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Selective Catalytic Reduction of Nitric Oxide with Ammonia on MFI-Type Ferrisilicate

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The catalytic properties of framework Fe^{3+} in MFI-type H-ferrisilicate for the selective reduction of nitric oxide with ammonia in the presence of oxygen have been investigated and compared with those of Fe-exchanged ZSM-5, iron oxide supported on silicalite and HZSM-5. H-ferrisilicate exhibited a high activity and selectivity for the reduction of nitric oxide into nitrogen. A side reaction, *i.e.* the oxidation of ammonia with oxygen into nitrogen, occurred only above 773 K. The activity and selectivity of Fe-exchanged ZSM-5 for the reduction of nitric oxide were comparable to those of H-ferrisilicate, while iron oxide supported on silicalite catalysed the oxidation of ammonia with oxygen into nitric oxide preferentially under the same reaction conditions. The catalytic activity of HZSM-5 for this reaction was much lower than that of H-ferrisilicate. Therefore, the framework Fe^{3+} ions in H-ferrisilicate are the active sites for the selective catalytic reduction of nitric oxide.

An isomorphous substitution of transition-metal ions for aluminium in the zeolite framework provides crystalline metallosilicates. In these metallosilicates, all metal cations occupy tetrahedral coordination sites similar to aluminium cations in zeolites. Therefore, they are isolated by SiO_4 tetrahedra, that is no metal–oxygen–metal bonds are present. On the other hand, in pure transition-metal oxides the metal cations are connected to each other by oxygen anions. As the metal cations in metallosilicates are present in chemical states different from those in pure metal oxide, it is expected that the metal cations of metallosilicates occupying tetrahedral framework sites will show unique catalytic properties.

Recently, we have reported the catalytic properties of framework Fe^{3+} ions in MFI-type ferrisilicate for the oxidation of carbon monoxide[1,2] and oxidative dehydrogenation of alkanes[3,4] in comparison with those of iron oxide supported on MFI-type silicalite and Fe^{3+}-exchanged ZSM-5. The Fe^{3+} ions in ferrisilicate exhibited very low activity for the CO oxidation[1] and the total oxidation of butane into carbon oxides but showed a higher selectivity than the other two catalysts for the oxidative dehydrogenation of butane into butenes[3] and that of propane into propene.[4] It was demonstrated by Mössbauer spectroscopy that the Fe ions in ferrisilicate are tetrahedrally coordinated Fe^{3+} and that those in iron oxide supported on silicalite are octahedrally coordinated Fe^{3+} in the form of small particles of α-Fe_2O_3; we could not determine the chemical states of Fe ions in Fe-exchanged ZSM-5 by Mössbauer spectroscopy owing to the low iron content of the sample.[1] Thus, we have revealed that the isolated and tetrahedrally coordinated Fe^{3+} in ferrisilicate has unique catalytic properties in the oxidation reactions. This prompted us to investigate the catalytic properties of ferrisilicate for the reduction of nitric oxide.

The selective catalytic reduction (SCR) of nitric oxide with ammonia in the presence of oxygen is an effective technique for removing NO from the effluent of chemical plants and stationary combustion sources. The catalytic reduction of NO with NH_3 has been studied extensively over various metals and metal oxides catalysts. Among them, vanadium-based catalysts have proven to be effective in selectively reducing NO with NH_3.[5–9] Iron oxides also exhibit significant activity for NO reduction with NH_3, though they are not as selective as vanadium oxide.[10–12] Recently, Fe-exchanged Y zeolite has been studied for the reduction of NO with NH_3 or CO.[13–15]

In the present work, we studied the catalytic properties of framework Fe^{3+} ions in MFI-type ferrisilicate for the selective reduction of NO with NH_3. A comparison of the activity and selectivity of ferrisilicate for this reaction with those of Fe^{3+}-exchanged ZSM-5, iron oxide supported on silicalite, and HZSM-5 has been made to clarify the relation between the chemical state of Fe^{3+} and its catalytic properties. The activity for a side reaction, *i.e.* oxidation of NH_3 with oxygen and the effect of acid sites, were investigated.

