

Synergistic Effect in Lean NO_x Reduction by CH₄ over Co/Al₂O₃ and H-Zeolite Catalysts

J.-Y. Yan, H. H. Kung, W. M. H. Sachtler, and M. C. Kung¹

V. N. Ipatieff Laboratory, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60208

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In the reduction of NO by CH₄ in the presence of a large excess of oxygen, the conversion to N₂ over a physical mixture of Co/Al₂O₃ and H-zeolite catalysts was found to be twice as high as that expected if these components acted independently. This synergistic effect was observed with both H-ZSM-5 and H-USY. By comparing the activities of these catalysts for NO oxidation and CH₄ reduction of NO₂, it was concluded that the synergistic effect could be explained by the participation of Co ions and proton sites in the reaction. NO is oxidized to NO₂ over the Co ions, and NO₂ is reduced by CH₄ to N₂ over the proton sites. © 1998 Academic Press

1. INTRODUCTION

Selective catalytic reduction (SCR) of NO_x to N₂ is an important industrial process to remove pollutants from exhaust fumes. For stationary sources of NO_x, the commercial SCR process uses NH₃ as a reductant over catalysts based on vanadium oxide. There are problems associated with the NH₃ SCR process, which include ammonia slip, equipment corrosion, as well as danger in transportation and storage of ammonia. An attractive alternative, pioneered by the work of Li and Armor, is to use CH₄ as a reductant (1). Numerous ensuing studies have shown that Co based catalysts, such as Co/ZSM-5, (2, 3) are among the most active for the reduction of NO_x by CH₄. However, substantial improvement is still needed for this process to be economically competitive with the NH₃ SCR process, and a better understanding of the reaction may facilitate this improvement.

Although Co/Al₂O₃ is a good SCR catalyst when C₃H₆ or C₃H₈ is used (4), its performance is poor with CH₄ as the reductant (1). In a previous study (4), it was proposed that the similar structural and chemical properties of the Co cations in Co/ZSM-5 and Co/Al₂O₃ catalysts are responsible for their comparable catalytic performances in the selective reduction of NO_x by C₃H₆ and C₃H₈. Since the I.E.P. (isoelectric point) of the Al₂O₃ support is 8 (5), and the acidity of Al₂O₃ is primarily Lewis in nature (6), a possible reason for the poor performance of the Co/Al₂O₃ catalyst in the CH₄

SCR process is the lack of Brønsted acidity. Brønsted acidity has been shown to be important in the CH₄ SCR of NO over Ga/ZSM-5, In/ZSM-5, and Pd/ZSM-5 catalysts (7–10). Loughran *et al.* (11) have shown that CH₄ SCR of NO can be promoted by Brønsted acid sites located on nonzeolitic material such as sulfated ZrO₂. Over the Pd/ZSM-5 catalyst, Nishizaka and Misono (9, 10) have proposed that the proton site is important in the reduction of NO₂ by CH₄, whereas over the Ga/ZSM-5 and In/ZSM-5 catalysts, oxidation of NO to NO₂ was proposed to occur over a H⁺ site with its subsequent reduction over the metal site (8). Thus, the objective of this study is to elucidate the functions of the metal cation and Brønsted acidity in the CH₄ SCR of NO, using a combination of Co/Al₂O₃ and H-zeolite.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Al₂O₃ was prepared as described previously (4). H-ZSM-5 was prepared by ion-exchange of Na/ZSM-5 (UOP, Si/Al=17) with NH₄NO₃ solution three times at 25°C and calcined in O₂ at 500°C for 2 h to decompose NH₄⁺. The H-USY was prepared by calcining NH₄-USY (UOP, LZY84) in air at 723 K for 16 h. This H-USY as characterized by XRD had 26 framework Al ions per unit cell and a unit cell dimension of 24.468 Å (12).

2 wt% Co/Al₂O₃ was prepared by incipient-wetness impregnation of Co(C₆H₆O₇) (Johnson-Matthey) onto Al₂O₃. The sample was calcined in air at 350°C for 2 h and activated in a reaction feed at 500°C for 2 h before use. Co/H-ZSM-5 was prepared by three times ion-exchange of Na/ZSM-5 (UOP, Si/Al=17) with 0.002 M Co(NO₃)₂ solution at 80°C. The pH of the suspension was between 5–6 in the first and second exchanges and 7.5 (adjusted by addition of NaOH solution) in the third exchange. The sample was calcined in O₂ at 500°C for 2 h before use. Its Co loading was 1.24 wt%, and the Co/Al=0.27, and Na/Al=0.02. The color of Co/H-ZSM-5 after calcination was pale purple, but it quickly turned to white after exposure to air. Co/H-USY was prepared by ion-exchange of H-USY with a 0.02 M Co(NO₃)₂ solution once at 80°C and pH between 5 and 6.

¹ Corresponding author. E-mail: m-kung@nwu.edu.

The resulting sample was calcined in O₂ at 500°C for 2 h before use. The Co loading was 0.64 wt% and Co/Al = 0.047. The color of the calcined Co/H-USY was light purple. The particle sizes of H-USY and H-ZSM-5 are very small as all the powder passed through a 200 mesh sieve. Approximately half of the Co/Al₂O₃ catalyst passed through the 200 mesh sieve.

