

The Selective Catalytic Reduction of NO₂ by NH₃ over HZSM-5

Scott A. Stevenson¹ and Jim C. Vartuli

ExxonMobil Research & Engineering Company, Corporate Strategic Research, Active Materials Laboratory/Materials Synthesis Section, 1545 Route 22 East, Annandale, New Jersey 08801-3059

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We have studied the reduction of NO₂ by NH₃ over HZSM-5 and find that this reaction is several hundred times faster than the corresponding reduction of NO under similar conditions. In addition, the kinetics of the reduction of NO₂ are strikingly different from the kinetics of NO reduction. Whereas the reduction of NO is inhibited by the adsorption of ammonia and is first order in oxygen concentration, the rate of conversion of NO₂ increases as NH₃ concentration increases and is independent of oxygen concentration. We believe that these results strongly support our earlier suggestion that the oxidation of NO is the rate-determining step in the selective catalytic reduction of NO over HZSM-5. © 2002 Elsevier Science (USA)

Key Words: selective catalytic reduction; HZSM-5; zeolite; NO; NO₂; NO_x.

INTRODUCTION

The selective catalytic reduction (SCR) of nitric oxide by ammonia is the most widely used process for the reduction of NO emissions from combustion flue gas (e.g., 1). Although a variety of materials show some catalytic activity for this reaction, catalysts based on mixtures of vanadia and titania are currently used in virtually all 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.

In a previous work (2), we reported kinetic data collected for the selective catalytic reduction of NO by NH₃ over HZSM-5 under a variety of conditions and developed a kinetic equation that accurately predicted the N₂ formation rate given the temperature and inlet NO, NH₃, and O₂ concentrations. Because the rate was first order in NO and oxygen and negative order in ammonia, and because only small amounts of NO₂ were observed in the

product gas stream, we suggested that the rate-determining step was the oxidation of NO by O₂. We proposed that the adsorption of ammonia on the active site inhibited the reaction and, based on the extent of this inhibition at 400°C and above, that the active site was extra-framework aluminum.

In order to further test these conclusions, we have studied the reduction of NO₂ by NH₃ under similar conditions over the same catalyst. In this paper, we report the results of these studies and discuss their implications for the mechanism of the SCR reaction over zeolites.

METHODS

The catalyst used in this 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 suggested that the actual Si/Al ratio in the final catalyst was roughly 22 : 1. The catalyst contained approximately 700 ppm sodium; this gives an Al/Na ratio of about 22 : 1. The average crystal size, as measured by TEM, was estimated to be 0.50 μm. Before testing, the catalyst was dried *in situ* in flowing helium for 30 min at 100°C, 2 h at 200°C, and 2 h at 300°C; this pretreatment was previously found to be important in obtaining reproducible results from run to run.

Rate data were collected using the same reactor system described in our previous studies of NO reduction (2); however, due to the significantly higher rate of NO₂ conversion, the space velocity was increased by using less catalyst and, in some cases, a higher gas flow rate. A fixed-bed reactor operated in a downflow configuration was used; a bypass loop allowed the measurement of feed concentrations. HZSM-5 (0.019 g), sized to 20/40 mesh, was mixed with 0.091 g of HiSil silica, also sized to 20/40 mesh, and loaded into a 3.49-mm inner diameter quartz tube reactor, where it was held in place with quartz wool. The total bed volume was approximately 0.41 cm³; from previous density measurements, we estimate the volume of zeolite to be approximately 0.035 cm³. Oxygen, nitrogen dioxide, and

¹ To whom correspondence should be addressed. Current address: SABIC Technology Center, 1600 Industrial Boulevard, Sugar Land, TX 77478. E-mail: scott.stevenson@sabicusa.com.

ammonia in balance helium, supplied from gas cylinders, were metered using mass flow controllers and mixed with helium to give the desired inlet concentrations. The NO₂ contained a small amount of NO (NO₂/NO ratio approximately 63); trace amounts of nitrogen (2–10 ppm) were also present in the feed mixture and were properly accounted for in the total mass balance. The total gas flow was set to either 500 or 1000 sccm, giving a space velocity based on zeolite of either approximately 870,000 or 1,740,000 h⁻¹, respectively.

