Lean selective catalytic reduction of NO_2 by methane over Co-zeolites

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The reaction of NO_2, CH_4 and O_2 was studied using low levels of methane compared to NO_2 and O_2 over protonic and cobalt-exchanged ferrierite, ZSM-5 and mordenite zeolites. Results suggest that two reaction pathways at low and high temperatures may be involved in the lean selective catalytic reduction (SCR) of NO_2 by methane. At low temperatures, the reduction of NO_2 to NO and N_2 might be the initial reaction step. It is likely that NO_2 or its adsorbed precursors initiate the reaction of methane at low temperatures. At high temperatures, the oxidation of NO and combustion of methane with oxygen might be involved. No appreciable differences were observed in the reduction of NO_2 over Co-zeolites as compared to known results of NO reduction over these materials. However, enhanced N_2 formation rate was observed on H-zeolites starting from NO_2 instead of data reported for NO. Furthermore, it appears that the active sites for SCR are both acid and metal sites.

Keywords: NOx abatement, lean SCR, Co-zeolites, ferrierite, ZSM-5, mordenite

1. Introduction

Cobalt-exchanged zeolite catalysts have been reported [1] to be active for the selective catalytic reduction (SCR) of NO with methane in the presence of excess oxygen. NO reduction activity was found to be proportional to the Co^{2+} exchange level in Co-ZSM-5, and the parent Na-ZSM-5 was inactive. Therefore, it was concluded [2] that the transition metal ion exchanged into the zeolite must be responsible for the NO reduction. Furthermore, zeolite topology as a support appears to be crucial. Activity differences of Co^{2+} ions into ferrierite, ZSM-5, mordenite and Y zeolites has been ascribed [3] to cation coordination and relative diffusivity in the zeolite channels, postulating [2] that certain types of zeolites are required to position the cobalt cations providing a suitable electronic environment to carry out the selective reduction of nitric oxide with methane.

Alternatively, the lean SCR of NO may also be performed over H-zeolites [4–6], and some authors [7] consider that redox chemistry is unnecessary. So, the transition metal cation is not needed. Yogo et al. [8] found that the order of selectivity for this reaction was the same as of decreasing acid strength, H-ferrierite $>$ H-mordenite $>$ H-ZSM-5 $\gg$ H-Y, suggesting that a relation exists between the SCR of NOx and acidity. Ribotta et al. [9] reported activity and selectivity of H-mordenite for this reaction and showed [10] a linear relationship between activity and aluminum content, concluding that the strong acid sites associated with lattice Al are directly involved in the lean catalytic reduction of NOx over H-mordenite.

The objective of this work is to better understand the role of zeolite topology for the lean SCR of NOx by methane over Co-loaded zeolites. Since most studies agree that gas-phase NO_2, formed via NO oxidation, may be involved in N_2 formation on the catalyst surface, we examined the lean selective catalytic reduction of NO_2 with methane over Co-exchanged mordenite, ZSM-5 and ferrierite catalysts and compared to the corresponding H-zeolites. Besides, most work has been conducted using excess methane compared to NOx. In this paper we report the results obtained using excess NO_2 and oxygen compared to the hydrocarbon.

2. Experimental

2.1. Catalyst preparation

The parent sodium zeolites ZSM-5, FER and MOR were synthesized in our lab by known procedures [11–13]. FER contained organic template which was burned by calcining the corresponding zeolite at 450–500 °C for three hours. The Co–NH_4-zeolites were prepared by exhaustive exchange of the sodium zeolites with NH_4NO_3 at room temperature overnight, followed by cobalt exchange with 0.05 M $Co(NO_3)_2$ at 80 °C for about 24 h. The number of cobalt exchanges varied between 1 and 3 to obtain different cobalt loadings. After exchange, the zeolite suspensions were filtered, and the cakes were washed by stirring in 1 l de-ionized water for 2 h. After another filtration, the solid products were dried at 100 °C in a convection oven overnight. Crystallinity of the exchanged materials was checked by X-ray diffraction. No extraneous phases

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Table 1
Catalyst compositions.