2.2. Catalytic Activity Measurement

The catalytic reactions were conducted in a flow microreactor, as described previously (4). The standard feed was 250 ml/min of 0.095% NO or NO₂, 0.3% CH₄, 2% O₂, balanced with He. The feed for NO oxidation or NO₂ decomposition was 0.095% NO or NO₂, 2% O₂, balanced with He to give a 250 ml/min flow rate. A gas-chromatograph with a TCD detector and a NO_x analyzer (Beckman, model 951) were used to analyze the exit gases. N₂, NO, and NO₂ were the only nitrogen-containing species detected in the exit gas in all experiments reported here. N₂ yield was defined as the selectivity for N₂ times NO_x conversion. The weight of the catalysts (unless otherwise specified) used in a reaction was 0.5 g (for example, 0.5 g of H-USY or 0.25 g of H-USY + 0.25 g of Co/Al₂O₃ in a physical mixture). When a physical mixture was used, the two catalysts were stirred with a spatula until the mixture appeared uniform (when H-ZSM-5 was a component, it was necessary to crush the mixture gently to break up the clumps of H-ZSM-5). The duration of the catalytic tests was around 5 h.

3. RESULTS

3.1. CH₄ SCR of NO

3.1.1. Co/H-ZSM-5, Co/Al₂O₃, and Co/H-USY. The activity for CH₄ SCR of NO over Co/H-ZSM-5, Co/Al₂O₃, and Co/H-USY are shown in Fig. 1. Co/Al₂O₃ was characterized in depth in a previous publication (4). Briefly the active Co species in a 2 wt% Co/Al₂O₃ is proposed to be a highly dispersed octahedral Co²⁺ ion. Co/H-ZSM-5 was the most active catalyst. Its N₂ yield reached 56% at 500°C, corresponding to an integral rate of 11.9 μmol/min-g cat. The activity of Co/Al₂O₃ was much lower, and its N₂ yield increased with increasing temperature. Co/H-USY was even less active below 600°C.

3.1.2. Co/Al₂O₃ and H-ZSM-5. The activities over a combination of Co/Al₂O₃ and H-ZSM-5 catalysts are compared with those of Co/Al₂O₃ and H-ZSM-5 in Fig. 2. When H-ZSM-5 (upstream) and Co/Al₂O₃ (downstream) were used as two layers separated by a layer of quartz wool, the overall N₂ yield (curve c) was simply the sum of the individual yield over Co/Al₂O₃ (curve a) and H-ZSM-5 (curve b). When the order of the Co/Al₂O₃ and H-ZSM-5 layers was reversed, the overall N₂ yield (curve d) was a little lower. This is because some CH₄ was consumed by

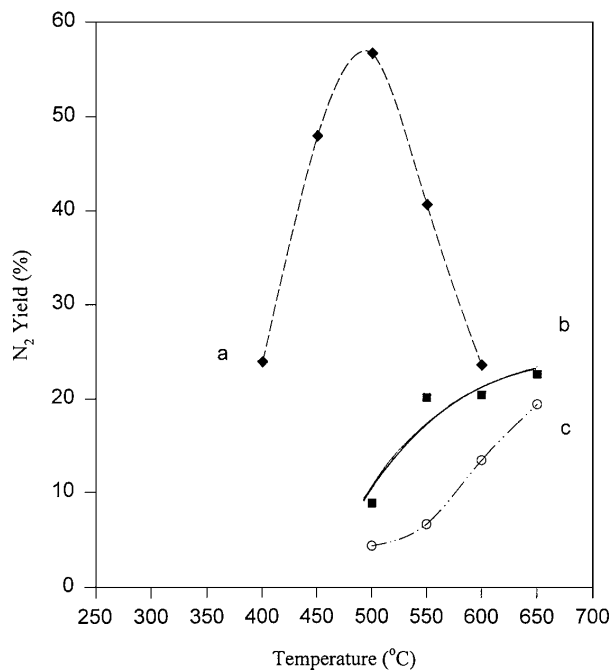


FIG. 1. CH₄ SCR of NO over: W = 0.5 g, (a) Co/H-ZSM-5 (1.24 wt% Co), (b) Co/Al₂O₃ (2 wt% Co), and (c) Co/H-USY (0.64 wt% Co).

the upper Co/Al₂O₃ layer and the actual feed reaching the H-ZSM-5 layer contained less CH₄ reductant. However, a significant enhancement in N₂ yield was observed over the physical mixture of Co/Al₂O₃ and H-ZSM-5 (curve e). The

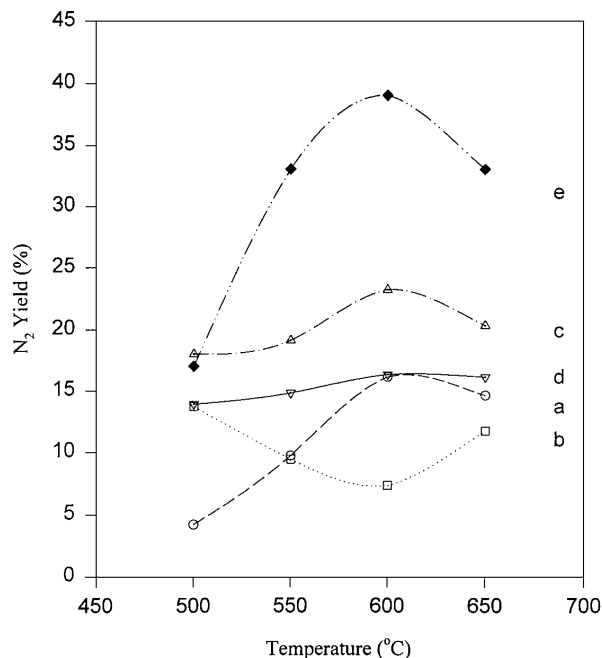


FIG. 2. CH₄ SCR of NO over: (a) Co/Al₂O₃ (0.25 g), (b) H-ZSM-5 (0.25 g), (c) H-ZSM-5//quartz wool//Co/Al₂O₃ (0.25 + 0.25 g), (d) Co/Al₂O₃//quartz wool//H-ZSM-5 (0.25 + 0.25 g), and (e) Co/Al₂O₃ + H-ZSM-5 (physical mixture, 0.25 + 0.25 g).