Standard inlet conditions were 500 ppm NO + NO₂, 500 ppm NH₃, and 1% O₂; variations of these concentrations were used to study the reaction kinetics. The catalyst activity was measured at 300, 350, and 400°C.

The catalyst was left on stream at each set of conditions for 90 min when the total flow rate was 1000 sccm and for 3 h when the flow rate was 500 sccm. The concentration of all products reached steady state in 20–60 min with the exception of the case where no oxygen was fed. In this case, the N₂ formed declined slowly but steadily during the 90-min reaction period. Effluent gas samples were recorded every 5 min. An MTI 200 Gas Chromatograph with a molecular sieve column was used to determine O₂, N₂, and N₂O concentrations; calibrations were made using cylinders of known concentration supplied by Matheson. Two Siemens NDIR analyzers were used to measure NO and NH₃ levels. NO₂ concentrations were estimated from an overall mass balance.

Some measurable conversion of NO₂ and NH₃ to N₂ was observed even when the gas flow bypassed the catalyst. We believe that this conversion is due to the homogeneous reaction of NO₂ and ammonia in the heated lines leading to the ammonia analyzer. Simple bypass tests showed that this background conversion is approximately first order in NO₂ and half order in NH₃; these results were used to correct the amount of N₂ formed over the catalyst during kinetic testing. This correction was typically small, only 1–10% of the N₂ formation rate over the catalyst. The HiSil used to dilute the zeolite bed was also tested for NO₂ and NH₃ conversion activity; its contribution to the observed conversion was found to be negligible.

RESULTS

Activity for Reduction of NO₂

Our measurements of the NO₂ reduction activity of HZSM-5 demonstrate that this reaction is much faster than the reduction of NO over the same catalyst. Table 1 compares conversion as well as N₂ and N₂O formed during NO₂ reduction with that observed during NO reduction (2). Even though the space velocity is approximately 50 times greater for NO₂ reduction, the conversions and amounts of N₂ and N₂O formed are 5–10 times higher. A simple rate calculation based solely on the amount of NO₂ or NO con-

TABLE 1

Activity for NO ₂ Reduction Compared to NO Reduction								
T (°C)	Conversion (%)		N ₂ formed (ppm)		N ₂ O formed (ppm)		NO ₂ /NO rate enhancement	
	NO	NO ₂	NO	NO ₂	NO	NO ₂	Unadjusted	Adjusted
300	3.8	31	14	98	4	86	490	570
350	5.6	55	26	190	5	135	520	870
400	10.3	57	54	220	7	126	270	500

Note. Conditions: inlet NO + NO₂ = inlet NH₃ = 500 ppm; inlet O₂ = 1%; GHSV = 36,000 h⁻¹ for NO, 1,740,000 h⁻¹ for NO₂. Adjusted rates calculated according to kinetics described in text.

verted per volume of catalyst per unit time (column labeled “unadjusted” in Table 1) suggests that the reduction of NO₂ is 250–500 times faster than the reduction of NO. However, despite the high space velocity used for the NO₂ reduction studies, nondifferential conversions were observed, so that this calculation with integral reactor data underestimates the rate enhancement due to NO₂ if the reaction order in NO₂ or NH₃ is nonzero. Using the kinetic assumptions discussed below, we calculate that the reduction of NO₂ is 500–900 times faster than the reduction of NO, depending on the temperature (column labeled “adjusted” in Table 1.)

Previous reports in the literature (3–5) have indicated that the reduction of NO₂ by NH₃ over H-mordenite catalysts is faster than the reduction of NO, although the magnitude of the rate increase seen by these authors is less than what we observe for our HZSM-5 catalysts.