Catalyst	Number of exchanges	Si/Al atomic ratio	Co/Al atomic ratio	Co (wt%)	Na/Al atomic ratio
NH_4-MOR	3	6.0	–	–	0.01
Co-MOR-6-40	1	6.0	0.20	1.63	0.02
Co-MOR-6-48	2	6.0	0.24	1.93	0.01
NH_4-ZSM-5	3	14	–	–	0.01
Co-ZSM5-14-50	1	14	0.25	1.08	0.01
Co-ZSM5-14-74	3	14	0.37	1.68	0.02
NH_4-FER	3	11	–	–	0.02
Co-FER-11-20	2	11	0.10	0.60	0.02
Co-FER-11-14	1	11	0.07	0.42	0.02

were observed. Elemental analysis of Si, Al, Na and Co were performed by atomic absorption spectroscopy. The atomic ratios and wt% Co of resulting Co–NH_4-zeolites together with those corresponding to the NH_4 parent zeolites are listed in table 1.

2.2. Reaction studies

The catalytic activities were measured at atmospheric pressure in a steady-state plugged-flow mode SS reactor (1/4″ o.d.). Catalysts were pelletized, crushed and sieved to 60–80 mesh before use. Typically, 25–50 mg of sample was packed into a bed held between plugs of quartz wool at the center of an electrical furnace. A catalyst was routinely dehydrated *in situ* in flowing He at 650 °C for 4 h. The temperature was monitored by a J-type thermocouple placed externally adjacent to the center of the catalyst bed. The usual temperature ramp was 5 °C/min, and the feed flow rate varied between 50–100 cm^3/min corresponding to gas hourly-space velocities of 120,000–60,000 h^{-1} assuming an apparent bulk density of zeolite catalyst of 0.5 g/cm^3. The gas mixtures fed into the reactor were obtained by blending previously prepared mixtures of NO_2/He, CH_4/He, O_2/He and helium. Each mixture was controlled by Brooks 5872 mass flow controllers. The composition of the reaction mixtures varied between 750–3000 ppm NO_2, 300–500 ppm CH_4 and 2.0–2.5% O_2 (balance He).

The feed and effluent gases were sampled and analyzed by an on-line gas chromatograph (Varian Star 3400) with a thermal conductivity detector (TCD) using a 5 A molecular sieve. During analysis, the GC oven program was hold at 37 °C for 20 min. The rates of N_2 production are expressed as the number of mol of N_2 formed per g of catalyst per second. The rate of methane consumption is expressed as the difference between the initial mol of CH_4 fed into the reactor and the mol of CH_4 at each temperature per g of catalyst per second. The CH_4 combustion rate was calculated as the difference between the total methane consumption rate and the nitrogen production rate.

3. Results

3.1. Extent of Co^{2+} ion exchange

As indicated in table 1, the ammonium forms of ZSM-5, FER and MOR were used before cobalt exchange to avoid precipitation of certain cobalt oxides or hydroxides. Full Co^{2+} ion exchange was not reached even after three exchanges with 0.05 M cobalt nitrate solutions. The difficulty of obtaining fully exchanged bivalent zeolites has been related [14] to the coordination ability of the bivalent ions and the type of coordination complex formed in the small and big cavities. We obtained over-exchanged Co-zeolites using dilute cobalt acetate solutions by reported procedures [1,2]. However, it has been shown [15] that CoO species on cobalt-exchanged materials were formed as a result of cobalt acetate hydrolysis. However, they seem to be highly dispersed since they were not identified by X-ray diffraction. Therefore, in this work we used the under-exchanged cobalt zeolites.

3.2. Reaction studies

Figure 1 illustrates the rate of N_2 production from NO_2 reduction with methane over H-FER and Co-FER catalysts in the presence of O_2 as a function of reaction temperature. The N_2 formation rate–temperature profile of Co-FER catalysts is proportional to the cobalt loading and increases monotonically with temperature. The rates did not bend over at 550 °C with increasing temperature similar to data obtained [3] for NO reduction in the presence of O_2. Interestingly, contrary to previous observations of NO reduction over a protonic ferrierite (Si/Al = 8), H-FER appears to be much more active for NO_2 reduction compared to Co-FER catalysts at temperatures below 450–500 °C.