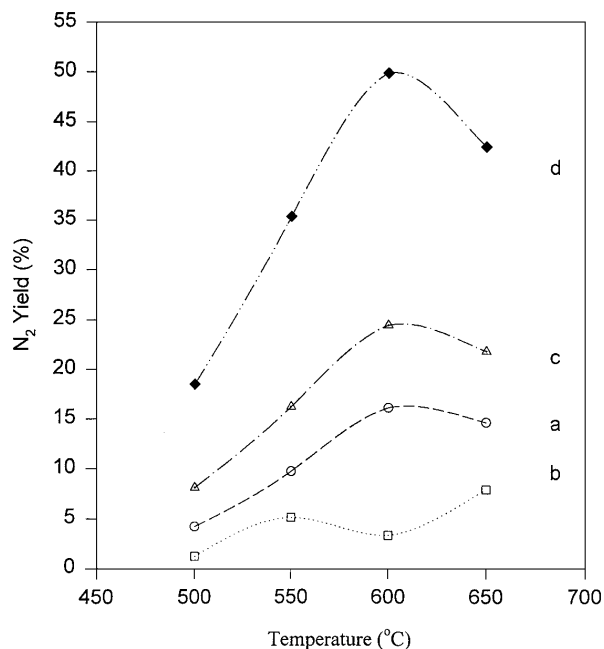


FIG. 3. CH_4 SCR of NO over: (a) $\text{Co}/\text{Al}_2\text{O}_3$ (0.25 g), (b) H-USY (0.25 g), (c) H-USY/quartz wool/ $\text{Co}/\text{Al}_2\text{O}_3$ (0.25 + 0.25 g), and (d) $\text{Co}/\text{Al}_2\text{O}_3$ + H-USY (physical mixture, 0.25 + 0.25 g).

maximum N_2 yield reached 39% at 600°C , or an integral rate of $8.3 \mu\text{mol}/\text{min}\cdot\text{g}\cdot\text{cat}$.

3.1.3. CH_4 SCR of NO over $\text{Co}/\text{Al}_2\text{O}_3$ and H-USY. Figure 3 shows that H-USY (curve b) was a poor catalyst

for the NO reduction by CH_4 , no better than $\text{Co}/\text{Al}_2\text{O}_3$ or H-ZSM-5. Exchange of Co into H-USY did not improve the CH_4 SCR activity significantly (curve c, Fig. 1). Significant enhancement in catalytic activity over the individual catalyst was observed for a physical mixture of $\text{Co}/\text{Al}_2\text{O}_3$ and H-USY (curve d), but not when the two catalysts were spatially separated (curve c). This was similar to the case of $\text{Co}/\text{Al}_2\text{O}_3$ and H-ZSM-5. The maximum N_2 yield reached 50% at 600°C (an integral rate of $10.6 \mu\text{mol}/\text{min}\cdot\text{g}\cdot\text{cat}$) for the physical mixture, a value comparable to that of $\text{Co}/\text{H-ZSM-5}$ (Fig. 1).

3.1.4. CH_4 SCR of NO over $\text{Co}/\text{H-ZSM-5}$ + $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Co}/\text{H-ZSM-5}$ + H-ZSM-5. Figure 4a compares the CH_4 SCR activity of $\text{Co}/\text{H-ZSM-5}$ with those of two different physical mixtures: $\text{Co}/\text{H-ZSM-5}$ and $\text{Co}/\text{Al}_2\text{O}_3$ mixture or $\text{Co}/\text{H-ZSM-5}$ and H-ZSM-5 mixture. The addition of 0.4 g of $\text{Co}/\text{Al}_2\text{O}_3$ to 0.1 g $\text{Co}/\text{H-ZSM-5}$ did not improve the activity significantly, which was low compared with 0.5 g of $\text{Co}/\text{H-ZSM-5}$. In contrast, the catalytic activity of a mixture of 0.1 g of $\text{Co}/\text{H-ZSM-5}$ and 0.4 g of H-ZSM-5 was comparable or superior to that of 0.5 g $\text{Co}/\text{H-ZSM-5}$ catalyst. Figure 4b shows the corresponding CH_4 conversion for the different catalysts.

3.2. CH_4 SCR of NO_2

Replacing NO with NO_2 in the feed affected the N_2 yield quite differently over various samples, as can be seen by comparing the data in Fig. 5 with those in Figs. 2 and 3.

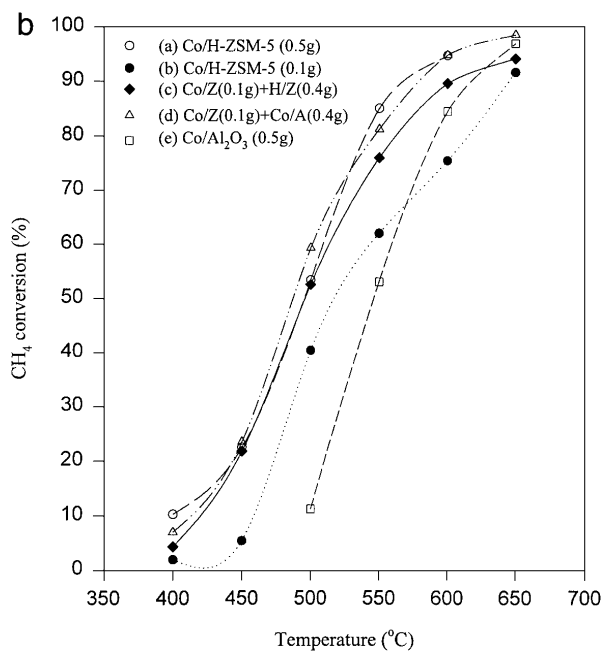
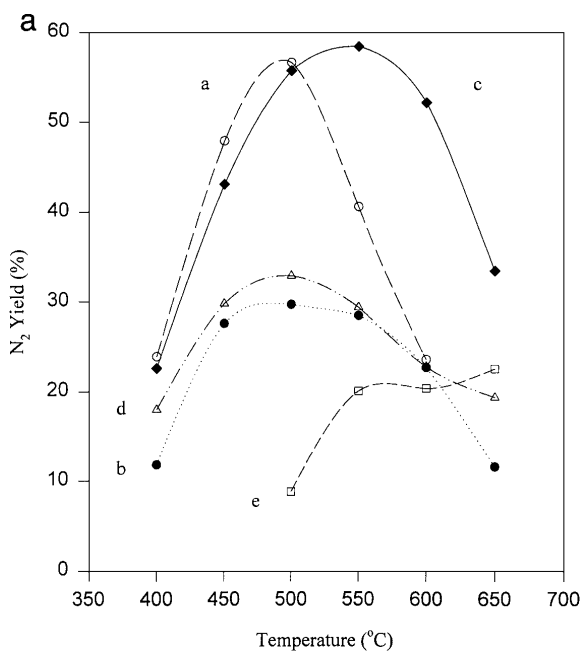


