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Selective Catalytic Reduction (SCR) of NO with Methane over CoZSM-5 and HZSM-5 Zeolites: On the Role of Free Radicals and Competitive Oxidation Reactions

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The reactions of CH_4 with NO, NO_2, and O_2, and with the mixtures of $NO_x + O_2$, were studied over CoZSM-5 and HZSM-5 zeolites. Based on the comparison of the "light-off" temperatures as well as the activation energies of these reactions, a conclusion is drawn that over both catalysts at temperatures below 500°C NO reduction into N_2 and CH_4 oxidation into CO_x are coupled and initiated by the reaction of CH_4 with NO_2. The results demonstrate that this reaction may be considered as a limiting reaction step of NO_2 reduction into N_2, and of the SCR reaction for the mixture of $CH_4 + NO + O_2$ when O_2 is present in large amounts. With the latter mixture when O_2 concentration is relatively low (up to about 1.5%) another reaction step, namely, the catalytic oxidation of NO by O_2 into NO_2 appears to control the rate of the SCR process. Thus, an important role of O_2 is to convert NO into NO_2. At low temperatures (below 400°C) O_2 does not compete with NO_x for CH_4, but even at these temperatures O_2 participates in oxidation of the intermediate reaction species decreasing in this way the selectivity of the SCR process. At higher temperatures (above 450°C) a strong competition between O_2 and NO_x for CH_4 is observed and this results in a further decrease in the process selectivity. It is shown that the higher SCR selectivity of HZSM-5 catalyst in comparison with CoZSM-5 is due to the stronger competition between O_2 and NO_2 for CH_4 over the latter catalyst. The effects of space velocity and reactor size were briefly explored. These results show that the reaction pathways are the same for both catalysts studied in this work. Based on these, and literature results, the formation of $CH_3\cdot$ free radical is postulated and possible reactions of this radical with NO_x and O_2, that form the pathways of the SCR process, are considered. Finally, the possible role of gas phase reactions in the SCR process is discussed.

INTRODUCTION

Reduction of NO_x (nitric oxide and nitrogen dioxide) to N_2 by hydrocarbons in the presence of excess oxygen (SCR) is potentially a very important process for environmental catalysis (1–3). This reaction proceeds with relatively high rates over a number of ZSM-5 catalysts with various metal cations and has been the subject of numerous investigations during the last several years. Most of this work has been performed on CuZSM-5 catalysts with C_2+ hydrocarbons as reductants (see reviews (2, 3)), but more recently, CoZSM-5 and HZSM-5 zeolites were reported (4–7) to be effective catalysts for the SCR of NO using CH_4 as the reductant. It was shown that O_2 greatly enhances the NO conversion into N_2, and an important role of NO_2 in the initiation of the SCR process over these and other ZSM-5 based catalysts has been delineated (6–15). Hence, the possibilities exist that either NO_2 or O_2 dominates in the initiation process. Evidence favoring the former has been presented (9–15), but the reaction of CH_4 with O_2 alone was not included in these studies. In addition, it has been suggested (7) that it might be better to look at SCR as a competitive co-oxidation of methane with NO_x and O_2, rather than as a selective reduction of NO in the presence of oxygen, i.e., to shift the focus from reduction of NO into N_2 to the competitive oxidation of hydrocarbons by NO_x and O_2. In the present work, the reactions of CH_4 over CoZSM-5 and HZSM-5 zeolites with the mixtures of $NO + O_2$ and $NO_2 + O_2$ have been studied and compared with the three oxidizing components tested separately. The same reactions were studied over NaZSM-5 zeolite. Based on these results possible pathways of the SCR process over CoZSM-5 and HZSM-5 catalysts have been suggested. The chemistry developed has led to a microscopic kinetic treatment that formally yields very similar results to those for the macroscopic reaction model used by Li and Armor (16) for CoFerr.