The NO₂ reduction rates implied by the data presented in Table 1 are so large that they raise the question of whether or not mass transport limitations may influence the observed rate. In fact, halving the space velocity decreases the measured rate by 25% at 300°C and 50% at 350°C, suggesting that mass transfer is limiting the rate of reaction. At 350°C, inlet concentrations of 500 ppm NH₃ and NO₂, and a space velocity of 1,740,000 h⁻¹, and using diffusion coefficients estimated according to the methods of Satterfield (6), we calculate the Damköhler numbers for interphase mass transport to be 0.24 and 0.33 for ammonia and NO₂, respectively; this implies that interphase mass transport does not significantly limit the reaction rate (7). However, we estimate the Damköhler number for mass transport in the macropores to be in the range of 1.5–5, depending on the value used for the tortuosity. This suggests that mass transport in the macropores is limiting the rate (7); we estimate effectiveness factors (8) in the range of 0.85–0.95 under these conditions. It is also possible that mass transport limitations in the zeolite pores also affects the reaction rate; however, without a reasonable value for the rate of diffusion of NO₂ in HZSM-5 it is difficult to estimate the importance of this process. If mass transport processes are indeed limiting the NO₂ reduction rate, the

rate-enhancement factors presented in Table 1 will underestimate the increase in rate when NO_2 is fed in place of NO .

One interesting difference between the reduction of NO_2 and the reduction of NO is the much larger amount of N_2O formed when NO_2 is fed. Under normal SCR conditions little NO is converted to N_2O ; in our previous work (2) N_2O concentrations did not exceed 10 ppm. When NO_2 was fed, however, much larger amounts of nitrous oxide were formed, with concentrations often greater than 100 ppm. We observed $\text{N}_2\text{O}/\text{N}_2$ ratios of approximately 0.9 at 300°C ; this ratio decreases as the temperature increases, falling to approximately 0.55 at 400°C . It is interesting that this ratio is not strongly dependent on the space velocity, suggesting that little N_2 is formed from the decomposition of gas phase N_2O .

Ammonia conversion was invariably higher than NO_2 conversion, as based on a comparison of the amounts of $\text{NO} + \text{NO}_2$ and NH_3 at the reactor exit. Additionally, the amount of ammonia converted always exceeded the amount of $\text{N}_2 + \text{N}_2\text{O}$ formed by 10–20%. This may suggest that some ammonia is oxidized to NO and NO_2 under these conditions.

NO (1–15 ppm) was observed in the product gas stream, depending on the conditions. Comparisons with the small amounts of inlet NO present in the NO_2 feed show that at 300°C there is a net formation of NO amounting to 1–3 ppm, while at 350°C there is net conversion of NO of 1–5 ppm. Thermodynamic equilibrium for 1% O_2 and 500 ppm $\text{NO} + \text{NO}_2$ would be 165 ppm NO at 300°C and 280 ppm at 350°C . However, using the rate of NO oxidation reported in our earlier work and the known equilibrium constant we can estimate the rate of conversion of NO_2 to NO at the high space velocities used for the $\text{NO}_2 + \text{NH}_3$ reaction. We calculate that when 500 ppm NO_2 is fed, roughly 3 ppm NO should be converted to NO at 350°C , suggesting that some NO may be converted even at 300°C .

Kinetics of NO_2 Reduction

In order to better understand the selective catalytic reduction of NO_2 over HZSM-5, we performed some limited kinetic experiments. Unfortunately this reaction is so fast that even at the high space velocities used the NO_2 and NH_3 conversions were large; to accurately analyze these data, we would need to know the true form of rate expression so that the observed activities could be corrected to account for the high conversions. Lacking this, the best we can do is to make some simple assumptions concerning the approximate form of the rate equation, adjust the observed rates to compensate for the nondifferential conversions, and see if the resulting rates justify the original assumptions. Best results were obtained by assuming a power-law rate equation; the power-law coefficients were adjusted by a trial-and-error process until the coefficients used to correct the measured integral rate data to account for the nondifferential conversions were approximately the same as those

obtained from fitting the adjusted data. Because we must also contend with the fact that the ammonia and NO_2 concentrations do not decrease in a 1:1 stoichiometry, the rate adjustments were made using the approximate form

$$r_{\text{true}} = r_{\text{meas}} \left(\frac{2r_{\text{inlet}}}{r_{\text{inlet}} + r_{\text{exit}}} \right), \quad [1]$$

where r_{true} is the actual reaction rate at the inlet conditions, r_{meas} is the measured rate, r_{inlet} is the rate calculated from the kinetic expression using the inlet NO_2 and NH_3 concentrations, and r_{exit} is the rate calculated from the kinetic expression using the NO , NO_2 , and NH_3 concentrations measured at the reactor exit. This expression, while not exact, is a reasonably good approximation and allows us to account for the nondifferential conversions in our integral reactor.