FIG. 4. (a) N_2 yield in CH_4 SCR of NO over: (a) $\text{Co}/\text{H-ZSM-5}$ (0.5 g), (b) $\text{Co}/\text{H-ZSM-5}$ (0.1 g), (c) $\text{Co}/\text{H-ZSM-5}$ (0.1 g) + H-ZSM-5 (0.4 g) (physical mixture), (d) $\text{Co}/\text{H-ZSM-5}$ (0.1 g) + $\text{Co}/\text{Al}_2\text{O}_3$ (0.4 g) (physical mixture), and (e) $\text{Co}/\text{Al}_2\text{O}_3$ (2 wt% Co, 0.5 g). (b) CH_4 conversion in CH_4 SCR of NO over: (a) $\text{Co}/\text{H-ZSM-5}$ (0.5 g), (b) $\text{Co}/\text{H-ZSM-5}$ (0.1 g), (c) $\text{Co}/\text{H-ZSM-5}$ (0.1 g) + H-ZSM-5 (0.4 g) (physical mixture), (d) $\text{Co}/\text{H-ZSM-5}$ (0.1 g) + $\text{Co}/\text{Al}_2\text{O}_3$ (0.4 g) (physical mixture), and (e) $\text{Co}/\text{Al}_2\text{O}_3$ (2 wt% Co, 0.5 g).

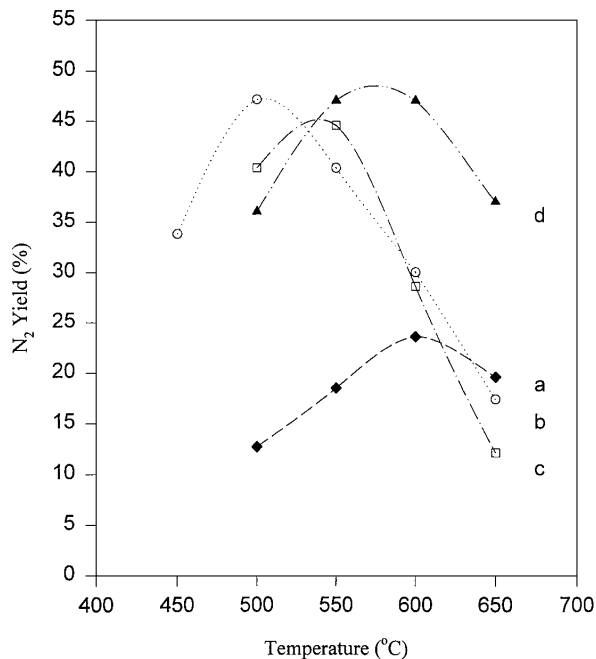


FIG. 5. CH₄ SCR of NO₂ to N₂ over: (a) Co/Al₂O₃ (0.5 g), (b) H-ZSM-5 (0.5 g), (c) H-USY (0.5 g), and (d) Co/Al₂O₃ + HZSM-5 (physical mixture, 0.25 + 0.25 g).

Compared to NO, the N₂ yield ranged from no significant difference over Co/Al₂O₃, to a mild increase over the physical mixture of Co/Al₂O₃ + H-ZSM-5, and to a significant increase over H-ZSM-5 or H-USY. The maximum N₂ yield increased from below 20% for H-ZSM-5 and H-USY with NO in the feed, to 47% and 45%, respectively, with NO₂ in the feed.

3.3. NO Oxidation and NO₂ Decomposition

Figure 6 shows the activities of various catalysts for NO oxidation to NO₂. The equilibrium composition under these conditions is also shown as a reference. Co/H-USY and H-USY were inactive for NO oxidation; the NO₂ concentrations of the exit gas were the same as from a reactor containing only quartz wool. Similarly, Na-ZSM-5 and Al₂O₃ were found to have very low activities. The NO oxidation activity followed the order: Co/H-USY ~ H-USY ~ Na-ZSM-5 < Al₂O₃ < Co/Al₂O₃ < H-ZSM-5 < Co/H-ZSM-5. In view of the low equilibrium NO₂ concentrations at high temperatures, NO₂ decomposition activities of the various catalysts were also examined to better distinguish the NO oxidation capability of the various catalysts in the high temperature region. As expected from the Principle of Microscopic Reversibility, the order for NO₂ decomposition activity was identical to NO oxidation. At 600°C, near equilibrium conversion was obtained for Co/Al₂O₃, but not for Co/H-USY.

Figure 7 shows the effect of 0.14% H₂O in the feed on the NO oxidation activity of H-ZSM-5 at 350, 450, and 550°C.