EXPERIMENTAL

The reactions were carried out in the steady state flow mode as in earlier work (15, 17). Three catalysts CoZSM-5, HZSM-5 and NaZSM-5 (Si/Al = 11) were studied in this work. The cation exchange level was 98% and 100% for CoZSM-5 and HZSM-5, respectively. The catalyst preparation and the standard pretreatment in O_2 used prior to

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reaction have been described previously (15, 17). Pretreatment was in flowing O_2 at increasing temperatures to 773 K for 12 h. The feed comprised CH_4 (0.28%), NO (0.21%) or NO_2 (0.21%), and/or O_2 (2.6%) in He. The flow rate was 75 ml/min and the gas hourly space velocity (GHSV) was varied between 4,500 and 225,000 h^{-1} by changing the weight of catalyst samples from 500 to 9 mg. The gases used were all of >99.9% purity.

RESULTS AND DISCUSSION

Reactions of CH_4 with Different Oxidizing Compounds

Figure 1 shows the effect of temperature and feed composition on the conversion of NO_x into N_2 and of CH_4 into CO_x over CoZSM-5 and HZSM-5 catalysts at a GHSV of 45,000 and 9,000 h^{-1}, respectively. These data demonstrate the very similar behavior of the two catalysts studied (note, however, that the CoZSM-5 was reacting at five times the SVH of the HZSM-5) and indicate that for every reaction of CH_4 with NO_x in the presence or absence of O_2 the "light-off" temperature of methane combustion coincides with the temperature at which N_2 formation is initiated. In the presence of O_2 this temperature was about 350°C regardless of the nitrogen oxide used. Moreover, in the absence of O_2 "light-off" occurred with NO_2 at the same temperature, but with NO 500° and 600°C were required for CoZSM-5 and HZSM-5 catalysts, respectively. Similarly, in the absence of NO_x, oxidation of CH_4 by O_2 was observed only above 450° and 500°C, respectively (see Figs. 1B and 1D).

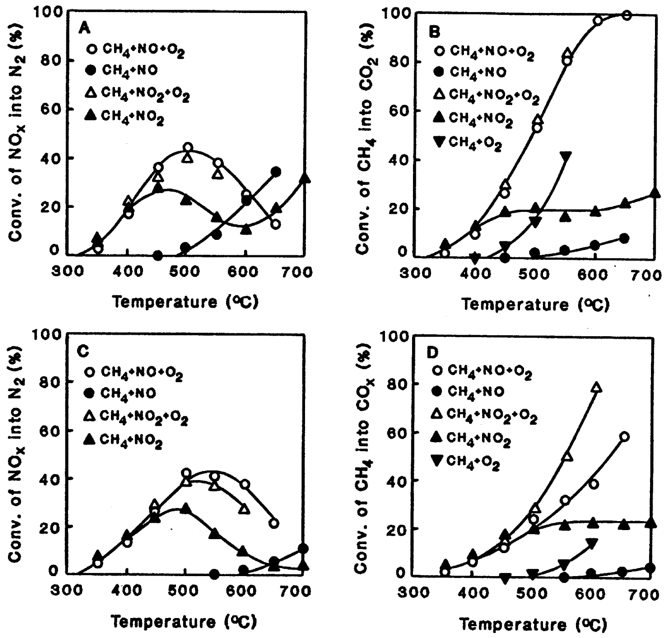

FIG. 1. Reactions of CH_4 with different oxidizing compounds over CoZSM-5 (A, B) and HZSM-5 (C, D) catalysts: conversion of NO_x into N_2 (A, C) and of CH_4 into CO_x (B, D) as function of temperature. Catalyst weight was 50 and 250 mg for CoZSM-5 and HZSM-5 samples, respectively. Feed contained 0.28% CH_4, 0.21% NO or 0.21% NO_2 (when used), and 2.6% O_2 (when used) in He at a flow rate of 75 ml/min.

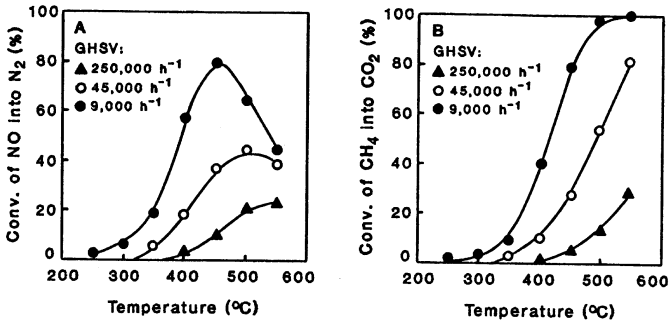

FIG. 2. Effect of temperature and space velocity on the conversion of NO into N_2 (A) and of CH_4 into CO_2 (B) over CoZSM-5 catalyst. Feed contained 0.21% NO, 0.28% CH_4 and 2.6% O_2 in He at a flow rate of 75 ml/min.