Figure 1 shows the effects of varying the inlet NO_2 concentration on the $\text{N}_2 + \text{N}_2\text{O}$ formation rate. The rate of $\text{N}_2 + \text{N}_2\text{O}$ formation is positive order in NO_2 concentration; the power-law rate expression used to fit the data suggests that the rate is proportional to the NO_2 concentration to the 0.68 power at 300°C and the 0.93 power at 350°C . This is less than the first-order dependence in NO observed in our previous work (2). Although it is possible that the NO_2 reaction order observed at 350°C is decreased by diffusional limitations or small errors in the adjustments made for nondifferential conversions, it appears that the rate at 300°C is intrinsically less than first order in NO_2 .

Figure 2 shows the dependence of the $\text{N}_2 + \text{N}_2\text{O}$ formation rate on inlet ammonia concentration. The power law fit gives rate orders of 0.13 and 0.82 at 300 and 350°C , respectively. This result stands in marked contrast to our earlier work using NO (2), where the rate was found to be negative order in NH_3 . This suggests that although ammonia is still adsorbed on the active site, it is no longer passively blocking

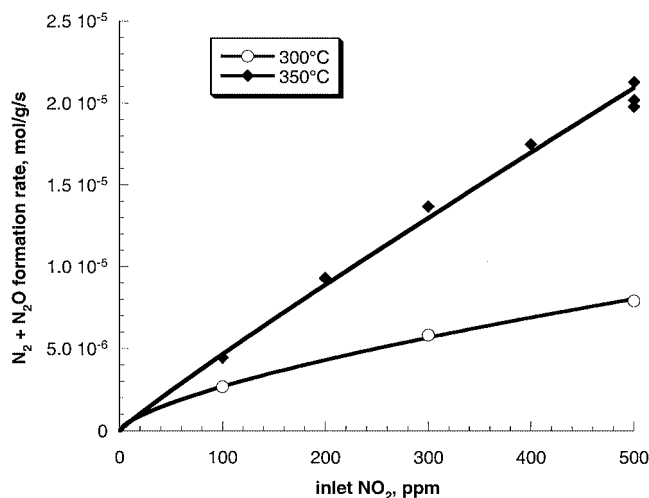


FIG. 1. Variation of $\text{N}_2 + \text{N}_2\text{O}$ formation rate with inlet NO_2 concentration. Inlet $\text{NH}_3 = 500$ ppm; inlet $\text{O}_2 = 1\%$; $\text{GHSV} = 1,740,000 \text{ h}^{-1}$.

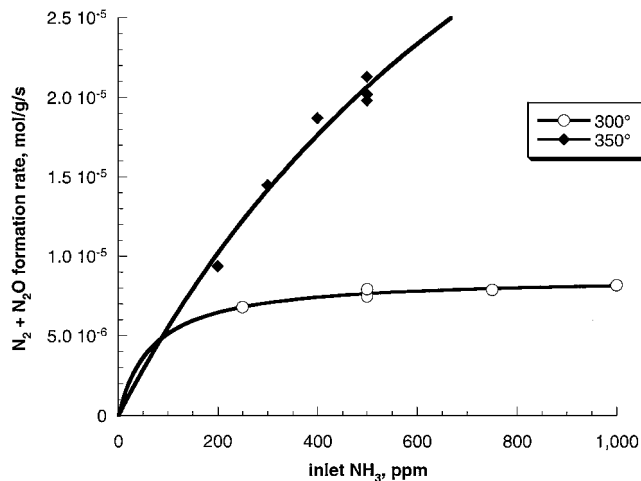


FIG. 2. Variation of N₂ + N₂O formation rate with inlet NH₃ concentration. Inlet NO₂ = 500 ppm; inlet O₂ = 1%; GHSV = 1,740,000 h⁻¹.

the active site, but participates in the rate-determining step or in some step leading up to the rate-determining step.