The H₂O concentration in the feed was chosen to be equivalent to the amount of H₂O that would be produced by a 23% conversion of CH₄ in the SCR reaction. Even at this low concentration of H₂O, significant suppression of the NO oxidation activity was observed at 350°C. This suppression became less severe at higher temperatures, and no observable effect was detected at 550°C. However, because of the low equilibrium concentration of NO₂ at 550°C, small changes in the oxidation activity would not be easily detectable. Upon removal of H₂O from the feed, the NO oxidation activity was slowly restored.

The effect of 0.14% H₂O on the NO₂ decomposition activity of Co/Al₂O₃ was also examined. The results showed that H₂O also suppressed the decomposition activity, but the effect was much milder than the effect with H/ZSM-5 shown in Fig. 7.

3.4. CH₄ Reduction of NO₂ to NO

Figure 8a shows the NO₂/NO_x (NO_x = NO + NO₂) ratio in the exit gas for a feed of NO₂/O₂/CH₄ over H-ZSM-5, H-USY, Co/H-ZSM-5, and Co/Al₂O₃. The equilibrium composition in the absence of CH₄ for the reaction of NO + O₂ >> NO₂ is also included. Below 500°C, the activity of NO₂ reduction to NO followed the order: Co/H-ZSM-5 > H-ZSM-5 >> H-USY ~ Co/Al₂O₃. Above 500°C, the order changed to H-ZSM-5 > H-USY > Co/H-ZSM-5 > Co/Al₂O₃. However, the low activity of Co/H-ZSM-5 above 500°C might be due to the rapid consumption

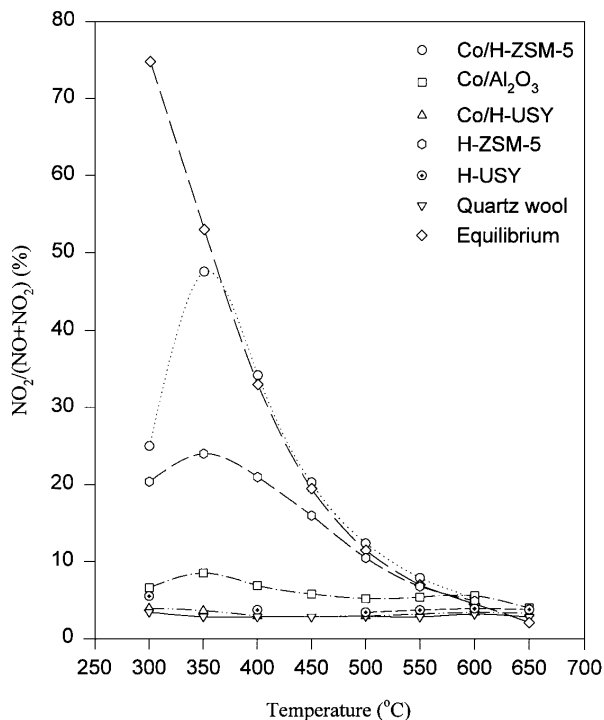


FIG. 6. NO oxidation to NO₂ over different samples, NO (0.095%)/O₂ (2%)/He, W = 0.5 g, baseline NO₂/(NO + NO₂) = 3%.

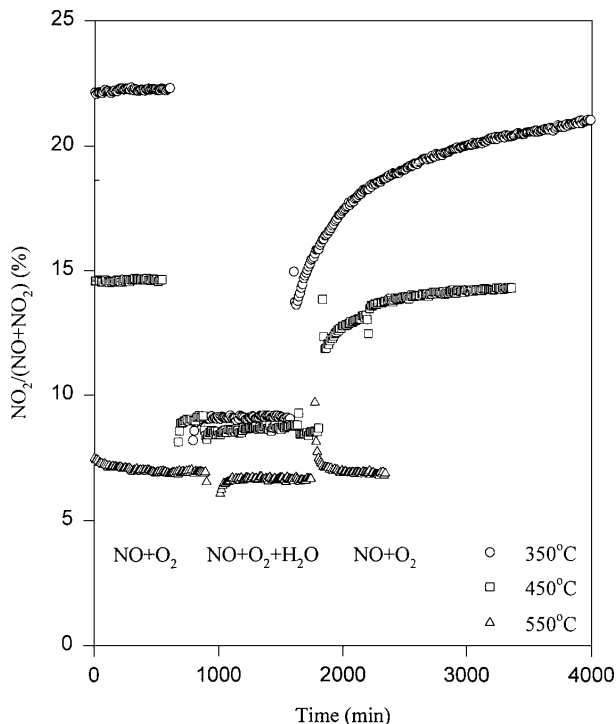


FIG. 7. Effect of H₂O on activity of the NO oxidation to NO₂ over H-ZSM-5 (0.5 g), NO (0.095%)/O₂ (2%)/H₂O (0.14%)/He.

of CH₄ (Fig. 8b). With H-ZSM-5 and H-USY, NO₂ is rapidly reduced to NO, and the resultant NO₂/(NO + NO₂) ratios at the reactor exit were significantly lower than the equilibrium composition in the absence of CH₄.

