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CoZSM-5: Why This Catalyst Selectively Reduces NO_x with Methane

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Methane oxidation with NO_2, NO, O_2 catalyzed by CoZSM-5 and CuZSM-5 was studied, as well as NO oxidation with O_2 to form NO_2. The efficacy of NO, NO_2, and O_2 for the oxidation of CH_4 has been evaluated. CuZSM-5 is very active for combustion and it is thus the dominant pathway for NO_x SCR with CH_4. CoZSM-5 is much less active than CuZSM-5 for the same reaction. Although CH_4 conversion with NO_2 is approximately the same for both catalysts, the paths of NO_2 conversion differ dramatically. Whereas with CoZSM-5, 50% of NO_2 converts to N_2 in the presence of CH_4 at temperatures below 450°C, only 10% of NO_2 is converted to N_2 with CuZSM-5. However, the selectivity toward N_2 for CuZSM-5 increases with temperature and reaches approximately 50% at 600°C. Despite the completely different behavior of both catalysts in the $CH_4 + NO_2$ reaction they are equally selective for the $CH_4 + NO$ reaction: only CO_2 and N_2 form but CuZSM-5 was more active.

The catalytic behavior of CuZSM-5 and CoZSM-5 under SCR conditions with CH_4 is related to the unique chemistry of Cu and Co species in the host ZSM-5. In CuZSM-5, dispersed Cu oxide clusters are highly active in a direct (reaction with O_2) and an indirect (reaction with NO_2 to form NO followed by its oxidation with O_2) methane combustion. The different intrinsic ability of Cu^{2+} and Co^{2+} ions to activate NO_x results in the formation of an adsorbed species that is reactive toward gaseous CH_4 and also has a significant impact on the origin of CoZSM-5's ability to selectively reduce NO_x with methane. © 1999 Academic Press

Key Words: **CoZSM-5; CuZSM-5; NO_x SCR; CH_4; oxide clusters; NO oxidation; kinetic isotope effect.**

INTRODUCTION

Developing methods to eliminate nitrogen oxides (NO_x) from stationary and mobile combustion exhaust streams has been a challenge since the late 1950s. The conversion of NO_x to N_2 with reducing agents such as CO (1–3), NH_3 (4–8), and hydrocarbons (9–11) has been studied using a variety of catalysts ranging from metals to metal oxides and zeolites. Particularly challenging has been the development of a catalyst that will selectively reduce NO_x with a low concentration of a reductant in the presence of a large excess of oxygen. Currently, NH_3 is used as the reductant in power plants (4, 12–14), but it is highly toxic. Hydrocarbons are viable and desirable replacements for NH_3, and many reports have shown that zeolites catalyze this selective reduction with C_1–C_4 hydrocarbons (15–31). Researchers have pursued possible reaction mechanisms for catalysts including zeolites (32–55). However, the reason why methane, a readily available reductant at power plants, is effective with only a few zeolite catalysts has not been clarified.

The specific type of zeolite (24) and charge compensating cations have a large impact on the preferential reaction of the reductant (e.g., hydrocarbon) with NO_x rather than with the excess O_2. For example, Iwamoto reported that CuZSM-5 was efficient for selective catalytic reduction (SCR) with C_3 hydrocarbon (58). Further investigations have shown that CuZSM-5 is efficient for reactions involving C_{2+} olefins (27, 30, 36, 37, 39, 43) and paraffins (30, 32, 40, 43, 45), but it is completely unselective when CH_4 is used (31, 57). However, Co containing ZSM-5, ferrierite, and mordenites (58–59), and a few other catalysts such as NiZSM-5, GaZSM-5, and InZSM-5 (24, 60, 61) are selective for NO_x reduction with CH_4. The reasons for the effective performance of the Co systems and for the inefficacy of CuZSM-5 for the SCR of NO_x with CH_4 remain uncertain.

The C–H bond cleavage to form methyl radicals catalyzed by CoZSM-5 is the rate determining step (RDS) of the NO_x SCR (62). Hence, elementary steps after the RDS are key to controlling selectivity. Witzel and Hall studied the catalytic properties of a series of zeolites for NO reduction by HCs containing up to nine carbons (63). Rather than viewing the reaction mechanism as a selective catalytic reduction (SCR), it was proposed that the process is more appropriately described as a competitive oxidation of hydrocarbons by three oxidants (NO, NO_2, O_2) (63). Thus, the relative rates of the parallel reactions that consume CH_3 radicals determine the selectivity toward N_2.

Why CuZSM-5 is unselective may be determined by evaluating the competitive oxidation proposed for CoZSM-5 to the CuZSM-5 system. The present study was designed to elucidate why CoZSM-5 selectively reduces NO_x in the presence of excess O_2 with CH_4. A new perspective on the mechanism is developed by comparing CoZSM-5 with

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CuZSM-5 for reactions in which CH_4 is oxidized by NO, NO_2, and O_2. This complex system is clarified by reacting each oxidant, individually, with CH_4 and with isotopic tracers.