The effect of oxygen concentration on the rate at 350°C is shown in Fig. 3. We observe no change in the reaction rate as the inlet oxygen concentration is varied between 0 and 1%. This observation is in agreement with the work of Hirsch (3), who reported that O₂ is not needed to reduce NO₂ with NH₃ over H-mordenite. This behavior is very different from the effect of oxygen on the reduction of NO, where the reaction was observed to be first order in O₂ (2).

Figure 4 shows the variation in rate observed at 350°C when the inlet NO₂ and NH₃ concentrations are changed equally together. The rate changes almost linearly with the inlet NO₂ and NH₃ concentration. This behavior is somewhat unexpected from the observed NO₂ and NH₃ kinetics discussed above; from those results we might have expected the rate to increase as the 1.7 power of the inlet NO₂ and NH₃ concentrations. It is not clear what the cause is of

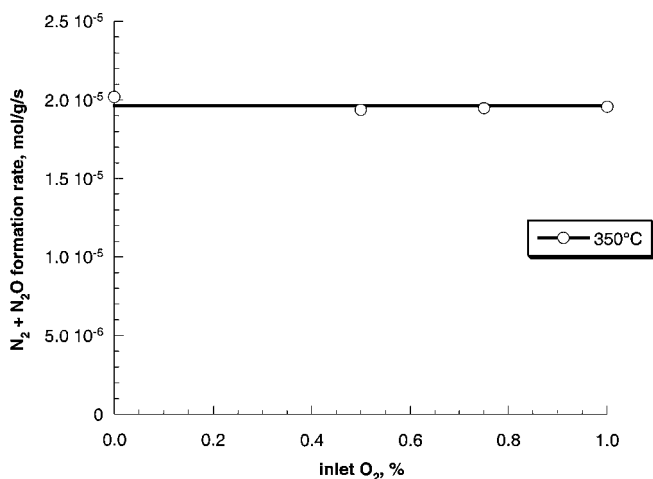


FIG. 3. Variation of N₂ + N₂O formation rate with inlet O₂ concentration. Inlet NO₂ = NH₃ = 500 ppm; GHSV = 1,740,000 h⁻¹.

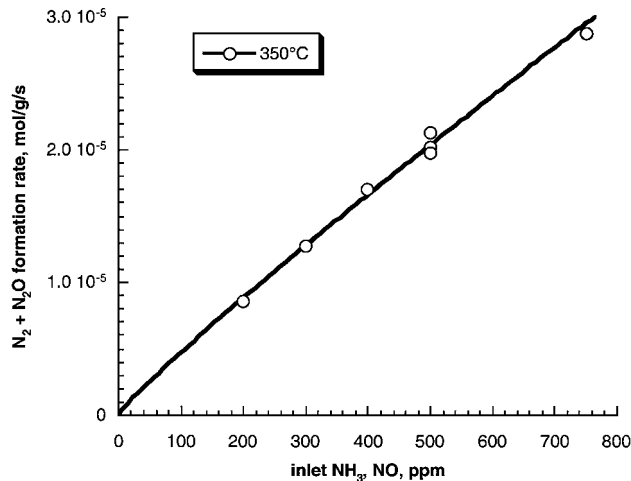


FIG. 4. Variation of N₂ + N₂O formation rate when inlet NO₂ and NH₃ are varied together. Inlet O₂ = 1%; GHSV = 1,740,000 h⁻¹.

this apparent change in order; possibilities include competitive adsorption, inaccuracies in the conversion adjustments, mass transfer limitations, or oversimplification of the rate expression.

DISCUSSION

In our previous work on the selective catalytic reduction of NO by NH₃ (2), we suggested that the rate-determining step was the oxidation of NO to NO₂. This conclusion was based on several observations. First, the rate of reduction of NO was first order in NO and O₂ but was negative order in ammonia, suggesting that ammonia did not participate in the reaction until after the rate-determining step. Second, the gas exiting the reactor contained little NO₂, even though the catalyst was shown to convert NO and O₂ to a near-equilibrium mixture of NO and NO₂ under the same conditions but in the absence of ammonia. Third, the kinetics of NO oxidation to NO₂ in the absence of NH₃ were observed to be similar to the kinetics of the SCR reaction, i.e., first order in NO and positive order in O₂. And finally, the forward rate constant calculated for NO oxidation agreed well with the rate constant calculated for the SCR reaction.