4. DISCUSSION

In this study, the most significant observation is that the CH₄ SCR activity of a physical mixture of Co/Al₂O₃ and H-ZSM-5 or H-USY is much higher than the sum of the activities of the individual components (Figs. 2 and 3). It can be ruled out that the improved catalytic performance originates from a Co/H-zeolite formed by migration of Co from alumina to the H-zeolite. Although transition metal zeolite can be prepared via solid state reactions, the introduction of cation into the zeolite is much easier with metal chloride than with metal oxide (13). On energetic grounds, it would be even more difficult for Co ions supported on alumina to migrate into the zeolitic channels. Alumina interacts strongly with cobalt oxide and this is reflected in the modified redox property of the cobalt cation. Whereas, Co₃O₄ reduces readily to cobalt metal at 217°C (14), no detectable uptake of H₂ was observed for a 2 wt% Co/Al₂O₃ at temperatures as high as 800°C (4). On the other hand, silica generally interacts much more weakly with transition metal oxides. Using laser Raman spectroscopy, Deo *et al.* (15) observed that the maximum V₂O₅ loadings,

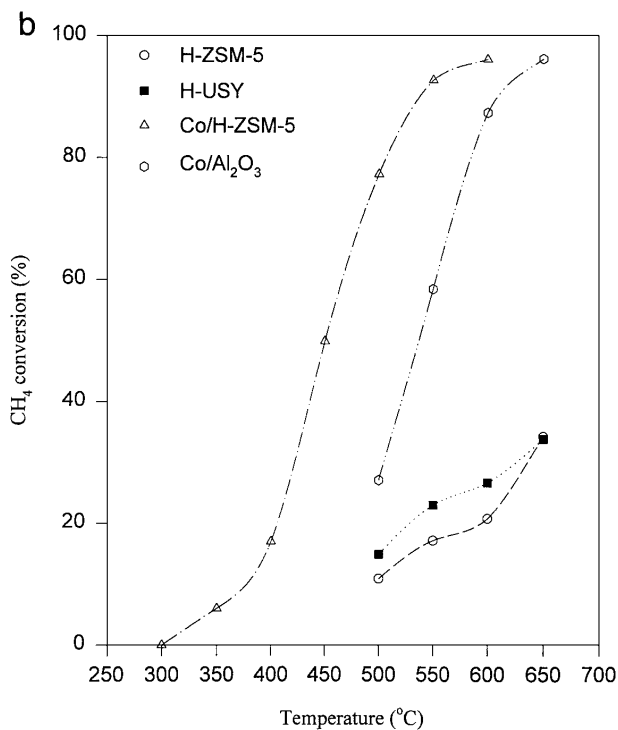
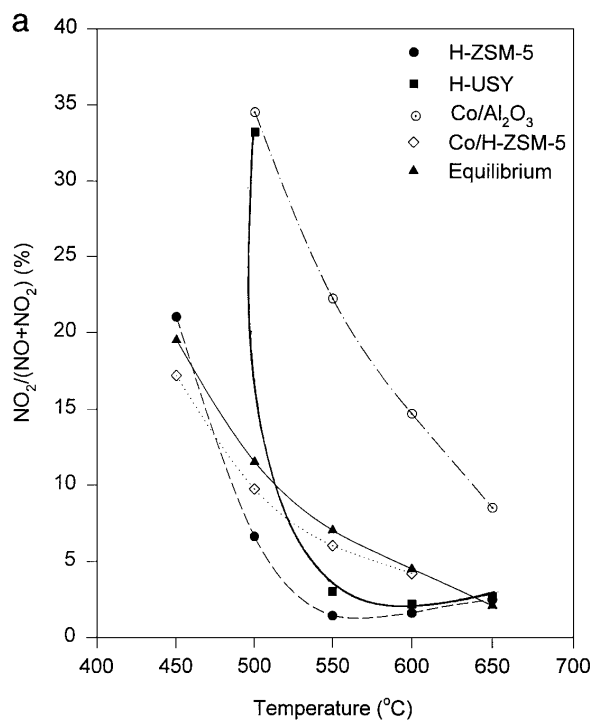


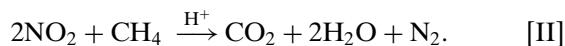
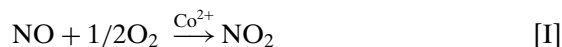
FIG. 8. (a) NO₂ reduction to NO by CH₄ over different samples, feed: NO₂ (0.095%)/O₂ (2%)/CH₄ (0.3%)/He. Baseline NO₂/(NO + NO₂) = 93%, W = 0.5 g. (b) CH₄ conversion in SCR of NO₂ over different samples, feed: NO₂ (0.095%)/O₂ (2%)/CH₄ (0.3%)/He, W = 0.5 g.

before detection of crystalline V₂O₅, are 3 wt% and 20 wt% for SiO₂ and Al₂O₃, respectively. The exterior of ZSM-5 is siliceous in nature, and thus there is no driving force other than entropy for cobalt to migrate from alumina to silica. For a low Co loading (2 wt%) sample, the entropic effect should be insignificant. The strength of cobalt–alumina interaction can partly be attributed to the ease of formation of a surface cobalt aluminate phase. As shown by UV-visible spectroscopy, this phase was present when the sample was heated only to 350°C (4), and its concentration increased dramatically after reactions at high temperatures (450–600°C). This diffusion of cobalt into the alumina to form the aluminate lowers the density of cobalt on the support surface and effectively decreases the concentration of cobalt available for migration. In summary, a number of factors, such as low surface density of cobalt, the low loading of cobalt on Al₂O₃, the strong interaction of cobalt with alumina and the ease of compound formation all combined to make migration of cobalt from alumina to the H-zeolite unfavorable. It is noteworthy, that direct observations have shown that no migration of Ag onto Al₂O₃ was detected for a physical mixture of 6 wt% Ag/Al₂O₃ and Al₂O₃ after the mixture was used in the selective catalytic reduction of NO at high temperatures (16). The conditions in the case of Ag are more conducive to ion migration than in the Co/Al₂O₃ and H-zeolite physical mixture: the surface density of Ag is higher due to its lack of tendency to form compound with alumina, the lower rate of bulk diffusion of Ag because of its larger size, and the higher weight loading of Ag used.