Methane combustion rate on the same H-FER and Co-FER materials as a function of reaction temperature is shown in figure 2. Methane combustion is high at 300 °C and decreases with increasing temperature reaching a min-

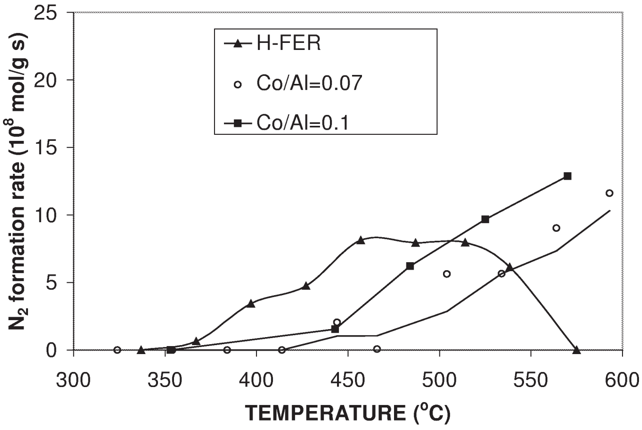

Figure 1. N_2 formation rate versus temperature as a function of Co/Al ratio in Co-FER compared to H-FER. The reaction was run on 25 mg sample with a feed containing 3000 ppm NO_2, 500 ppm methane, 2.0% O_2, balance He. GHSV = 60,000.

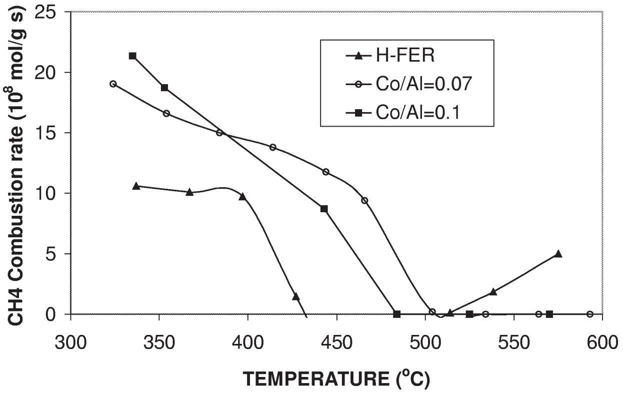

Figure 2. Methane combustion rate versus temperature as a function of Co/Al ratio in Co-FER compared to H-FER. The reaction was run on 25 mg sample with a feed containing 3000 ppm NO_2, 500 ppm methane, 2.0% O_2, balance He. GHSV = 60,000.

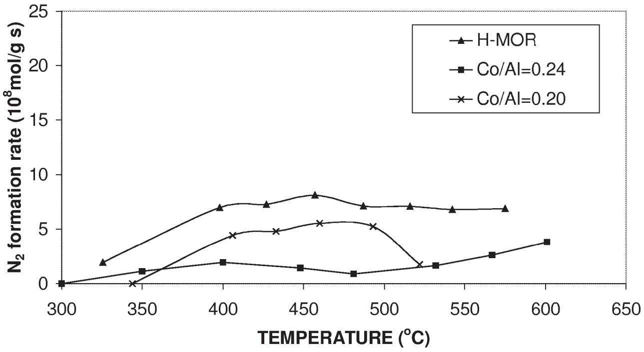

Figure 3. N_2 formation rate versus temperature as a function of Co/Al ratio in Co-MOR compared to H-MOR. The reaction was run on a 25 mg sample with a feed containing 3000 ppm NO_2, 500 ppm methane, 2.0% O_2, balance He. GHSV = 60,000, except for a GHSV = 120,000 for the material with Co/Al = 0.24.

