brønsted acid sites play little or no role in this reaction and indicating that extra-framework species are most likely the active site. The extent of sodium exchange does, however, strongly affect the activity of the catalysts for NO_2 reduction; although the fully exchanged sample is still active for this reaction, it is observed to be as much as 20 times less active than catalysts containing less sodium. We would suggest that both framework and extra-framework acid sites are active for the reduction of NO_2. Since NO oxidation is the rate-determining step for NO reduction, the framework aluminum may play some role in converting NO_2 after it is formed at the extra-framework sites, especially at higher temperatures, where NO_2 is more likely to desorb from these sites and readsorb on the framework acid sites.

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