Even if migration of Co does take place, the observed enhancement for the physical mixture of Co/Al₂O₃ and H-USY cannot be explained by the formation of Co/H-USY. We have prepared a low loading Co/H-USY and found that it is a poor catalyst for CH₄ SCR of NO (Fig. 1). This agrees with a similar observation by Li and Armor, who have studied a higher Co loading HY catalyst (1). Similarly, for the Co/Al₂O₃ and H-ZSM-5 physical mixture, the degree of migration has to be extensive to explain the enhancement. In order to compare with the available data on Co/H-ZSM-5 catalyst, we assume that in a physical mixture of 0.25 g of Co/Al₂O₃ and 0.25 g of H-ZSM-5, 0.1 g of the H-ZSM-5 is in intimate contact with 0.25 g of Co/Al₂O₃ and an ensuing solid state reaction results in a physical mixture of 0.25 g of 1.5 wt% Co/Al₂O₃, 0.15 g of H-ZSM-5 and 0.1 g of 1.24 wt% Co/H-ZSM-5. In the absence of a synergistic effect, the contributions of the Co/Al₂O₃ catalyst and H-ZSM-5 catalyst to the overall catalytic performance are small. Then the overall N₂ yield from this “new” catalytic mixture would be approximated by the performance of 0.1 g of the 1.24 wt% Co/H-ZSM-5 catalyst (Fig. 4a(b)). Experimentally, the performance of 0.1 g of Co/H-ZSM-5 in the high temperature region is significantly lower than that of the physical mixture of 0.25 g of Co/Al₂O₃ and H/ZSM-5 (Fig. 2).

Thus, Co migration from Co/Al₂O₃ to the zeolite is insufficient to explain the observations, and the synergistic effect observed with the physical mixture must be due to other causes. For the purpose of this discussion, the synergistic effect is defined as the enhanced SCR activity of the physical mixture over the sum of the activities of the components.

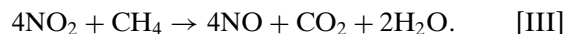
It is probable that the synergistic effect requires participation of active sites on both H-zeolite and Co/Al₂O₃. Most likely, the active sites are the zeolitic protons and the Co²⁺ ions. We propose that the following scheme represents the principal pathway in the selective reduction of NO_x over the physical mixture:



In discussing this proposal, the following experimental observations are particularly relevant:

1. In the CH₄ SCR of NO₂ over H-ZSM-5 and H-USY, the ratios of the rate of N₂ production to CH₄ consumption are generally high, being about 0.4 at 550°C to about 0.2 at 600°C, implying that a significant portion of the CH₄ is consumed by the productive reaction (Eq. [II]).

2. There is also a nonproductive route for the consumption of CH₄ in the CH₄ SCR of NO₂ over the H-zeolite, which results in the reduction of NO₂ to NO (Fig. 8a):



H-ZSM-5 is more active than H-USY for this route. The exit gas of the reactor contains very little NO₂ at temperatures above 500°C for H-ZSM-5, and above 550°C for H-USY (Fig. 8a).

3. Whereas H-ZSM-5 is quite active for NO oxidation to NO₂, H-USY is much less active (Fig. 6).

4. Co/Al₂O₃ is a poor catalyst for the selective reduction of NO as well as NO₂ by CH₄ (Fig. 5).

5. The largest enhancement in activity for the physical mixture is generally observed at about 600°C.

Point 1 suggests that the H-zeolite would be very effective CH₄ SCR catalysts for NO if NO can be rapidly oxidized to NO₂ first. Points 2 and 3 justify the need for Co to catalyze NO oxidation. H-USY is not active for NO oxidation. Consequently, it is not an effective CH₄ SCR catalyst (Fig. 3). On the other hand, even taking into account of the effect of H₂O suppression, H-ZSM-5 is quite active for NO oxidation, especially at the higher temperatures. However, it is also active for the reduction of NO₂ to NO, with the activity increasing with increasing temperature (Fig. 8a). The net effect is a low N₂ yield in the CH₄ SCR of NO that changes little with temperature. This also applies to H-USY. The presence of Co/Al₂O₃ in the physical mixture changes

this scenario substantially. Co/Al₂O₃ is able to maintain a certain ratio of NO₂/(NO + NO₂) throughout the catalyst bed because it can rapidly generate NO₂ *in situ* at 550°C and above (Fig. 6). NO₂ formed is subsequently reduced to N₂ over the H-zeolite. The importance of the H⁺ in this reaction scheme is further emphasized by the observation that Co ions on alumina is not effective in catalyzing the reduction of NO₂ (point 4).

The data in Figs. 2 and 3 show that the synergistic effect of H-zeolite and Co/Al₂O₃ is much greater with a physical mixture than when the two catalysts are separated. When H-ZSM-5 was placed upstream of Co/Al₂O₃, the overall SCR activity was similar to the sum of the activity of the individual catalyst. This is expected; the low SCR activity of H-ZSM-5 only results in minor changes in the gas mixture when it reaches the Co/Al₂O₃ catalyst. When Co/Al₂O₃ is upstream of H-ZSM-5 or H-USY, it catalyzed both the NO oxidation and the CH₄ combustion reactions such that the gas mixture reaching the zeolite layer would be higher in NO₂ concentration and lower in CH₄ concentration. However, the increase in NO₂ concentration, as limited by equilibrium, is very modest and the higher N₂ production that would have resulted is offset by the lower CH₄ concentration reaching the zeolite and by the rapid reduction of NO₂ to NO by the zeolite. The net result is that the overall N₂ production is not changed substantially.

The high activity of CH₄ SCR of NO₂ observed over H-ZSM-5 and H-USY samples (Fig. 5), suggests that the H⁺ sites, rather than the zeolite structure play an important role in the CH₄ SCR of NO₂. How NO₂ is reduced to N₂ over a H⁺ site is not clear. One possibility is that NO₂ is adsorbed to form a nitronium ion, which then reacts with a hydrocarbon molecule to form nitroalkane that eventually forms N₂ (17). The importance of nitromethane or nitrosoalkane as an intermediate, formed by reaction of hydrocarbon with adsorbed NO₂, has been suggested by various investigators (18–21). Another possibility is that the Brønsted acid site protonates CH₄ to form a transient CH₅⁺, which reacts with gas phase NO₂ to form CH₃NO⁺ and H₂O.