Experimental

MFI-type ferrisilicates with Si : Fe atomic ratios of 44, 77 and 88 were prepared by hydrothermal crystallization of a basic reaction mixture using a method similar to that described previously.[3] The calcined form of ferrisilicates were converted into hydrogen form (H-ferrisilicate) by a conventional ion-exchange technique using an aqueous solution of NH_4NO_3 followed by calcination in air at 773 K. Preparation of MFI-type aluminosilicate (ZSM-5) with an Si : Al ratio of 29 was carried out according to the procedure described in Mobil's patent.[16] The hydrogen form of ZSM-5 (HZSM-5) was prepared in a similar manner to H-ferrisilicate. Fe-exchanged ZSM-5 (FeZSM-5) was obtained by an ion-exchange method using an aqueous solution of $FeCl_3$ and HZSM-5 followed by washing and calcination. Silicalite with an MFI structure was prepared by hydrothermal crystallization.[17] Iron oxide was supported on silicalite (FeO_x/Sil) by a conventional impregnation method using an aqueous solution of $Fe(NO_3)_3$ and silicalite followed by calcination at 773 K in air. Elemental analyses were carried out by atomic absorption spectrophotometry. The amount of iron oxide supported on silicalite corresponded to an Si : Fe atomic ratio of 50. For FeZSM-5, the percentage degree of ion-exchange as Fe^{3+} was 27%, which corresponds to an Si : Fe atomic ratio of 315.

The catalytic reduction of NO with NH_3 was carried out under atmospheric pressure in a fixed-bed flow-type reactor of 17 mm i.d. Feed-gas mixture was prepared by mixing three certified gases; 10.0% NO in helium, 9.65% NH_3 in helium, and pure O_2. Helium was added when necessary to further dilute the reaction gas mixture. In a typical reaction run, the catalyst was dehydrated in flowing helium by increasing the temperature slowly from room temperature to 773 K and maintaining it for 2 h. The temperature was then adjusted to the reaction temperature and the reaction was started by the introduction of feed gas containing NO, NH_3 and O_2 diluted with helium. The oxidation of NH_3 was carried out similarly using a mixture of NH_3, O_2 and helium. The reactor effluent gas was analysed by a gas chromatograph (Tylan M-200) with molecular sieve 5A and Plot Q columns for the separation of N_2, N_2O and O_2. NO and NO_2 were analysed by an NO_x analyser (Yanaco ECL-77A) with a chemiluminescent detector. Unreacted ammonia in the effluent gas was periodically trapped by passing through a 2×10^{-5} mol l^{-1} hydrochloric acid solution. The amount of unreacted ammonia was determined by colorimetry using Nessler's reagent.

Results and Discussion

Reduction of NO with NH_3 on Various Iron Catalysts

The catalytic activities and selectivities of H-ferrisilicate (Si : Fe = 44), FeZSM-5 (Si : Fe = 315), HZSM-5 (Si : Al = 29) and FeO_x/Sil (Si : Fe = 50) for the reduction of NO with NH_3 in the presence of O_2 were examined in the temperature range 473–923 K. The feed gas consisted of 0.1% NO, 0.1% NH_3 and 2.0% O_2 diluted in He with a total flow rate of 500 ml min^{-1} (STP). The weights of the catalysts were 0.1, 0.7, 0.7 and 0.1 g for ferrisilicate, FeZSM-5, HZSM-5 and FeO_x/Sil, respectively. The amounts of the iron-containing catalysts were adjusted to obtain the same amount of iron in all cases, though the different W/F may influence the reactions slightly. The reaction products containing N-atoms were mainly N_2 and a negligible amount of N_2O. The reaction was allowed to stabilize for 0.5 h on stream before the first sample was analysed. No significant deactivation of the catalyst with time on stream was observed for all the catalyst. The results obtained after 1 h on stream at a particular temperature are compared hereafter.