EXPERIMENTAL

Catalyst Preparation

NaZSM-5, CoZSM-5, and CuZSM-5 catalysts were used in this investigation. The NaZSM-5 (template free) was provided by Air Products and Chemicals and was used as received. The CuZSM-5 and CoZSM-5 were prepared from the NaZSM-5 by ion-exchange as follows. Fifteen grams of the NaZSM-5 were added to 1500 ml of 0.02 M aqueous solution of $Co(OAc)_2$ (Aldrich) with pH 7.0 or to 0.01 M solution of $Cu(OAc)_2$ (Aldrich) with pH 6.0. The pH of the starting solution was adjusted by adding acetic acid. The mixture was stirred for 24 h at 80°C. Then, the solid was recovered by filtration and washed three times with 500 ml of distilled H_2O. In the case of CuZSM-5, the entire ion-exchange procedure was repeated three times. Finally, the material was dried overnight in atmospheric air at 80°C. The catalyst compositions were analyzed using ICP (Co, Na, Si, Al) and XRF (Cu) (Galbraith Laboratories). The Si/Al ratio (10.8) and ion exchange levels (100, 70, and 103% based on M^{n+}/nAl ratio for NaZSM-5, CoZSM-5, and CuZSM-5, respectively) were calculated from the weight percentages.

Gases

The NO and NO_2 (each 1% in He, 99.5% purity), CH_4 (1% in He, 99.97% purity, higher hydrocarbon impurity was <1% of CH_4), O_2 (10% in He, 99.994% purity), and He (99.999% purity) were obtained from Praxair and were used as received. The deuterated methane (CD_4, 99% CD_4, deuterium purity >98%) was provided by Cambridge Isotope Laboratories in a 3 liter cylinder at atmospheric pressure. It was subsequently pressurized with He to achieve a final concentration of 1% CD_4 in He. Analysis by gas chromatography showed no detectable impurities in the CD_4 and NO_2 tanks, while the NO tank contained impurities of CO_2 (~0.0075%) and N_2O (~0.01%).

Kinetics Experiment

Prior to each experiment, all samples were pretreated *in situ* with 2.5% O_2 (balance He) flowing at 75 cm^3/min (GHSV $\approx$ 42,000 h^{-1}). During this pretreatment, the temperature was increased to 500°C at 4°C/min, stablilized there for 14 h, and then cooled to room temperature.

Methane (deuteromethane) oxidation with O_2, NO, or NO_2, as well as NO oxidation with O_2 were conducted at 200–600 ± 1°C in a quartz reactor. A stainless steel gas line was used to supply a continuous flow to the quartz U-tube reactor (inner diameter 4 mm) which contained 50 mg of catalyst. A gas mixture of 2000 ppm CH_4 (CD_4) and 2000 ppm NO (NO_2) or 2.5% O_2 in He or a mixture of 2000 ppm NO and 2.5% O_2 in He at atmospheric pressure was introduced into the reactor at a flow rate of 75 ml min^{-1}. To minimize the homogeneous gas phase reaction of NO and O_2 that is thermodynamically favorable below 500°C, the free space between the reactor and the NO/NO_x analyzer was minimized to 12.6 cm^3 ($t = 0.21$ min). The homogeneous oxidation of NO to NO_2 that occurred in this volume at 25°C was approximately 1.6%.

NO_2, NO, N_2O, N_2, CO, CO_2 were the only products for all reactions studied. Effluent NO and NO_2 were analyzed with a chemiluminiscent NO/NO_x analyzer (Rosemount Analytical Model 955). All other products were analyzed by gas chromatography (Varian GC 3300). Nitrogen, N_2O, O_2, CO, and CO_2 were quantified with an Alltech 6′ CTR I column connected to a TCD and a Supelco 30′ Chromosorb P AW column connected to a FID was used to quantify the hydrocarbons.

As the primary goal of the investigation was to determine reaction rates and kinetic isotope effects, the conversion was maintained under 10% so that rate data were obtained in the differential regime. Steady state conversion at each temperature was defined by consecutive measurements in which the standard deviation in CH_4 concentration was less than 0.6% of the average value. The NO/NO_x analyzer (maximum error was 2.6% conversion) recorded continuous measurements. In this case steady state was defined as a deviation of less than 1.3% in conversion after 20 min.

RESULTS

NO Oxidation

Figure 1 shows the oxidation of NO to NO_2 in the presence of excess O_2 when catalyzed by CoZSM-5, CuZSM-5, and NaZSM-5. A maximum conversion of 2.4% at room temperature and 5% at 200°C due to homogeneous oxidation (64) is evident from the empty reactor experiment. The activity of the NaZSM-5 was approximately the same as that for the empty reactor. The other two zeolites, CuZSM-5 and CoZSM-5, exhibited higher activity and similar qualitative behavior. At temperatures less than 375°C, the conversion was substantially below equilibrium. The NO conversion reached a maximum of 35% for CuZSM-5 and 26% for CoZSM-5 at approximately 375°C. Thermodynamic equilibrium was achieved in the temperature range of 400–450°C for both catalysts and was obeyed thereafter. The error associated with each point includes the homogeneous conversion at room temperature (~1.6%). Thus, the data above the equilibrium curve are within experimental error.

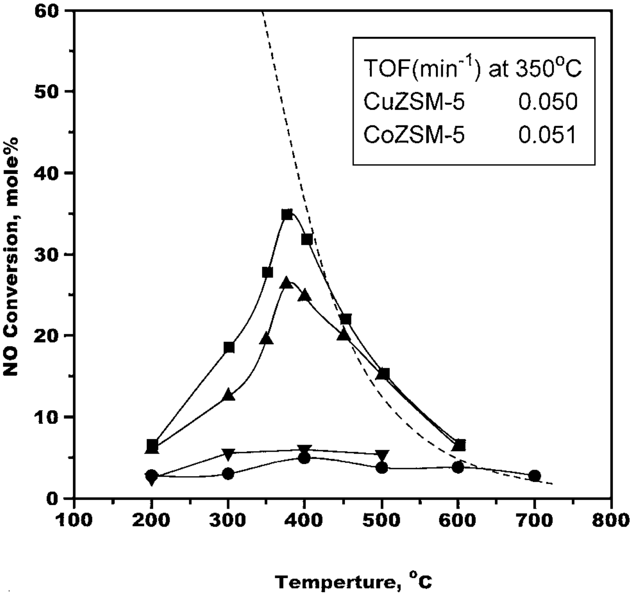

FIG. 1. NO oxidation with oxygen over CuZSM-5 (■), CoZSM-5 (▲), and NaZSM-5 (▼) catalysts and in the empty reactor (●). The dotted curve represents the thermodynamic equilibrium. Inset: Turnover frequency on a per metal ion basis at 350°C for Cu and CoZSM-5 samples.