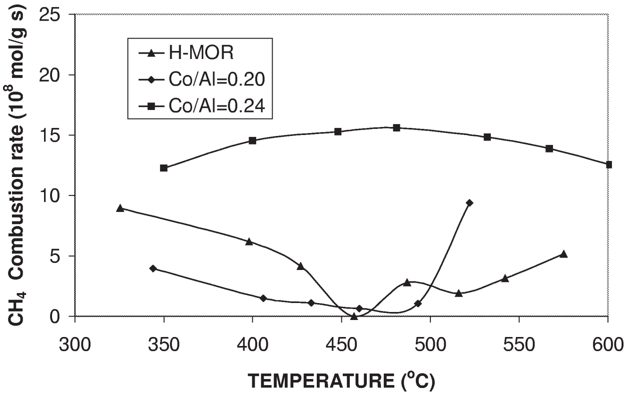

Figure 4. Methane combustion rate versus temperature as a function of Co/Al ratio in Co-MOR compared to H-MOR. The reaction was run on a 25 mg sample with a feed containing 3000 ppm NO_2, 500 ppm methane, 2.0% O_2, balance He. GHSV = 60,000, except for a GHSV = 120,000 for the material with Co/Al = 0.24.

imum between 487–500 °C on Co-FER catalysts and at about 430 °C on H-FER. Correspondingly, below 450 °C, N_2 formation rate on Co-FER catalysts is low (see figure 1). Since methane is not likely to react with O_2 at these temperatures, it probably reacted with NO_2 and the latter mainly reduced to NO on these catalysts. The decreasing profile on methane combustion rate may be explained by a lower level of NO_2 species with increasing temperature due to thermodynamic limitations. Although the same trend on methane combustion is observed over H-FER, the production of N_2 starts at 340 °C suggesting that protons are active sites for NO_2 reduction by methane to produce N_2. At higher temperatures, the curve of N_2 formation rate on H-ferrierite bends over. The bending over has been associated with experimental conditions and can be avoided by making the kinetic runs at higher space velocities [3]. The decrease in the nitrogen formation rate over H-ferrierite at temperatures higher than 500 °C leads to an increase in the methane combustion rate. No appreciable methane combustion is observed over Co-FER materials at temperatures higher than about 500 °C. Therefore, methane appears to react mainly with nitrogen containing species, rather than with oxygen, to produce N_2. This result is consistent with the high selectivity of Co-FER for SCR.

Figure 3 shows that N_2 formation rate is inversely proportional to Co loading over mordenite catalysts. These results coincide with recently reported [16] observations that conversion of NO_2 to N_2 occurs on the support rather than on the cobalt ions, showing that the rate of N_2 formation and selectivity increase linearly with the number of protons and is proportional to the acid strength. The rate of CH_4 combustion on mordenite type catalysts is illustrated in figure 4. Here methane combustion rate is proportional to Co loading and the selectivity for NO_2 reduction decreases with Co loading. At temperatures below 450 °C, methane combustion rate on H-MOR and Co-MOR-6-40 decreases resembling the behavior seen over H-FER. Again, methane appears to interact with NO_2 adsorbed on proton sites to produce N_2. As the temperature increases above 450 °C, NO_2 species decrease. Correspondingly, N_2 formation decreases and methane combustion by oxygen increases. The space velocity for Co-MOR-6-48 was twice the space velocity of the other mordenite catalysts used and the rate of N_2 formation is the smallest compared to the other two mordenite catalysts. Under these conditions, it appears that the NO produced by reaction of NO_2 with methane was reoxidized back to NO_2 on the metal sites. Although methane combustion predominated over the entire temperature range studied, no change in the oxygen concentration was observed. This suggests that methane was mainly burned by the oxygen released from the NO_2 decomposition as the temperature increased.