Fig. 1 shows the percentage conversions of NO and NH_3 and the percentage yield of N_2 as a function of the reaction temperature for H-ferrisilicate (a), FeZSM-5 (b) and HZSM-5 (c), respectively. The NO conversion increased with temperature and reached maxima at 873 and 823 K on ferrisilicate and FeZSM-5, respectively, then decreased at higher temperatures. On HZSM-5, the NO conversion kept increasing up to the highest temperature studied (923 K). For H-ferrisilicate, [Fig. 1(a)], at temperatures lower than 773 K, the ratio of NO conversion, NH_3 conversion and N_2 yield was 1 : 1 : 1. It has been suggested[18] that for vanadium oxide catalysts the selective reduction of NO with NH_3 in the presence of O_2 proceeds according to the following reaction stoichiometry:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

The above results indicate that the reduction of NO occurred selectively according to the stoichiometry in eqn. (1). However, at higher temperatures, NH_3 conversion was higher than NO conversion with the N_2 yield in between the two. A similar tendency was observed in the case of FeZSM-5 [Fig. 1(b)] and HZSM-5 [Fig. 1(c)] at higher temperatures. During NO reduction with NH_3 in the presence of O_2 a portion of NH_3 may be oxidized with O_2 according to either or both of the following reaction stoichiometries:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (2)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (3)$$

The differences in NO conversion, NH_3 conversion and N_2 yield at the high temperatures are probably due to the oxidation of NH_3 by O_2 into N_2 [eqn. (2)] occurring simultaneously with the NO reduction [eqn. (1)]. At low temperatures, where the reaction occurred selectively, the activities of H-ferrisilicate and FeZSM-5 for NO reduction were almost the same, while at higher temperatures, FeZSM-5 exhibited a higher activity than H-ferrisilicate. This higher activity of FeZSM-5 could be partially due to an additional contribution of the activity of acidic protons remaining unexchanged with Fe^{3+}. HZSM-5 [Fig. 1(c)], which contained no iron, showed significantly lower activity than either H-ferrisilicate or FeZSM-5. It has been reported that HZSM-5 and H-mordenite are active in the selective reduction of NO with NH_3, and that in these zeolites, acid sites are the active sites.[19–22] In spite of the larger amount of HZSM-5 (0.7 g) used, H-ferrisilicate (0.1 g) was much more active than HZSM-5, which indicates that the framework Fe^{3+} ions in ferrisilicate possess higher activity for NO reduction than the acid sites of HZSM-5. FeZSM-5 also showed markedly higher activity than the parent HZSM-5, which indicates that the Fe^{3+} ions in FeZSM-5 are also much more active than the acid sites of HZSM-5.

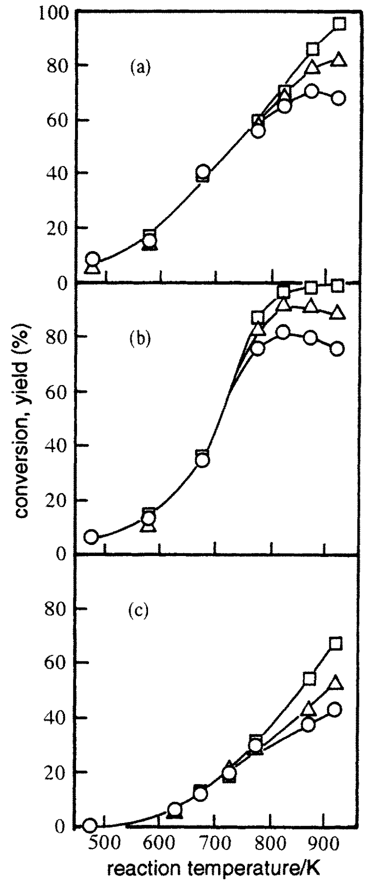

Fig. 1 Reduction of NO with NH_3 in the presence of O_2 on H-ferrisilicate (a), FeZSM-5 (b) and HZSM-5 (c). Change in NO conversion (○), NH_3 conversion (□) and N_2 yield (△) with reaction temperature. Reactant containing NO (0.1%), NH_3 (0.1%), O_2 (2.0%) and He (balance) was fed at a flow rate of 500 ml min^{-1}.