CH_4 Oxidation by O_2 (Combustion)

While the activity of Cu and CoZSM-5 for NO oxidation by O_2 was similar, their ability to oxidize CH_4 with O_2 differed substantially. This comparison is shown in Fig. 2. The temperature at which the conversion reached 1%, the "light-off temperature," for the CuZSM-5 catalyst was 312°C. This was 115°C lower than the light-off temperature for CoZSM-5. At the temperature where NO oxidation to NO_2 was at a maximum (400°C, Fig. 1), the rate of combustion was approximately 13% for CuZSM-5 and below the detection limit for CoZSM-5. The CH_4 conversion with CoZSM-5 reached 43% at 600°C and it was nearly 95% for CuZSM-5. In the absence of a catalyst, conversions were below the detection limit of the GC (0.2%) for reaction temperatures up to 600°C.

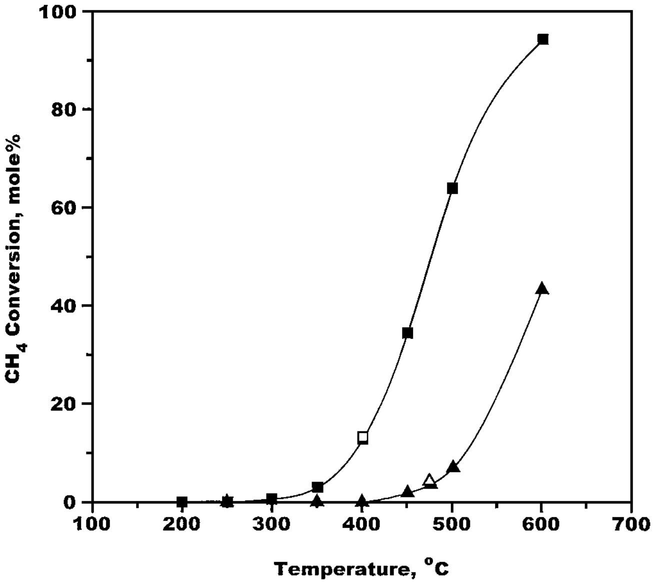

FIG. 2. Methane combustion over CuZSM-5 (■) and CoZSM-5 (▲) catalysts. Open symbols refer to the measurements performed after reaction at 600°C.

TABLE 1

Kinetic Isotope Effect for the Methane Oxidation with Oxygen

Catalyst	T, °C	r_{CH_4} μ mol min^{-1} g^{-1}	r_{CD_4} μ mol min^{-1} g^{-1}	r_{CH_4}/r_{CD_4}
CuZSM-5	350	3.6	1.5	2.4
	370	7.5	2.9	2.6
	400	15.7	7.7	2.0
CoZSM-5	426	1.1	0.6	1.9
	450	2.3	1.2	1.9
	476	4.4	2.5	1.8
	500	8.6	4.9	1.8

After the catalyst was held at 600°C for 40 min, the reaction temperature was lowered. This resulted in a conversion equal to the value previously measured. In Fig. 2 the open symbols correspond to measurements taken after the temperature was lowered to 400°C for CuZSM-5 and to 475°C for CoZSM-5. This result shows that the catalyst did not change irreversibly while the temperature was increased. Replacing CH_4 with CD_4 had a pronounced effect on the combustion rate. The ratios of hydrocarbon conversion rates (r_{CH_4}/r_{CD_4}) were 1.8–2.6 for both catalysts (Table 1).

CH_4 Oxidation by NO_2

The stoichiometry of the $CH_4 + NO_2$ reaction to form N_2 requires that one CH_4 molecule is consumed for every two molecules of NO_2 converted to N_2. Accordingly, a maximum of 1000 ppm of CH_4 will react with 2000 ppm of NO_2, placing a theoretical limit for CH_4 conversion of 50% for equal feed concentrations. The highest CH_4 conversions obtained were 38 and 37% for CoZSM-5 and CuZSM-5, respectively (Fig. 3). However, as shown in Fig. 3A (CuZSM-5), the CH_4 conversion catalyzed by CuZSM-5 was higher than the allowed stoichiometric ratio of 1 CH_4 molecule converted for 2 NO_2. The light-off temperature for CH_4 conversion was also lower (340°C) than that for NO_2 conversion to N_2 (370°C). In contrast, the ratio of CH_4 to NO_2 conversions was approximately equal for the CoZSM-5 up to 450°C, and the same light-off temperature of 290°C was observed (Fig. 3B). Above 450°C with CoZSM-5, the conversion to N_2 decreased while the conversion of CH_4 remained essentially constant.