We believe the data presented in this paper on the reduction of NO₂ by NH₃ support our conclusion that NO oxidation to NO₂ is the rate-determining step for the selective catalytic reduction of NO to N₂. We observe that the rate of reduction of NO₂ is roughly 500 times faster than the rate of reduction of NO or the rate of oxidation of NO to NO₂. This implies that once NO₂ is formed under normal SCR conditions it will be rapidly converted to N₂.

A second important difference between the reduction of NO and NO₂ can be seen in the kinetics. The rate of NO reduction was observed to be first order in NO but was strongly inhibited by ammonia, suggesting that ammonia blocked the active site by adsorption and did not participate in any step up to and including the rate-determining step.

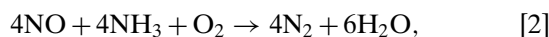
TABLE 2
Stoichiometry of NO₂ Reduction

T (°C)	Conditions	Observed stoichiometry	Ratio NH ₃ /NO _x converted
300	500 NO ₂ + 500 NH ₃ + 1% O ₂	1.55 NO _x + 2.21 NH ₃ = 1.0 N ₂ + 0.88 N ₂ O	1.42
350	500 NO ₂ + 500 NH ₃ + 1% O ₂	1.45 NO _x + 1.97 NH ₃ = 1.0 N ₂ + 0.71 N ₂ O	1.36
350	500 NO ₂ + 500 NH ₃ + 0% O ₂	1.49 NO _x + 1.89 NH ₃ = 1.0 N ₂ + 0.69 N ₂ O	1.26
350	500 NO ₂ + 200 NH ₃ + 1% O ₂	1.55 NO _x + 2.14 NH ₃ = 1.0 N ₂ + 0.84 N ₂ O	1.38
350	200 NO ₂ + 500 NH ₃ + 1% O ₂	1.04 NO _x + 2.09 NH ₃ = 1.0 N ₂ + 0.58 N ₂ O	2.02
400	500 NO ₂ + 500 NH ₃ + 1% O ₂	1.28 NO _x + 1.86 NH ₃ = 1.0 N ₂ + 0.57 N ₂ O	1.45

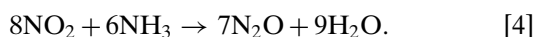
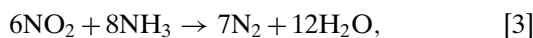
Note. GHSV = 1,740,000 h⁻¹.

In contrast, however, NO₂ reduction is positive order in ammonia. In fact, at 350°C the rate of N₂ and N₂O formation is 0.8 order in ammonia, suggesting that the activation of ammonia plays an important role in the reaction during or before the rate-determining step. Likewise, the effect of oxygen on the two reactions also suggests differences in the mechanism; while the reduction of NO is nearly first order in oxygen concentration, the rate of reduction of NO₂ is unaffected by the amount of oxygen present. It appears that the primary role of oxygen in SCR is to oxidize NO; in the case of NO₂ this function is no longer needed. The fact that feeding NO₂ instead of NO changes the reaction kinetics suggests that it also changes the rate-determining step by removing the primary barrier to NO reduction. We would propose that the rate-determining step for NO reduction is the oxidation of NO, while for the reduction of NO₂ the rate-determining step involves the combination of adsorbed NH₃ and NO₂ species in some form.