As shown in figure 5 the rate of N_2 formation is proportional to Co loading on Co-ZSM-5 materials. The curve bends over at about 500 °C on H-ZSM-5 and on the high Co-loaded material (Co-ZSM-5-14-74). However, the curve has a propensity to increase above 550 °C on Co-ZSM-5-14-50. Observations on the latter material are similar to those reported [17] for a Co-ZSM-5 (Si/Al = 11) catalyst. Methane combustion rate versus temperature profile on ZSM-5-type catalysts is illustrated in figure 6. Again, at low temperatures, methane combustion rate decreases to

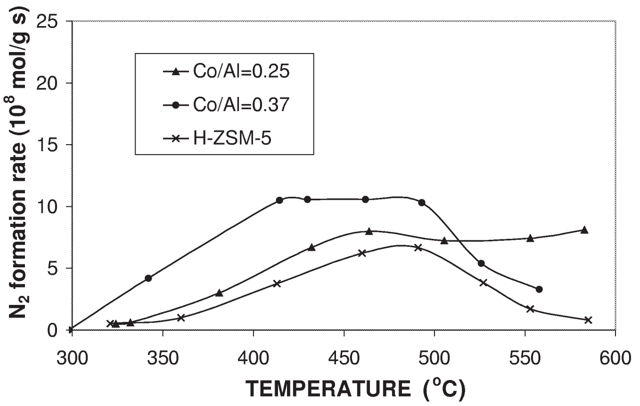

Figure 5. N_2 formation rate versus temperature as a function of Co/Al ratio over Co-ZSM-5 compared to H-ZSM-5. The reaction was run on a 25 mg sample with a feed containing 3000 ppm NO_2, 300 ppm methane, 2.0% O_2, balance He. GHSV = 60,000.

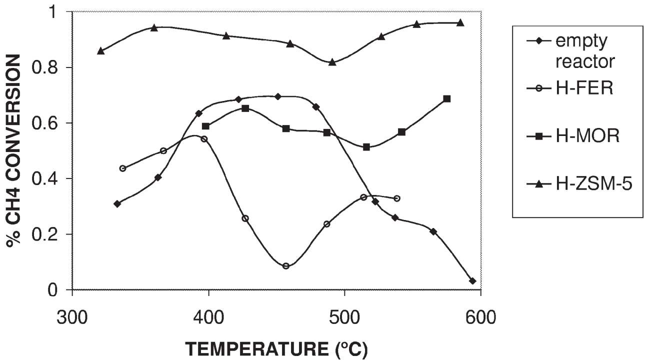

Figure 7. Methane conversion versus temperature over H-zeolites compared to the empty reactor. The reaction was run on a 25 mg sample with a feed containing 3000 ppm NO_2, 500 ppm methane, 2.0% O_2, balance He. The feed used on H-ZSM-5 contained 3000 ppm NO_2, 300 ppm CH_4, 2.0% O_2, balance He. GHSV = 60,000.

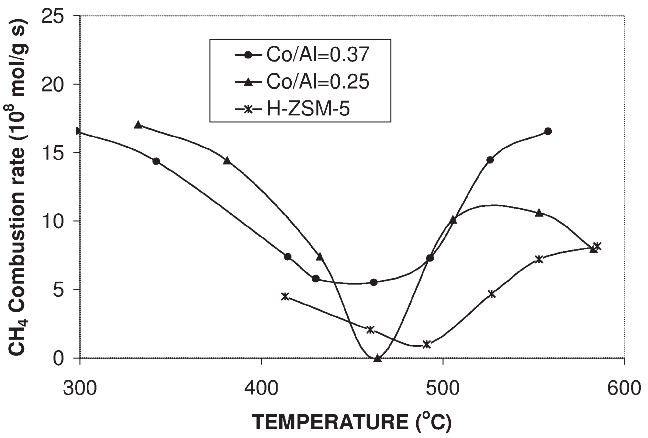

Figure 6. Methane combustion rate versus temperature as a function of Co/Al ratio over Co-ZSM-5 compared to H-ZSM-5. The reaction was run on a 25 mg sample with a feed containing 3000 ppm NO_2, 300 ppm methane, 2.0% O_2, balance He. GHSV = 60,000.