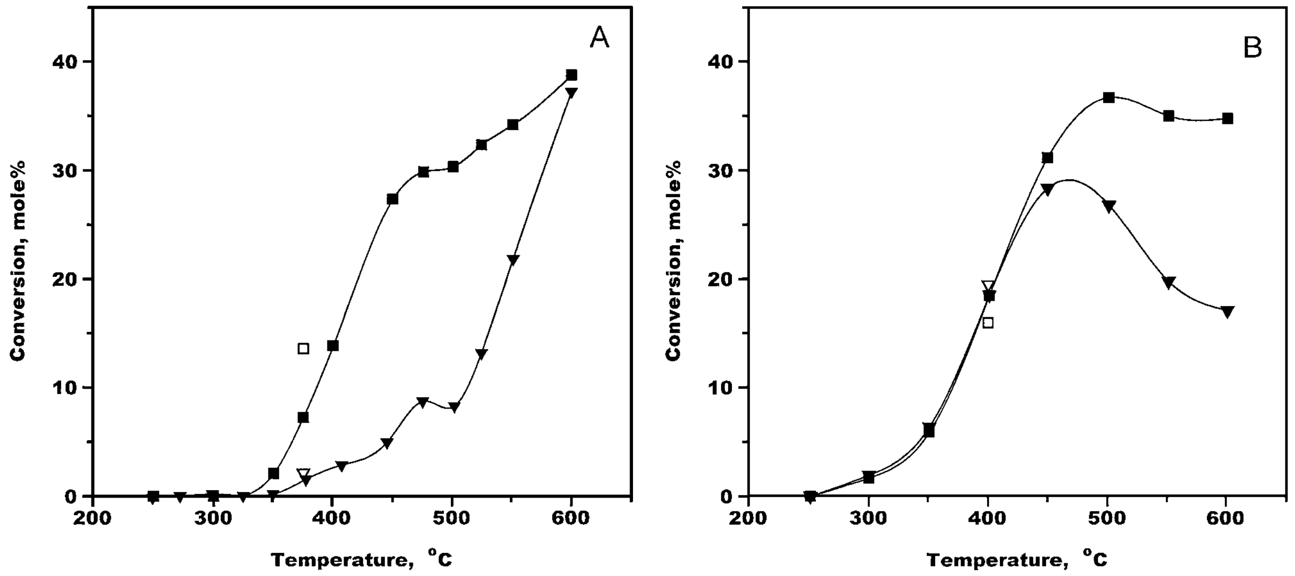

FIG. 3. Methane oxidation with NO_2 over CuZSM-5 (A) and CoZSM-5 (B) catalysts. ▼, the conversion of NO_2 to N_2; ■, the conversion of CH_4 to CO_x. Open symbols refer to the measurements performed after reaction at 600°C.

The conversion of NO_2 to N_2 as a function of temperature exhibited an absolute maximum for the CoZSM-5 and a local maximum for the CuZSM-5. The NO_2 conversion to N_2 for CoZSM-5 (Fig. 3B) progressed to a maximum of 28% at 450°C and then decreased to 17% at 600°C. The maximum for CuZSM-5 at 475°C was not as distinct (Fig. 3A). After the reaction temperature reached 500°C, the NO_2 conversion increased again to 38% at 600°C.

The decrease in conversion with CoZSM-5 was not due to deactivation. The open symbols correspond to the conversions measured after the temperature was increased to 600°C and lowered to 375°C for CuZSM-5 and 400°C for CoZSM-5. The same conversions, within experimental error, were obtained with CoZSM-5. In the case of CuZSM-5, the CH_4 conversion increased by 6%, but the NO_2 conversion into N_2 remained essentially the same. Thus, the behavior was reversible with temperature for CoZSM-5 whereas CuZSM-5 changed irreversibly only for CH_4 oxidation.

This reaction behavior has been clarified in the context of previous research. The typical dependence of NO_x conversion into N_2 vs temperature under conditions of SCR can be described as follows (17, 18, 26, 61, 65–69). First the conversion increases with temperature to approximately 500°C and decreases at higher temperatures due to a lack of NO_2, because at higher temperatures thermodynamic equilibrium of the reaction $NO_2 \Leftrightarrow NO + 1/2\ O_2$ favors NO formation. Thus, the conversion of NO_2 into N_2 shown in Fig. 3A for CuZSM-5 is simply a superimposition of two reactions: NO_2 conversion into N_2 and NO and NO conversion into N_2 (Fig. 4). The rate of the latter reaction becomes significant at temperatures above 500°C (Fig. 4). Because oxygen released in the NO_2 decomposition reaction is consumed to oxidize CH_4, the maximum dependence of CH_4 conversion to CO_x on temperature is less pronounced (Fig. 3A). It would be difficult to observe a maximum in NO_2 conversion into N_2 under conditions of the $CH_4 + NO_x + O_2$ reaction, because at temperatures above 500°C the reactivity of molecular oxygen toward CH_4 is much higher than NO. No more N_2 forms under these conditions.

As for the $CH_4 + NO_2$ reaction catalyzed by CoZSM-5, the decrease in NO_2 conversion to N_2 as the temperature increases above 450°C (Fig. 3B) can be interpreted in terms of an increased impact of NO_2 conversion into NO compared with NO_2 conversion into N_2 (68). The fact that increasing the temperature does not increase N_2 selectivity can be attributed to the impact of the $CH_4 + NO$ reaction. CoZSM-5 is less active for this reaction. However, the selectivity toward N_2 increased again at temperatures above 600°C (68).