The enhancement in N₂ yield for a physical mixture of Co/Al₂O₃ and H-zeolite is larger than expected for the observed NO oxidation activity on Co/Al₂O₃; the equilibrium distribution of NO and NO₂ is not reached even at 550°C (Fig. 6). We propose that the NO oxidation activity for this catalyst is suppressed by NO₂. That is, in the absence of NO₂, the NO oxidation activity would be significantly higher. Therefore, over a mixture of Co/Al₂O₃ and H-zeolite, the gaseous NO₂ concentration is lowered through the continuous consumption of NO₂ by both the SCR reaction and by the reduction of NO₂ to NO by CH₄ catalyzed by the H-zeolite. The reduced gas phase NO₂ concentration removes the suppression of NO₂ production by Co/Al₂O₃.

In our scheme for the physical mixture of Co/Al₂O₃ and H-ZSM-5, the proposed principal role of Co is to catalyze

NO oxidation. The Co/ZSM-5 system however is more complex. Lukyanov *et al.* (22) reported that Co/ZSM-5 (98% exchange level) is substantially more active than H-ZSM-5 in NO₂ reduction by CH₄. Thus, it appears that some or all of the Co ions in the ZSM-5 channel can catalyze NO₂ reduction to N₂ by CH₄. The situation is further complicated by the fact that when the Co/H⁺ ratio is varied, by changing the Co exchange level, the distribution of the different Co species is varied. Li and Armor (23), using NO TPD and SO₂ poisoning studies, proposed that the Co sites in Co/ZSM-5 are not homogeneous. Stakheev *et al.* (24) observed that Co/H-ZSM-5 catalysts with low levels of Co exchange are not active in NO oxidation. In fact, H-ZSM-5 is more active than Co/H-ZSM-5 with a 30% Co exchange level in the NO oxidation reaction. Thus the proposed reaction cycle (Eqs. [I] and [II]) cannot be optimized for a Co/H-ZSM-5 catalyst, if a low Co/H⁺ ratio is desirable, because H-ZSM-5 with low Co loading is not efficient in NO oxidation. The Co/H⁺ ratio can, however, be changed without altering the distribution of the various Co species by using mixtures of Co/Al₂O₃ and H-ZSM-5, or Co/H-ZSM-5 and H-ZSM-5. The lowest activity is observed with the highest Co/H⁺ ratio (0.4 g Co/Al₂O₃ and 0.1 g Co/H-ZSM-5) (Fig. 4a). At a lower Co/H⁺ ratio, with a 50:50 mixture of Co/Al₂O₃ and H-ZSM-5, the NO reduction activity is substantially improved (Fig. 2). A mixture of 0.1 g Co/H-ZSM-5 and 0.4 g H-ZSM-5 has the lowest Co/H⁺ ratio in this study. Its NO reduction activity is comparable or superior to 0.5 g of Co-ZSM-5 at all temperatures. In order to have the same Co/H⁺ ratio in a Co/H-ZSM-5 as in the physical mixture of 0.1 g Co/H-ZSM-5 and 0.4 g H-ZSM-5, the Co exchange level would have to be around 10%. Campa *et al.* (25) showed that the rates of NO reduction increase with Co loadings, and that the rate of N₂ production is very low for a 11% exchanged sample. This is in sharp contrast to the observed high activity in the physical mixture of 0.1 g Co/H-ZSM-5 and 0.4 g H-ZSM-5.

In addition to Co/Al₂O₃ and H-zeolite, other catalytic systems have been reported to show similar bifunctional properties. Nishizaka and Misono (10) observed that proton sites are important in the reduction of NO₂ by CH₄ over a low loading Pd/H-ZSM-5 catalyst. In that system, both Pd and H⁺ are necessary for the NO₂ reduction to N₂ as this reaction proceeds much faster over Pd/H-ZSM-5 than over either Pd/Na-ZSM-5 or H-ZSM-5. For the Ga/H-ZSM-5 system (7, 8), NO oxidation was proposed to take place over H⁺ sites and NO₂ reduction over Ga sites, since the rate of the latter reaction increases with Ga loading. Our observation that NO oxidation over H⁺ sites is suppressed by H₂O is consistent with the observation that CH₄ SCR over Ga/H-ZSM-5 is very sensitive to the presence of H₂O (7). Thus, in all these catalytic systems, including the physical mixture of Co/Al₂O₃ and H-zeolite, the NO oxidation and NO₂ reduction functions are satisfied by a combination

of H⁺ and cation sites. That dual active sites of different functions are needed probably reflects the demanding nature of the CH₄ SCR process.

5. CONCLUSION

A strong promotional effect is observed for NO reduction to N₂ by CH₄ over physical mixtures of Co/Al₂O₃ and H-zeolite (H-ZSM-5 or H-USY) at temperatures above 500°C. A proposed scheme for the enhancement involves NO oxidation over the Co cation sites and the subsequent reduction of NO₂ by CH₄ over the proton sites. Thus, a major role of Co is to generate NO₂ *in situ* and maintain a nonnegligible concentration of NO₂ throughout the catalyst bed. The idea of a need for a bifunctional catalyst for CH₄ SCR has been proposed in the literature in various forms, but they all involve a NO oxidation and a CH₄ activation function. Since CH₄ SCR is such a demanding reaction, it is not surprising that many more bifunctional catalysts have been documented for this reaction than for other hydrocarbon SCR reactions.

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