The observed values of the "light-off" temperature of CH_4 catalytic combustion and of the temperature at which N_2 formation is initiated should be a function of the space velocity. Figure 2 and Table 1 confirm this expectation and show that the temperature shifts caused by the space velocity change are the same for all reactions studied. Taken together with the fact that over CoZSM-5 (18) and HZSM-5 (14) catalysts NO can be oxidized by O_2 into NO_2 at temperatures as low as 200–300°C, our results suggest that the SCR of NO into N_2 and CH_4 oxidation into CO_x are coupled and initiated by NO_2 reaction with CH_4. There is ample IR evidence showing that strongly adsorbed NO_2 is formed and exists on the surface of Cu- and CoZSM-5 and reaction temperatures (18, 24). On the other hand one would not expect CH_4 to adsorb nondissociatively under these conditions. Therefore it will be assumed that CH_4 (g) reacts with NO_2

TABLE 1

Effect of Space Velocity and Feed Composition on the "Light-Off" Temperature (°C) at Which N_2 Formation is Initiated over CoZSM-5 Catalyst

		GHSV (h^{-1})		
Feed[a]	Reaction	22,500	45,000	250,000
$CH_4 + NO$	NO into N_2	450°C	500°C	550°C
	CH_4 into CO_2	450°	500°	550°
$CH_4 + NO + O_2$	NO into N_2	300°	350°	400°
	CH_4 into CO_2	300°	350°	400°
$CH_4 + NO_2$	NO_2 into N_2	300°	350°	400°
	CH_4 into CO_2	300°	350°	400°
$CH_4 + NO_2 + O_2$	NO_2 into N_2	300°	350°	—
	CH_4 into CO_2	300°	350°	—
$CH_4 + O_2$	CH_4 into CO_2	400°	450°	500°

[a] Feed contained 0.28% CH_4, 0.21% NO or 0.21% NO_2 (when used) and 2.6% O_2 (when used) in He at a flow rate of 75 ml/min.

(ads) to initiate the reaction. This idea is supported by the work of Cant and co-workers (19, 20) who showed a first order isotope effect on the rates of both methane coupling and N_2 formation by SCR over CoZSM-5 when CD_4 was substituted for CH_4. This pinpoints the rate determining step as the breaking of a CH vs a CD bond in the formation of $CH_3\cdot$ in both reactions.

Reaction of CH_4 with NO_2

It follows from the above results that the interaction of CH_4 with NO_2 is a key reaction step in the SCR process. Consequently, this reaction was studied in detail and some typical results are shown in Fig. 3. Previously, we have found (15) that in the absence of methane, NO_2 decomposes into $NO + \frac{1}{2}O_2$ over CoZSM-5 and HZSM-5 catalysts at temperatures higher than about 350°C. At 400°C this reaction under our conditions produces comparable amounts of NO and NO_2. With methane in the feed additional reactions occur (Fig. 3): (i) reduction into NO, and (ii) reduction into N_2. The O_2 formed during these reactions and by disproportionation of NO_2 is used to oxidize CH_4 into CO_2 over CoZSM-5 or into $CO_2 + CO$ over HZSM-5. The highest conversion of NO_2 was reduction into NO. At low temperatures (300–400°C) the rate of this reaction, as determined under conditions of a differential reactor, was about two times higher than the rate of N_2 formation (Table 2). With increasing temperature (see Figs. 3A, 3B and 3C) the concentration of O_2 first increased to about 400°C and then decreased, and at temperatures higher than 500°C oxygen was not observed in the reaction products. Simultaneously, the total conversion of NO_2 (into NO and N_2) reached 100%. An increase in temperature above 500°C resulted in an increase in formation of NO at the expense of N_2. Perhaps this behavior resulted from the gas phase reaction of NO_2 with CH_4 (Fig. 3D). This reaction occurred at temperatures higher than 450°C and increased in rate steeply with temperature, producing NO only; N_2 formation was not observed (15).