CH_4 Oxidation by NO

When NO was the oxidant, CuZSM-5 was more active than CoZSM-5 (Fig. 4). The difference was most pronounced in the temperature range from 375–550°C. The light-off temperature for NO conversion was lower for CuZSM-5 (270°C) than for CoZSM-5 (330°C). A similar trend was observed for CH_4 conversion. The reaction stoichiometry was $CH_4 : NO = 1 : 4$ for both catalysts. For CuZSM-5, there was a local maximum at 450°C, and the NO conversion increased again at temperatures greater than 500°C (Fig. 4). A hysterisis was observed for CH_4 and NO conversions with CuZSM-5 when the temperature was lowered after 40 min at 600°C. This indicated that the catalyst

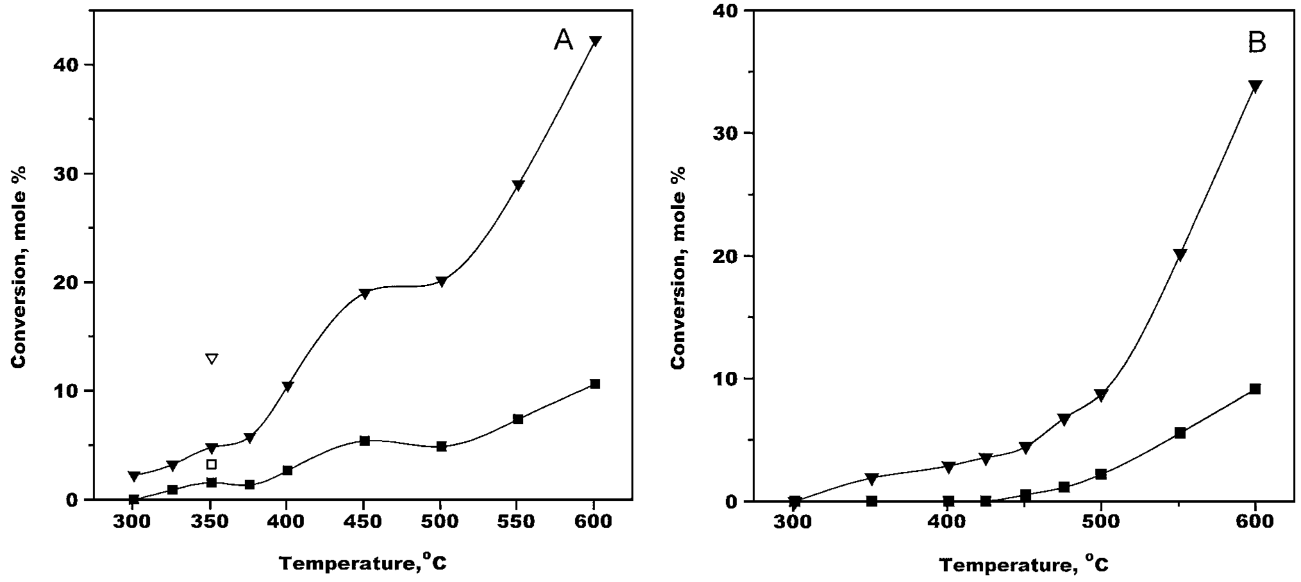

FIG. 4. Methane oxidation with NO over CuZSM-5 (A) and CoZSM-5 (B) catalysts. ▼, the conversion of NO to N_2; ■, the conversion of CH_4 to CO_x. Open symbols refer to the measurements performed after reaction at 600°C.

underwent an irreversible change that resulted in a higher activity.

Isotope experiments were performed for the CH_4 reaction with NO. Table 2 lists the rate ratios for the $CH_4 + NO$ and $CD_4 + NO$ reactions with respect to CH_4 conversion to CO_x (Column 3) and NO conversion to N_2 (Column 4) catalyzed by CuZSM-5 and CoZSM-5, respectively. A value of ~2.5 was established for CH_4 conversion ($CH_4 + NO$) over CuZSM-5 in the range of 351–401°C (Table 2) and the ratios were within 0.5 of those obtained for CH_4 combustion ($CH_4 + O_2$) (Table 1). For the formation of N_2 catalyzed by CuZSM-5, the rate ratio of 1.3 was observed, substantially lower than that for CH_4 conversion. With CoZSM-5 (Table 2), the rate ratio of ~1.3 for CH_4 conversion was ~0.5 lower than that for CH_4 combustion (Table 1). Also, the rate ratios for CH_4 conversion were similar to those for N_2 formation when catalyzed by CoZSM-5.

Lastly, another nitrogen-containing product, N_2O, was observed for the $CH_4 + NO$ reaction. Figure 5 shows the concentration of N_2O as a function of temperature for the two catalysts. The concentration of N_2O reached a maximum at 375°C with CuZSM-5 (a small amount of N_2O was present in the feed). Figure 5 and Table 2 demonstrate the

TABLE 2

Kinetic Isotope Effect for the Methane Oxidation with NO

Catalyst	T, °C	r_{CH_4}/r_{CD_4}	$r_{N_2(CH_4)}/r_{N_2(CD_4)}$	$r_{N_2O(CH_4)}/r_{N_2O(CD_4)}$
CuZSM-5	301	—	1.1	1.4
	326	—	1.4	1.6
	351	2.5	1.3	1.3
	401	2.4	1.3	1.0
	451	1.3	—	—
CoZSM-5	401	—	1.2	1.1
	425	—	2.0	0.7
	451	—	1.3	1.1
	476	1.2	1.3	—
	500	1.3	1.0	1.1
	551	1.3	—	—