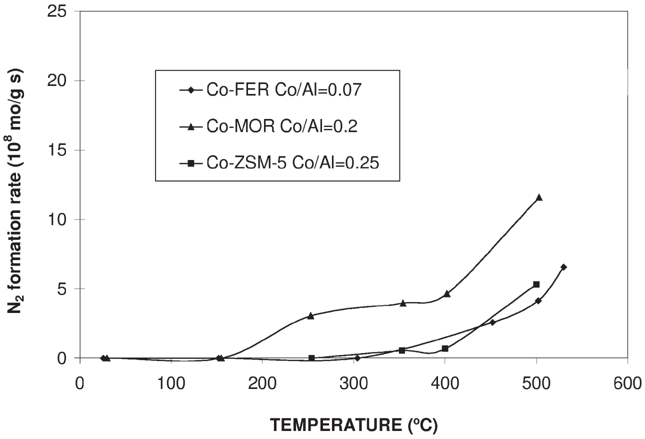

Figure 8. N_2 formation rate over Co-loaded zeolites. The reaction was run on a 50 mg sample with a feed containing 750 ppm NO_2, 300 ppm methane, 2.5% O_2, balance He. The feed used on Co-ZSM-5 contained 1000 ppm NO_2, 300 ppm CH_4, 2.5% O_2. GHSV = 60,000.

reach a minimum between about 500 °C. Methane combustion rate increases at higher temperatures and is proportional to Co loading, as expected from previously reported results [1,2].

In the empty reactor no nitrogen was formed, but methane conversion increased with temperature to about 450 °C (see figure 7) and then decreased to obtain almost no conversion at 600 °C. This result suggests that NO_2 should be supplying virtually all of the oxygen required for methane combustion. The trend observed on H-zeolites, compared to the empty reactor in figure 7, and the fact that almost no N_2 was produced in the homogeneous reaction, demonstrate that the formation of nitrogen is the result of the interaction of methane with adsorbed NO_2.

Nitrogen formation rates for a 100 cm^3/min feed containing 750 ppm NO_2, 300 ppm CH_4 and 2.5% O_2 on 50 mg samples of different cobalt-loaded zeolites are compared in figure 8. It is interesting to observe that nitrogen formation rate is enhanced over Co-MOR-6-40. Besides, although having different Co loads, the formation of nitrogen over Co-FER-11-14 is similar to Co-ZSM5-14-50 suggesting, again, that conversion of N_2 occurs on the support rather that on the cobalt ions. The corresponding curves for methane combustion over these materials are shown in figure 9. Under these conditions, the temperatures at which the increasing methane combustion profile starts on each zeolite type are lower than those observed in figures 2, 4 and 6. The differences observed may be due to different experimental conditions used. Furthermore, it can be observed that the order of methane combustion is MOR > ZSM-5 > FER, which is consistent with previous observations [3] related to the different channel systems of these zeolites.

In order to determine intrinsic activities of acid sites in H-MOR, H-FER and H-ZSM-5, the rates of nitrogen formation and methane combustion were determined using 25 mg samples and a 100 cm^3/min feed mixture containing 1000 ppm NO_2, 300 ppm CH_4 and 2.5% O_2. The results in figure 10 show higher nitrogen formation rates over H-MOR, and, within experimental error, these rates

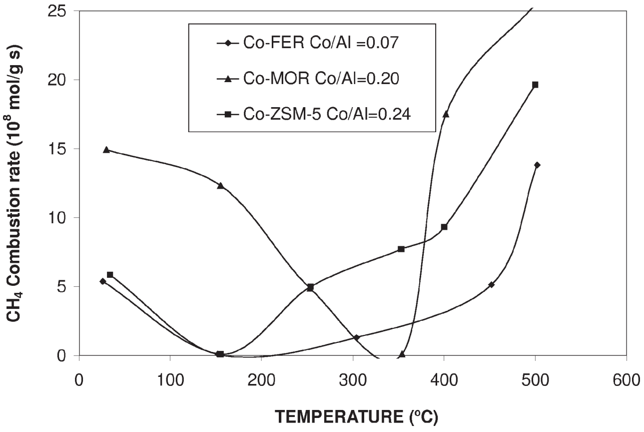

Figure 9. Methane combustion rate versus temperature over Co-loaded zeolites. The reaction was run on a 50 mg sample with a feed containing 750 ppm NO_2, 300 ppm methane, 2.5% O_2, balance He. The feed used on Co-ZSM-5 contained 1000 ppm NO_2, 300 ppm CH_4, 2.5% O_2. GHSV = 60,000.