Fig. 2 shows the results of the reaction of NO with NH_3 over FeO_x/Sil. Below 673 K, NO conversion and NH_3 conversion increased slightly with temperature and small amounts of N_2 were produced. When the temperature rose above 673 K, NH_3 conversion increased greatly, N_2 yield remained low and NO conversion declined to apparently 'negative' conversions, *i.e.* the concentration of NO in the effluent exceeded that in the reactant. This may be due to the oxidation of NH_3 by O_2 to form NO [eqn. (3)] occurring preferentially to the reduction of NO.

In previous studies, we have reported that the activity of ferrisilicate for CO oxidation[1] is much lower than that of

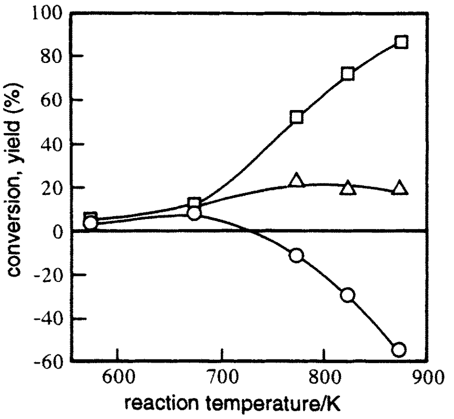

Fig. 2 Reduction of NO with NH_3 in the presence of O_2 on FeO_x/Sil. Change in NO conversion (○), NH_3 conversion (□) and N_2 yield (△) with reaction temperature. Reactant was the same as for Fig. 1.

FeO_x/Sil or FeZSM-5 and that in the oxidative dehydrogenation of butane,[3] ferrisilicate catalyses the dehydrogenation of butane into butenes more selectively than does FeO_x/Sil or FeZSM-5, which mainly catalyse the total oxidation into CO_2. Therefore, it has been concluded that the catalytic activity and selectivity of ferrisilicate for the oxidation reactions are different from those of FeO_x/Sil and FeZSM-5. We have also revealed the difference in the iron species by Mössbauer spectroscopy.[1] The iron species in ferrisilicate was almost exclusively Fe^{3+} with a tetrahedral coordination, indicating that Fe^{3+} was in the framework of ferrisilicate, while that in FeO_x/Sil consisted of small particles of α-Fe_2O_3 having octahedral coordination. In the present study on the NO reduction with NH_3, however, the activity and selectivity of H-ferrisilicate are quite similar to those of FeZSM-5 but totally different from those of FeO_x/Sil. On FeO_x/Sil, the oxidation of NH_3 proceeded preferentially to the NO reduction.

Oxidation of NH_3 with O_2

In order to evaluate the contribution of side reactions to the above results of the NO reduction experiment, the oxidation of NH_3 with O_2 was carried out under the same reaction conditions as for the SCR reaction, but without the addition of NO to the feed gas. Fig. 3 shows the change in yields of NO and N_2 for NH_3 oxidation against reaction temperature on H-ferrisilicate (a), FeZSM-5 (b) and FeO_x/Sil (c). In all cases, the N-containing products were N_2 and NO. Below 673 K the yields of both NO and N_2 were very low on all the catalysts. However, above this temperature, on H-ferrisilicate and FeZSM-5 the yield of N_2 increased with the temperature rise, while the yield of NO remained remarkably low. Therefore, it is clear that on H-ferricilicate and FeZSM-5, oxidation of NH_3 with O_2 producing N_2 [eqn. (2)] occurs significantly at high temperatures. This reaction should occur during the reduction of NO with NH_3, which leads to a higher conversion of NH_3 than that of NO shown in Fig. 1. It can also be seen from Fig. 3 that the activity of FeZSM-5 for the oxidation of NH_3 is higher than that of H-ferrisilicate. In the case of the oxidation of CO, we have reported[1] that FeZSM-5 is also more active than H-ferrisilicate. However, the difference in the oxidation activities of these catalysts were much higher for CO oxidation.