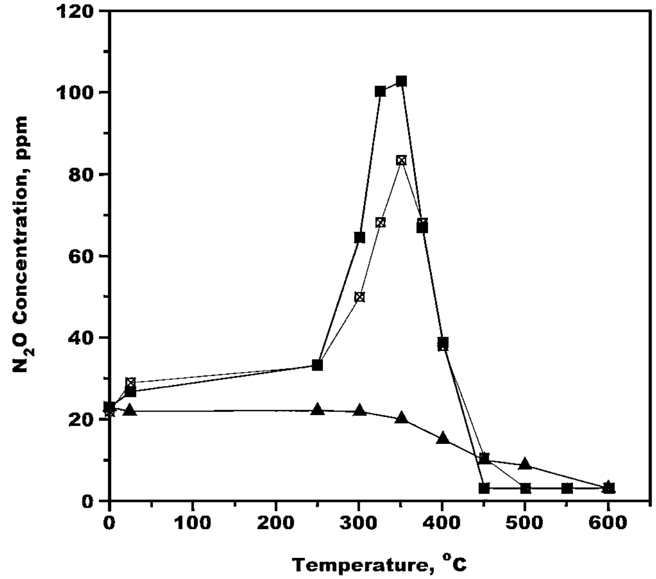

FIG. 5. N_2O concentration vs temperature during CH_4 (■, ▲) and CD_4 (☒) oxidation with NO over CuZSM-5 (■, ☒) and CoZSM-5 (▲) catalysts. N_2O concentration at 0°C refers to the feed concentration.

rates of N_2O formation depended on whether CH_4 or CD_4 was used as a reactant. For CoZSM-5, the concentration of N_2O decreased as a function of temperature.

DISCUSSION

Nature of the Catalyst

The term "excessively ion-exchanged" was introduced in 1989 by Iwamoto *et al.* as a signature of Cu-containing zeolites that showed high activity for NO decomposition (70). Typically, when metal ions are introduced by means of ion-exchange into zeolites with a relatively high Si/Al ratio, isolated metal ions form after high temperature oxidation (71). For CuZSM-5 this was confirmed by ESR (72–74). However, there are at least two copper–oxygen species in stoichiometric and excessively exchanged CuZSM-5 after calcination in O_2 at 773 K: CuO and $[Cu–O–Cu]^{2+}$ (35 , 75, 76). Even samples with less than 70% exchanged have a redox capacity (77), suggesting that copper–oxygen species are present in under-exchanged CuZSM-5.

Similar to CuZSM-5, excessively exchanged CoZSM-5 ($Co^{2+}/Al = 0.75$) forms metal oxide species (Co_3O_4 and perhaps $[Co^{2+}–O–Co^{2+}]^{2+}$) during pretreatment with O_2 in addition to isolated Co^{2+} ions (78). However, stoichiometric and underexchange samples ($Co^{2+}/Al < 0.5$) contain only Co^{2+}; neither crystalline Co_3O_4 nor CoO are detectable by XRD or TPR (79–80). The lack of "bulk" Co_3O_4 for ratios $Co^{2+}/Al < 1$ was confirmed by magnetic susceptibility measurement (81). Thus, it is reasonable to suggest that the fraction of Co oxide species is much lower than Cu oxide species in ZSM-5 with a comparable degree of ion exchange. One can also anticipate that more oxide clusters form for both Cu and CoZSM-5 under conditions of NO_x selective catalytic reduction or complete hydrocarbon oxidation because water formed during the reaction hydrolyzes M^{2+}–OZ bonds. The importance of these oxide species for different reactions of CH_4 oxidation will be discussed below.

NO Oxidation by O_2

It has been emphasized in the literature that most likely NO_2, rather than NO, is the nitrogen-containing species participating in the steps following CH_4 activation (20, 21, 24, 40, 45, 58, 63, 69, 82–86). Oxidation of NO by O_2 to form NO_2 is effectively catalyzed by HZSM-5 (83, 84, 87, 88), HMOR (89, 90), FeMOR (89), CuMOR (89), CuX (91), CuZSM-5 (36, 83), Cu/Al_2O_3 (83), CoZSM-5 (88, 92), and Co/SiO_2 (88). The NaZSM-5 exhibits negligible activity (61, 66, 88, 93), although Co-NaZSM-5 and Cu-NaZSM-5 decompose NO_2 comparably, the reverse reaction of NO oxidation (94).

The nature of sites responsible for NO oxidation are possibly the Lewis acid sites of the zeolite. In this case, O_2 adsorbs onto the acid site and is activated by the electrostatic polarization induced by the zeolite framework. Gas phase NO molecules attack the activated oxygen to form NO_2 (95). Several authors have presented evidence supporting this role of the zeolite for the $NO + O_2$ reaction, rather than the presence of transition metal ions in NO oxidation (45, 61, 87, 96). However, Co^{2+} ions also are responsible for NO oxidation over CoZSM-5 catalysts (92, 97, 98). NO oxidation can occur on both zeolite Lewis sites and transition metal ions, as well as on dispersed oxide particles. Under the reaction conditions employed in the present investigation, NO oxidation to NO_2 is not expected to be the rate determining step (68). Thus, the results for NO oxidation by O_2 obtained in the present work are consistent with those available in literature. The CuZSM-5 and CoZSM-5 catalysts cannot be expected to react similarly in NO_x SCR based on their close activity in the $NO + O_2$ reaction.

Methane Combustion

It is well established that the activity of bulk Co_3O_4 in CH_4 oxidation by O_2 at temperatures between 300 and 500°C is almost two orders of magnitude higher than that of bulk CuO (99), consistent with the strength of the metal–oxygen bond in these solids (100, 101). However, CuZSM-5 is more active than CoZSM-5 (Fig. 2), in agreement with previously published investigations (63, 68, 79, 81, 92, 102). This difference in activity for the bulk oxide in comparison to the zeolite systems can be explained in terms of the fraction of metal in the form of ions or metal oxide clusters. In general, the catalytic activity for total oxidation reactions catalyzed by oxides is significantly higher than that of metal ions in zeolites. For example, the TOFs for CO oxidation catalyzed by bulk oxides are four orders of magnitude higher than CuY and CoY with low metal loadings (103). Such significant differences in the activity of the metal cation in contrast to the metal oxide might be due to several factors (103): (i) limitations imposed on electron transfer between the metal cations in a zeolite framework, (ii) the effect of the ligand field in altering the energy required for electron donations from the cation, and (iii) changes in the metal to oxygen bonding in the surface layer of the catalyst.