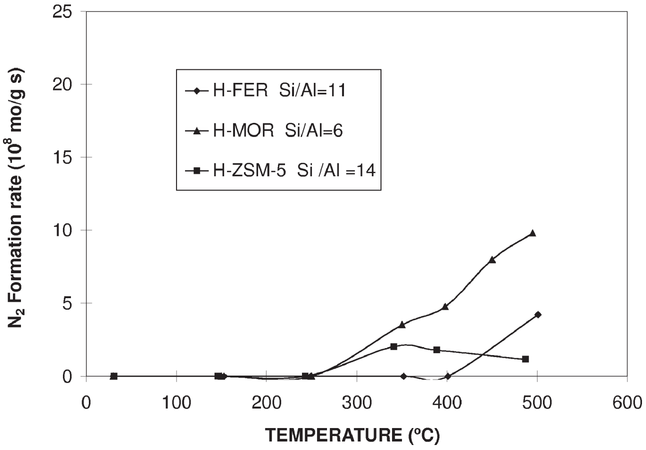

Figure 10. N_2 formation rate versus temperature over H-zeolites. The reaction was run on a 25 mg sample with a feed containing 1000 ppm NO_2, 300 ppm methane, 2.5% O_2, balance He. GHSV = 120,000.

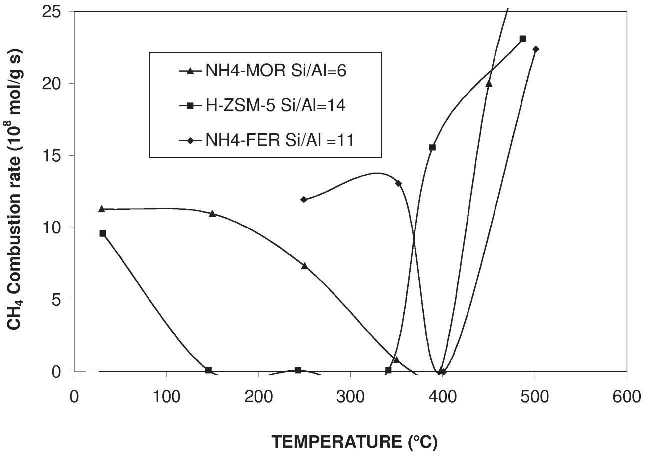

Figure 11. Methane combustion rate versus temperature over H-zeolites. The reaction was run on a 25 mg sample with a feed containing 1000 ppm NO_2, 300 ppm methane, 2.5% O_2, balance He. GHSV = 120,000.

are similar to those obtained over Co-MOR-6-40 confirming that acidity is essential for the SCR of NOx with methane. Figure 11 illustrates the corresponding rates of methane combustion. At this high space velocity enhanced methane combustion rates are observed on these materials as compared to Co-zeolites over the temperature range studied.

Table 2 shows the apparent activation energies for N_2 formation and methane combustion at GHSV 60,000 and 120,000. The lowest apparent activation energies for N_2 formation are obtained over the supported mordenite materials. It is interesting to observe that diffusion limitations appear to be stronger over ferrierite supported catalysts, likely due to the 8- and 10-ring channel system of this zeolite. The apparent activation energies shown in table 2 for methane combustion were calculated from the portions of the curves where the rates increase with temperature. As observed in table 2, the apparent activation energies decrease with cobalt loading on each zeolite type. At temperatures lower than 450–500 °C, the rate of methane combustion is high and decreases with increasing temperature. The apparent negative activation energy suggests that methane combustion is non-catalytic and may be caused by the rapid non-selective reaction of strongly adsorbed NO_2 in the zeolite pores with methane to produce mainly NO. As the temperature is increased, adsorption of NO_2 becomes weaker and both NO and N_2 are produced leading to a decrease in methane combustion.