On the other hand, the results for FeO_x/Sil differed greatly from those of the above two catalysts. The yield of NO was higher than that of N_2 and both increased with increasing temperature. These results suggest that on FeO_x/Sil, two different oxidation reactions of NH_3 [eqn. (2) and (3)] proceeded simultaneously to produce N_2 and NO. It should be noted that the oxidation of NH_3 into NO is predominant over that into N_2. In the case of the reaction of NO (Fig. 2), the oxidation of NH_3 into NO could be predominant also over the reduction of NO into N_2. As a result, the 'negative' NO conversion and low N_2 yield were observed over FeO_x/Sil. It is concluded that the catalytic activity and selectivity of H-ferrisilicate are comparable to those of FeZSM-5 but totally different from those of FeO_x/Sil for both the reduction of NO with NH_3 and the oxidation of NH_3. This is in contrast to the oxidation of CO and the oxidative dehydrogenation of alkanes, where FeZSM-5 and FeO_x/Sil are much more active for the formation of CO_2 than H-ferrisilicate.

Active Sites in H-Ferrisilicate

Results of Fig. 1(a) and (c) indicate that the activity of the framework iron in H-ferrisilicate for the reduction of NO with NH_3 is much higher than those of the acid sites of HZSM-5. In order to ascertain the role of the framework iron as an active site, the SCR reaction was carried out using H-ferrisilicates with varying Si : Fe atomic ratio. Fig. 4 shows the N_2 yields measured in the SCR reaction on ferrisilicate having Si : Fe atomic ratio of 44, 77 and 88 as a function of the reaction temperature. In all cases, the reduction of NO

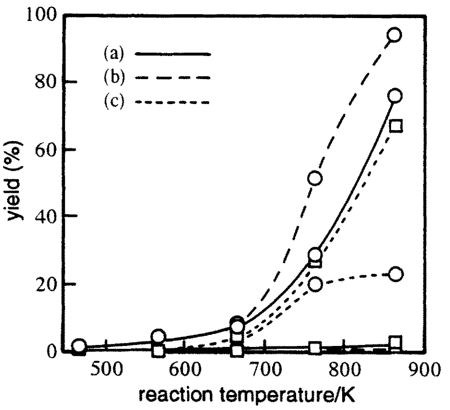

Fig. 3 Oxidation of NH_3 with O_2 on H-ferrisilicate (a), FeZSM-5 (b) and HZSM-5 (c). Change in the yields of N_2 (○) and NO (□) with reaction temperature. Reactant containing NH_3 (0.1%), O_2 (2.0%) and He (balance) was fed at a total flowrate of 500 ml min^{-1}.

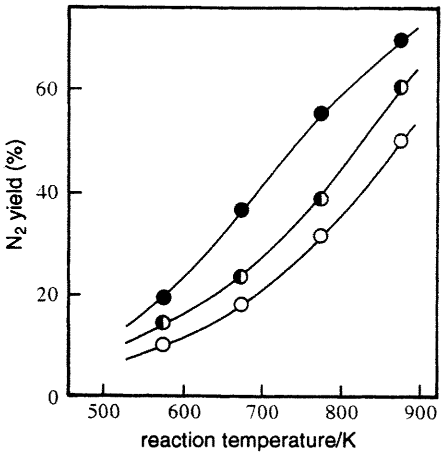

Fig. 4 Change in N_2 yield for NO reduction on H-ferrisilicate having Si : Fe ratios of 44 (●), 77 (◐) and 88 (○). Reactant was the same as for Fig. 1.

with NH_3 proceeded almost selectively to form N_2 and the yield of N_2 increased at higher temperatures. It is clear that the higher the iron content, the higher the N_2 yield. When silicalite, which contains no iron, was used as a catalyst under the same reaction conditions N_2 yield was less than 10% at 873 K. These results confirmed that the framework Fe ions in ferrisilicate are the active sites for the reduction of NO with NH_3.