In a consecutive reaction mechanism of CH_4 combustion, the bonding of one diatomic oxygen molecule to the catalyst requires the transfer of four electrons from a catalyst to oxygen atoms. Bonding one oxygen atom to a CH_4 molecule results in the back transfer of two electrons to the active site. Given that the complete oxidation of one CH_4 molecule to form CO_2 and H_2O requires two molecules of O_2, it is not likely that isolated metal cations can provide this high rate of multielectron transfer. This suggests that the difference in activity for complete oxidation of CH_4 catalyzed by CuZSM-5 and CoZSM-5 is related to the concentration of bulk metal oxide. The higher concentration of oxide in CuZSM-5 (35, 75–77), compared to CoZSM-5 (78–80), accounts for the higher activity of CuZSM-5.

Methane Oxidation by NO_2

The results of CH_4 oxidation by NO_2 catalyzed by CuZSM-5 and CoZSM-5 (Figs. 3A and 3B) demonstrate that CH_4 conversions to carbon oxides are similar at temperatures between 300 and 450°C. However, the difference in the N_2 yields is significant. These results confirm previous research on the nonselective nature of copper ions (18, 24, 31, 58). Although NO_2 is the only oxidant in the feed stream, several overall reactions must be considered:

$$CH_4 + 2NO_2 \rightarrow CO_2 + N_2 + 2H_2O \quad [1]$$

$$4CH_4 + 6NO_2 \rightarrow 4CO + 3N_2 + 8H_2O \quad [2]$$

$$CH_4 + 4NO_2 \rightarrow CO_2 + 4NO + 2H_2O \quad [3]$$

$$CH_4 + 3NO_2 \rightarrow CO + 3NO + 2H_2O \quad [4]$$

With both Cu and CoZSM-5, carbon monoxide does not form at NO_2 conversions far from 100%. Thus, only reactions [1] and [3] need to be taken into account. The stoichiometry of reaction [1] requires that two molecules of NO_2 are consumed for each CH_4. Results from the present investigation and others show that it is only 1 : 1 for CoZSM-5 at temperatures below 450°C (63, 68, 69, 85). For CuZSM-5 the ratio is approximately 0.2 : 1 at temperatures between 350 and 450°C and increases to 1 : 1 as the temperature increases to 600°C (Fig. 3). Therefore, the nonselective reaction [3] in which NO is formed impacts more strongly on the overall CH_4 conversion catalyzed by CuZSM-5 compared with that of CoZSM-5 at temperatures below 500°C.

Previous research has suggested that the reduction of NO_2 to N_2 with CH_4 occurs on isolated Co ions (79, 92, 97, 104, 105). Much less is known about the interaction of CH_4 and NO_2 to form NO (reaction [3]). One possibility, as proposed by Hall and co-workers (63, 68, 85), is that CH_4 is activated by the catalyst surface to form "free" radicals:

$$CH_4(g) + NO_2(ads) \rightarrow CH_3^{\bullet}(g) + NO(ads) + HO^{\bullet}(g) \quad [5]$$

with subsequent oxidation of methyl radicals in the gas phase. This is supported by observations that (i) NO_2 can oxidize methane in the gas phase with no N_2 formation (68, 85); (ii) the kinetics of NO_x SCR by CH_4 is consistent with the formation of free methyl radicals (68); and (iii) typical catalysts for oxidative methane coupling, which generate $CH_3^{\bullet}$ radical intermediate (106–109) exhibit activity in NO_x SCR reactions (110–112). However, the light-off temperature of reaction [3] is only 350°C for both CuZSM-5 and CoZSM-5 catalysts (Fig. 3). A significant impact of gas phase free radical reactions on the overall conversion at temperatures below 500°C is not expected. At such low temperatures the kinetic energy of a methane molecule is not likely to remain high enough after it hits the surface and the C–H bond dissoicates to allow such reactive species as methyl radicals to desorb from the surface. The typical temperatures of methane coupling are 600–800°C (113, 114), and at these conditions methyl radicals are "hot" enough that desorption significantly impacts the homogeneous steps of the reaction (115). This interpretation is supported by the selectivity of NO_x toward N_2 in the reaction of $CH_4 + NO + O_2$ catalyzed by HZSM-5. It is close to 100% at temperatures below 500°C (68, 82, 85), suggesting that free radical reactions, which decrease the selectivity of SCR process, are insignificant.

It is interesting that CH_4 oxidation by NO_2 to form NO under conditions of SCR ($NO + O_2 + CH_4$ mixture) is similar to CH_4 oxidation with O_2; in both reactions only O_2 is consumed. In reaction [3] NO is released and can be oxidized easily by molecular oxygen to form NO_2 which will further oxidize CH_4. The cycle in which NO_2 acts as a "catalyst" is then repeated. The correlation between catalytic activity for complete oxidation of CH_4 by O_2 and by NO_2 to form NO suggests that these two reactions may occur on the same surface species, namely on dispersed metal oxide clusters. The high selectivity of HZSM-5 in NO_x SCR with CH_4 is consistent with this hypothesis, because HZSM-5 does not contain metal oxide clusters (68, 82, 85). Thus, it can be concluded that the higher fraction of Cu oxide in the zeolite in comparison to the fraction of Co oxide contributes to the degree to which these two catalysts accelerate the combustion pathway. This interpretation, of course, does not exclude the participation of metal cations. In particular, CuZSM-5 is unselective for NO_x SCR with CH_4 even when only Cu ions are present. Other researchers have suggested that NO_y adsorbed on Cu^{2+} are much less reactive toward gas phase CH_4 than NO_y adsorbed on Co^{2+} (79).