Table 2
Apparent activation energies for N_2 formation and CH_4 combustion over H- and Co-zeolites.

Catalyst	E_{app} for N_2 production (kcal/mol)		E_{app} for CH_4 combustion (kcal/mol)	
	GHSV = 60,000	GHSV = 120,000	GHSV = 60,000	GHSV = 120,000
NH_4-MOR	4.22	6.84	34.81	22.35
Co-MOR-6-40	4.02	–	33.59	–
Co-MOR-6-48	3.28	3.72	17.51	–
NH_4-ZSM-5	16.35	–	29.40	33.33
Co-ZSM5-14-50	9.46	–	43.72	–
Co-ZSM5-14-74	5.89	–	15.20	–
NH_4-FER	19.04	13.03	44.05	32.26
Co-FER-11-14	21.40	11.19	–	–
Co-FER-11-20	24.70	10.29	–	15.17

4. Discussion

The present work shows that the selective catalytic reaction of NO_2 with methane proceeds via two different reaction pathways at low and high temperatures. In agreement with previous observations [18], it is likely that NO_2 or its adsorbed precursors initiate the reaction of methane at low temperatures. As proposed before [18,19], the interaction of methane and NO_2 is probably a homogeneous heterogeneous process at low temperatures over the tested catalysts. Figure 7 demonstrates that this reaction requires a catalyst at our reaction conditions, because the homogeneous reaction of NO_2 led to methane combustion but no N_2 was formed. At high temperatures, homogeneous radical reactions involving both NO and NO_2 were suggested [18,19] to be rate determining. Besides, the oxidation of methane by oxygen is probably an initial reaction step in the SCR process at high temperatures. Although methane combustion by O_2 can proceed homogeneously, this process requires a catalyst at our reaction conditions.

Reduction of NO_2 takes place at high NO_2/methane ratios over the zeolites studied. Under these conditions NO_2 conversions to N_2 are below 20%. However, methane conversions show two different trends, at low and high temperatures. At temperatures below 450–500 °C, conversions decrease with temperature giving apparent negative activation energies, likely due to non-selective reaction between adsorbed NO_2 and methane to produce mainly NO. Depending on the operating conditions and the type of catalyst, there is a temperature at which methane combustion starts to increase with increasing temperature.

The reduction of NO_2 over Co-zeolites does not significantly differ from that reported [1,2] for NO. Probably because in the presence of methane NO_2 is rapidly converted to NO. Nitrogen production rates over H-zeolites are higher using NO_2 rather than NO, likely due to higher surface coverages of adsorbed NO_2. At low temperatures N_2 formation rates are enhanced on H-zeolites compared to the corresponding Co-zeolites suggesting that reduction of NO_2 occurs at the support acid sites. As the temperature increases, equilibrium favors NO_2 decomposition to NO and the activity of Co-zeolites increases. Studies of NO oxidation indicate [1–3,20,21] that NO oxidation occurs at the metal-ion sites. Therefore, it suggests that metal sites are required to reoxidize NO and maintain a continuous supply of adsorbed NO_2 species as the temperature increases. On the other side, metal sites are also active for metane combustion by oxygen. In general, we did not observe appreciable changes in the oxygen concentration with increasing temperature. Therefore, we speculate that methane mainly reacted with the adsorbed oxygen released from the decomposition of NO_2 to NO and O as the temperature increased.

5. Conclusions

- Two reaction pathways, at low and high temperatures, appear to be involved in the lean selective catalytic reaction of NO_2 by methane over Co-zeolites.
- Reduction of NO_2 to N_2 occurs on the support rather than on the cobalt sites and appears to be proportional to the support acidity.
- Since NO_2 decomposition to NO and oxygen is favored as the temperature increases, cobalt sites may reoxidize NO back to NO_2. Therefore, acid and metal sites are required for the SCR of NOx with methane.

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