While there is general agreement that the selective catalytic reduction of NO occurs with a one-to-one NO/NH₃ stoichiometry, i.e.,



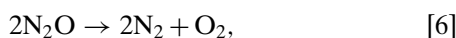
the appropriate stoichiometry for the reduction of NO₂ is not clear. If O₂ is neither consumed nor formed, there are two independent forms (and an infinite number of linear combinations) for the reduction of NO₂ by NH₃:



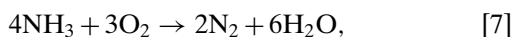
If combined to give a 1 : 1 ratio of ammonia and NO₂ consumption, a 1 : 1 ratio of N₂ and N₂O is also obtained:



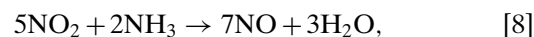
If O₂ can be activated, then other possibilities must be considered, including the decomposition of nitrous oxide,



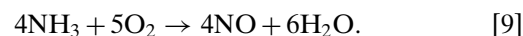
the oxidation of ammonia to N₂ by O₂,



or the oxidation of ammonia to NO by NO₂,



or by O₂,



Of course linear combinations of Eqs. [6]–[9] with reactions [3] and [4] are also possible.

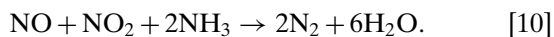
Table 2 shows the average stoichiometries we observed under several conditions. From these stoichiometries, it seems probable that more than one reaction pathway is involved. The ratio of N₂O to N₂ formed falls from 0.88 at 300°C to 0.57 at 400°C. Because the N₂/N₂O ratio is not greatly affected by space velocity, declining only 6–8% as the space velocity was doubled from 870,000 or 1,740,000 h⁻¹, we do not believe that the decomposition of N₂O, Eq. [6], plays a significant role in this process; instead, it appears that the N₂/N₂O ratio is determined primarily by the kinetics of NO₂ reduction. The observed decrease in this ratio as the inlet NH₃/NO₂ ratio decreases is consistent with the stoichiometries of Eqs. [3] and [4]. The fact that the N₂/N₂O ratio is unaffected by the presence or absence of molecular oxygen is in agreement with the conclusion that O₂ plays no direct role in the reaction of NH₃ and NO₂.

When equal amounts NO₂ and NH₃ are fed, approximately 1.4 mol of ammonia are consumed for every 1 mol of NO₂ consumed. Hirsch (3) observed that the conversion of NO₂ over H-mordenite was highest with an inlet ratio of NH₃/NO₂ of approximately 1.3. As might be expected, the ratio of NH₃/NO₂ consumed that we observed increases as the inlet NH₃/NO₂ ratio increases. The amount of ammonia consumed is too large to be accounted for by Eqs. [3] and [4] and suggests that ammonia oxidation is taking place. In our earlier work (2), we determined the rate of ammonia oxidation occurring during the reduction of NO over the same catalyst; this rate is much too slow to account for the excess ammonia consumed during the reduction of NO₂. This would seem to suggest, therefore, that NO₂ initiates this oxidation, although the stoichiometry indicates that even if this is so, then molecular oxygen must be involved in some role, perhaps to remove hydrogen from the catalyst surface or to activate NO₂ toward ammonia oxidation. It is noteworthy

that the ratio of NH₃/NO₂ converted falls when no oxygen is fed. It is also interesting that this was the only feed condition where steady state was not reached quickly, suggesting perhaps that under these conditions the reaction was slowly removing small amounts of oxygen from the catalyst.

While the reduction of NO₂ is nearly zero order in ammonia at 300°C, suggesting that ammonia coverage on the active site is high, it is not far from first order at 350°C, suggesting that at this temperature ammonia coverage on the active site is fairly low. This contrasts sharply with the temperature dependence of ammonia inhibition on the reduction of NO, where it was inferred that ammonia coverage on the active site was high even at 450°C. This may imply that the active site is different for the reduction of NO₂ than for the reduction of NO. Although the kinetic data presented above are not sufficient to extract accurate adsorption constants, estimates made from the ammonia reaction order data, assuming that the rate is proportional to a simple Langmuir–Hinshelwood term for adsorbed ammonia, suggest that the ammonia coverage is roughly 90% at 300°C and 30% at 350°C; this is much lower than the 85% coverage estimated for the active site for NO reduction at 350°C (2). For comparison, calorimetric data (9) suggest that the ammonia coverages on the framework Brønsted sites in the presence of 500 ppm ammonia would be 97 and 68% at 300 and 350°C, respectively. This suggests the possibility that the active site for NO₂ reduction is the framework Brønsted acid site. However, in the absence of spectroscopic evidence or a fully developed kinetic model, such a suggestion is only speculation. In contrast, our earlier work (2) indicated that the active site for the reduction of NO is highly acidic extra-framework alumina.