The role of Brønsted acid sites was also studied because proton-exchanged zeolites by themselves are reported to be active for the SCR of NO.[19–22] The H-ferrisilicate having an Si : Fe ratio of 44 was exchanged with Na^+ ions to obtain ferrisilicates with various proton-exchange levels. Using these ferrisilicates as catalysts, the SCR of NO with NH_3 was carried out at 773 K, where NO reacted with NH_3 and O_2 almost selectively to form N_2 [Fig. 1(a)]. Fig. 5 shows the change in N_2 yields against proton-exchange levels. Na^+-exchanged ferrisilicates also catalysed the NO reduction into N_2 selectively at this temperature. The exchange with Na^+ did not make any difference in N_2 yield when about half of the H^+ was exchanged. Further exchange below 20% proton-exchange level lowered the N_2 yield only slightly. Generally, the number of Brønsted acid sites in ferrisilicate declines with the decrease in proton-exchange level. Therefore, it is evident that the acid sites of H-ferrisilicate have a very minor effect on the SCR of NO with NH_3, which also indicates that the main active sites of ferrisilicate for NO reduction are the Fe^{3+} ions.

Effect of Oxygen

It has been reported that the reduction of NO with NH_3 on H-mordenite and HZSM-5 does not take place in the absence of oxygen.[9,10] In the case of the SCR of NO on CuZSM-5,[23] the rate of N_2 formation was about half order with respect to the concentration of O_2. In order to determine the effect of oxygen, we have carried out the SCR of NO using different oxygen concentrations. Fig. 6 shows the change in NO conversion on H-ferrisilicate and FeZSM-5 measured at 623 K. It can be seen that in the absence of oxygen, little reduction occurred on both catalysts. This result indicates that the reduction of NO with NH_3 on H-ferrisilicate and FeZSM-5 occurs only in the presence of oxygen. This is expected from the reaction stoichiometry expressed by eqn. (1). As the concentration of O_2 rose, the NO conversion increased monotonously. This suggests that the rate-determining step of the SCR of NO involves oxygen as a reactant.

From a survey of the literature, it is known that supported iron oxides are active in the reduction of NO with NH_3.[10–12] As shown above, in the presence of oxygen, iron oxide impregnated on silicalite (FeO_x/Sil) displayed very little activity for NO reduction at lower temperatures and no activity at higher temperatures (Fig. 2). In order to understand the role of O_2 for FeO_x/Sil, the reduction of NO was carried out in the absence of O_2 with 0.1% NO and 0.1% NH_3 in He (total flow rate: 500 ml min^{-1}) in the temperature range 473–873 K. Fig. 7 shows the change in NO conversion, NH_3 conversion and N_2 yield against the reaction temperature on FeO_x/Sil. The conversions of NO and NH_3, as well as the yield of N_2, increased with increasing temperature. These results indicate that the reduction of NO with NH_3 occurred on FeO_x/Sil in the absence of O_2. The reduction activity was slightly low compared with H-ferrisilicate and FeZSM-5 in the presence of O_2 [Fig. 1(a) and (b)]. Little activity of H-ferrisilicate and FeZSM-5 obtained in the absence of O_2 indicates the absence of oxide-like iron species in both catalysts. The ratio of NO-conversion : NH_3-conversion : N_2-yield was *ca.* 6 : 4 : 5, giving a stoichiometric reduction as follows:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad (4)$$