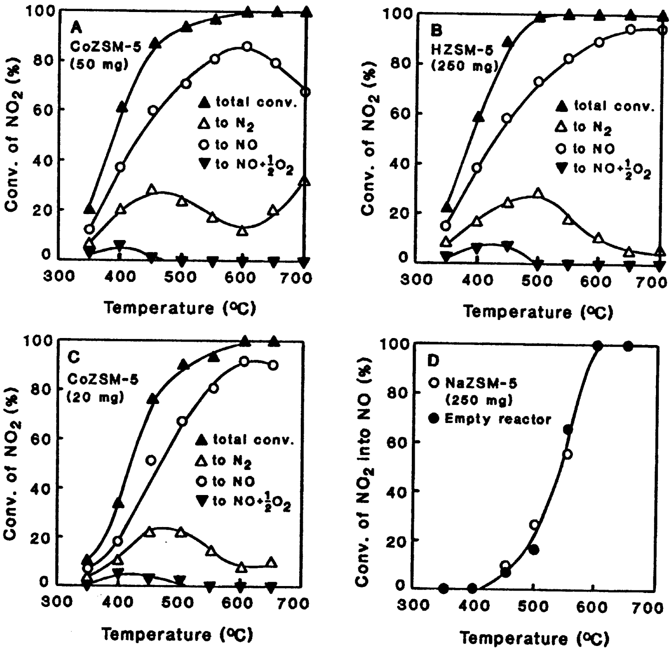

FIG. 3. Conversion of NO_2 into different products by reaction with CH_4 over CoZSM-5 (A, C), HZSM-5 (B) and NaZSM-5 (D) catalysts, and in the empty reactor (D). Catalyst weight was 50 mg (A), 250 mg (B, D) and 20 mg (C). Feed contained 0.21% NO_2 and 0.28% CH_4 in He at a flow rate of 75 ml/min. Data obtained in the empty reactor were taken from Ref. 15.

TABLE 2

Activation Energies and Differential Rates (μmol/g min) of NO_2 Reduction and of CH_4 Oxidation over CoZSM-5 and HZSM-5 Catalysts[a]

	Temperature (°C)				E_a
	300	350	400	450	(kcal/mol)
CoZSM-5					
A. Rate of NO_2 to N_2	2.0	8.8	37.4	—	22
B. Rate of NO_2 to NO	3.4	17.8	64.8	—	22
C. Rate of CH_4 to CO_2	1.9	8.3	34.9	—	22
HZSM-5					
D. Rate of NO_2 to N_2	—	2.5	5.7	11.0	13.5
E. Rate of NO_2 to NO	—	5.4	12.9	29.5	14
F. Rate of CH_4 to CO_2	—	2.7	5.6	12.0	13.5

[a] Feed contained 0.21% NO_2 and 0.28% CH_4 in He at a flow rate of 75 ml/min.

It is clear from Fig. 3 that formation of NO and N_2 is initiated at the same temperature. Moreover, Table 2 demonstrates that both reactions proceed with the same activation energy. Taken together, these two facts lead us to the conclusion that reactions of NO_2 reduction into NO and N_2 are coupled and have the same limiting step, namely, the activation of methane by NO_2. Figs. 3A, 3B and 3C as well as Table 2 demonstrate that at temperatures up to 400°C the ratios of the rates of conversion of NO_2 into NO and N_2 do not change significantly and are near 2. With further increase in temperature more NO_2 is converted into NO at the expense of the N_2 formed. This shows that, while the limiting step is the same for both reactions, the pathways of these reactions include different reaction steps and, consequently, different intermediate species. The last statement agrees completely with the previously reported data (15) on the homogeneous reaction between CH_4 and NO_2 where formation of NO only was observed.