As discussed above, we see a small net increase (1–3 ppm) in the NO concentration across the reactor at 300°C and a small net decrease (1–5) at 350°C. From our data on the rate of NO oxidation and the known equilibrium constant for NO oxidation, we have further estimated that under these conditions approximately 3 ppm NO₂ should be catalytically converted into NO; the extent of this reaction is limited by the very high space velocity used. Given the low conversion of NO₂ to NO expected, we cannot support the hypothesis of Andersson *et al.* (4) that this reaction is rate determining for NO₂ reduction. Under our conditions, it is clear that some NO is reduced to N₂ or N₂O at 350°C, and possibly also at 300°C. Hirsch (3) observed that in the presence of excess NH₃ mixtures of NO and NO₂ are converted with a 1 : 1 stoichiometry of NO₂/NO. Likewise, it has been reported (4, 5) that the reduction of NO_x over H–mordenite was faster when the NO₂/NO ratio was approximately 1 : 1 than it was when either NO or NO₂ was fed alone, leading to the suggestion that NO and NO₂ combined with ammonia to give N₂:



Experiments with labeled NO₂ and NH₃ provide support for this hypothesis (10). This reaction is probably occurring under our conditions, but the amount of NO involved is so small that it makes little difference to the overall rate or kinetics of the process.

SUMMARY

The reduction of NO₂ by NH₃ over HZSM-5 is two to three orders of magnitude faster than the reduction of NO by NH₃ under the same conditions. The reduction of NO₂ is so fast that high conversions are obtained even at gas hourly space velocities of 800,000 h⁻¹ and greater and that mass transfer may limit the observed rate. The reaction order in NO₂ is 0.68 and 0.93 at 300 and 350°C, respectively; the reaction order in NH₃ is 0.13 and 0.82 at 300 and 350°C, respectively. The reaction is zeroth order in oxygen. Large amounts of N₂O are formed under all conditions studied; the N₂O/N₂ ratio decreases from approximately 0.9 at 300°C to 0.55 at 400°C. The stoichiometry of NO₂ reduction is complicated and suggests that multiple reaction pathways are present. Approximately 1.4 mol of ammonia is converted for every 1 mol of NO₂ converted. Part of this higher conversion of ammonia is most likely due to the stoichiometry of NO₂ reduction, while some appears to be due to ammonia oxidation, possibly initiated by NO₂. The large increase in rate coupled with the change in kinetics strongly supports our earlier suggestion that the rate-determining step in the reduction of NO by ammonia is the oxidation of NO. We believe that the rate-determining step in NO₂ reduction involves the combination of adsorbed NH₃ and NO₂ species, possibly on a framework Brønsted alumina site.

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REFERENCES

1. Bosch, H., and Janssen, F., *Catal. Today*, **2**, 1 (1987).
2. Stevenson, S. A., Vartuli, J. C., and Brooks, C. F., *J. Catal.* **190**, 228 (2000), doi:10.1006/jcat.1999.2747.
3. Hirsch, P. M., *Environ. Prog.* **1**, 24 (1982).
4. Andersson, L. A. H., Brandin, J. G. M., and Odenbrand, C. U. I., *Catal. Today* **4**, 173 (1989).
5. Brandin, J. G. M., Andersson, L. A. H., and Odenbrand, C. U. I., *Catal. Today* **4**, 187 (1989).
6. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis," Krieger, Malabar, FL, 1981.
7. Mears, D. E., *Ind. Eng. Chem. Process Des. Dev.* **10**, 541 (1971).
8. Levenspiel, O., "Chemical Reaction Engineering." Wiley, New York, 1972.
9. Sharma, S. B., Meyers, B. L., Chen, D. T., Miller, J., and Dumesic, J. A., *Appl. Catal. A* **102**, 253 (1993).
10. Eng, J., and Bartholomew, C. H., *J. Catal.* **171**, 27 (1997).