However, in the presence of O_2 the oxidation of ammonia occurred predominantly (Fig. 2). This unique catalysis of FeO_x/Sil may result from the high reactivity of the lattice oxygen (O^{2-}) of supported Fe_2O_3 particles. We have revealed[2] that the CO oxidation on FeO_x/Sil proceeds *via* a redox mechanism, where the lattice oxygen attacks CO molecules to form CO_2. On the other hand, the lattice oxygen in

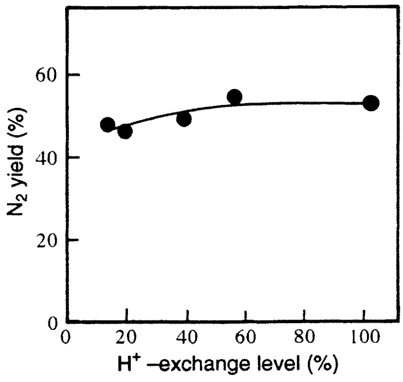

Fig. 5 Effect of Brønsted acid site in HNa-ferrisilicate for SCR at 773 K. Reactant was the same as for Fig. 1.

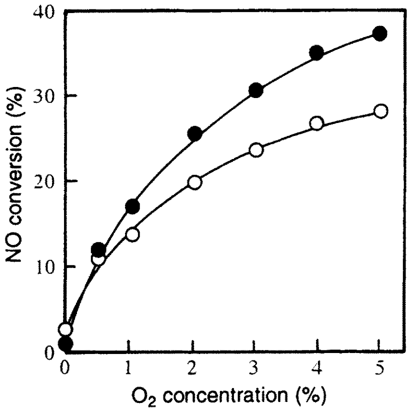

Fig. 6 Effect of O_2 concentration on NO conversion in SCR on H-ferrisilicate (●) and FeZSM-5 (○) at 623 K. Reactant containing NO (0.1%). NH_3 (0.1%), O_2 (0–5.0%) and He (balance) was fed at a total flow rate of 500 ml min^{-1}.

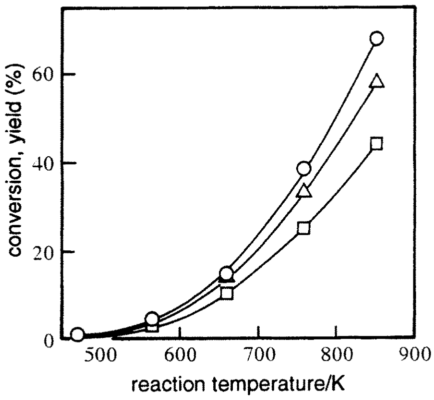

Fig. 7 Reduction of NO with NH_3 in the absence of O_2 on FeO_x/Sil. Change in NO conversion (○), NH_3 conversion (□) and N_2 yield (△) with reaction temperature. Reactant containing NO (0.1%), NH_3 (0.1%) and He (balance) was fed at a total flow rate of 500 ml min^{-1}.

H-ferrisilicate does not react with CO. From this study, it is also understood that the lattice O^{2-} in FeO_x/Sil is more reactive for the NH_3 oxidation than for the reduction of NO with ammonia in the presence of oxygen.

Conclusion

H-ferrisilicate is active for the selective reduction of NO with NH_3 in the presence of oxygen. At higher temperatures (>773 K), however, the oxidation of NH_3 with O_2 into N_2 occurs simultaneously, which lowers the selectivity for NO reduction. The activity and selectivity of H-ferrisilicate for the NO reduction is comparable to those of Fe-exchanged ZSM-5 and much higher than those of HZSM-5, while iron oxide supported on silicalite catalyses the oxidation of NH_3 into NO preferentially. Therefore, isolated Fe^{3+} ions, which are contained in both ferrisilicate and Fe-exchanged ZSM-5, are the active sites for the SCR reaction.

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