Methane Oxidation by NO

Both CuZSM-5 and CoZSM-5 can catalyze CH_4 oxidation by NO to form N_2 in the absence of O_2 with the following stoichiometry (31, 58, 68, 69, 97):

$$CH_4 + 4NO \rightarrow CO_2 + 2N_2. \quad [6]$$

This is consistent with results of the present study (Fig. 4). The $CH_4 + NO$ reaction is the least studied NO_x reduction reaction in SCR, as its significance is questionable when O_2 is present in the reaction mixture. Nevertheless clarification of how this reaction occurs can be useful to understand general trends of NO_x SCR with CH_4.

In the present study, both CH_4 and CD_4 were used as a reductant of NO to determine whether these methane molecules react at different rates over CuZSM-5 and CoZSM-5. A significant difference in rate (a factor of 2 or more, depending on the reaction temperature) would demonstrate a primary deuterium kinetic isotope effect (116). A high KIE value when CD_4 was used as the reductant in methane combustion instead of CH_4 (Table 1) suggests that the C–H bond scission is the rate determining step in methane combustion. This is consistent with the results published previously (101). The results in Table 2 indicate that a KIE is present for methane oxidation by NO catalyzed by CuZSM-5 at 351 and 401°C with its value being close to the theoretical prediction. However, the low value and the absence of a distinct temperature dependence for $r_{N_2(CH_4)}/r_{N_2(CD_4)}$ and $r_{N_2O(CH_4)}/r_{N_2O(CD_4)}$ ratios suggest that no KIE is present during the formation of nitrogen-containing products. For the same reasons, a KIE would not be suggested for the reaction of methane oxidation with NO over CoZSM-5 (Table 2).

The C–H bond rupture is most likely the rate determining step of methane oxidation by NO catalyzed by CuZSM-5 at temperatures below 450°C, but not by CoZSM-5. These experimental observations can be understood as follows. CuZSM-5 is an active catalyst for NO decomposition at temperatures above 300°C (32, 65, 70, 117–119), and the multiatomic Cu_n sites are required (120, 121); N_2O is formed as an intermediate (122). CoZSM-5 exhibits negligible activity for NO decomposition (31, 58, 94, 97, 119). Thus, CH_4 oxidation over CuZSM-5 may occur by two paths: first is NO decomposition followed by N_2 formation and second is CH_4 oxidation by O_2 generated during NO decomposition. If the rate of NO decomposition is higher than methane oxidation, the rate of CO_2 formation would depend on whether CH_4 or CD_4 is used, the rates of formation of N_2 and N_2O would not. In the case of CoZSM-5 it is reasonable to suggest that the $CH_4 + NO$ reaction proceeds by means of the Mars–van Krevelen mechanism with active site reoxidation by NO being the rate determining step (123). Nevertheless, it has also been suggested (97) that the $CH_4 + NO$ reaction over CoZSM-5 might proceed as

$$3NO \rightarrow NO_2 + N_2O \qquad [7]$$

followed by CH_4 oxidation by NO_2. However, no NO disproportionation was observed (94) with CoZSM-5 in the absence of O_2. Moreover, CoZSM-5 is a less active catalyst than CuZSM-5 for nitrous oxide decomposition (58, 124, 125). If N_2O formed under conditions of methane oxidation with NO, it would be experimentally detectable.

Some experimental results obtained in the present study for CuZSM-5 need additional consideration. These are (i) the unexpectedly low value of the KIE for $CH_4 + NO$ reaction at 451°C (Table 2), (ii) the absence of N_2O in effluent reaction mixture at temperatures above 450°C (Fig. 5), and (iii) the presence of a maximum at 450°C in the correlation between conversion in the $CH_4 + NO$ reaction vs temperature for both CO_2 and N_2 yield (Fig. 4A). The first two observations suggest that two mechanisms of methane oxidation with NO, low temperature and high temperature, might exist in the case of CuZSM-5. The low-temperature mechanism has been described above; the high-temperature one might be the same as for CoZSM-5. However, the reason for the maxima shown in Fig. 4A still remains unclear.

CONCLUSIONS

There have been many investigations devoted to the selective catalytic reduction of NO_x catalyzed by CuZSM-5 and CoZSM-5. However, the present investigation has clarified another facet of this important reaction, namely why the Co catalyst is selective toward the formation N_2 when CH_4 is the reductant in comparison with the Cu catalyst. Most significant is the extent to which CH_4 combustion catalyzed by CuZSM-5 impacts the overall CH_4 conversion during NO_x reduction in the presence of O_2. CuZSM-5 catalysts possess a larger fraction of Cu oxides than Cu ions in comparison to CoZSM-5. These dispersed oxide clusters readily catalyze direct (reaction with O_2) and indirect (reaction with NO_2 to form NO followed by its oxidation with O_2) methane combustion. Thus, higher concentrations of metal oxides will lower the selectivity toward N_2. It can also be acknowledged that the intrinsic ability of Cu^{2+} and Co^{2+} ions to activate NO_x to form an adsorbed species that is reactive toward gaseous CH_4 can also play a significant role in the origin of CoZSM-5's ability to selectively reduce NO_x with CH_4.

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