Additional information on the reaction system ($NO_2 +$ CH_4) follows from Fig. 3A. These data were obtained over CoZSM-5 catalyst at a GHSV of 45,000 h^{-1}. As shown in Fig. 1A, at this space velocity and at temperatures higher than 500°C the direct reaction between NO and CH_4 occurs resulting in N_2 formation. Obviously, this reaction occurs also in the system of $NO_2 + CH_4$ and explains a decrease in NO_2 conversion into NO and a corresponding increase in NO_2 conversion into N_2 observed at temperatures higher than 600°C (see Figs. 1A and 3A). However, in the SCR of NO_x in the presence of O_2, the reaction between NO and CH_4 does not play a significant role since it proceeds only at high temperatures and with rates much lower than the rate of CH_4 oxidation by O_2.

SCR of NO with CH_4 in the Presence of O_2 as a Competitive Oxidation of CH_4

An important role of O_2 in the SCR process is to convert NO into NO_2. This view stems from the above discussion as well as the literature (8–18) and is further supported by Fig. 4 where NO conversion into N_2 is shown to depend strongly on the O_2 concentration up to values of about 1.5% O_2. At higher O_2 concentrations NO conversion into N_2 becomes invariant with O_2 concentration. Similar results were obtained earlier over CoZSM-5 catalysts by Li and Armor (4) and by Petunchi *et al.* (17) over CuZSM-5 using i-C_4H_{10}. In these cases the leveling off of NO conversion into N_2 at high O_2 concentrations was not explained. In contrast to NO, NO_2 conversion into N_2 is completely independent of O_2 content in the feed (solid points of Fig. 4).

These results show that O_2 does not play an appreciable role in the initiation process when NO_2 is present in the feed stream (the same conclusion follows from Fig. 1). With NO in the feed, the presence of O_2 is required for NO_2 formation. In this case, an increase in O_2 concentration up to about 1.5% results in an increase in the rate of NO_2 formation and, consequently, in an increase in its concentration. In this range of O_2 concentrations the rate of NO oxidation by O_2 into NO_2 controls the rate of the overall process. At a certain O_2 concentration (under our conditions, at about 2%) the rate of NO_2 formation exceeds the rate of NO_2 consumption and a change of the limiting step of the SCR process occurs. At this point the reaction of NO_2 with CH_4 becomes the rate limiting step of the overall process, and a further increase in O_2 concentration does not alter the observed rate (Fig. 4).

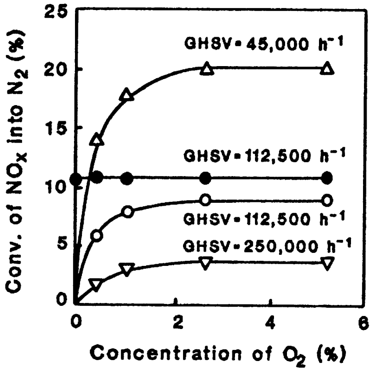

FIG. 4. Effect of O_2 concentration and space velocity on the conversion of NO_x into N_2 over CoZSM-5 catalyst at 400°C. Feed contained 0.28% CH_4, 0.21% NO or 0.21% NO_2 (solid points), and x% O_2 in He at a flow rate of 75 ml/min.

TABLE 3

Activation Energies and Differential Rates (μmol/g min) of NO Reduction and of CH_4 Oxidation during the SCR Reaction over CoZSM-5 and HZSM-5 Catalysts[a]

	Temperature (°C)						E_a
	350	400	450	500	550	600	(kcal/mol)
CoZSM-5							
A. NO reduction rate[b]	6.4	27	78	173	188	—	21
B. CH_4 oxidation rate[b]	3.9	18	54	140	300	—	21
C. CH_4 oxidation rate[c]	0.30	1.8	8.8	37	115	—	31
D. Ratio B/C	13.0	10.0	6.1	3.8	2.6	—	
HZSM-5							
E. NO reduction rate[b]	1.8	4.2	8.4	15.9	18.3	17.3	14.5
F. CH_4 oxidation rate[b]	1.0	2.4	5.0	9.5	15.0	19.5	14
G. CH_4 oxidation rate[c]	n.d.	n.d.	0.17	0.61	1.8	5.3	29
H. Ratio F/G	—	—	29.4	15.6	8.3	3.7	

Note. The flow rate was 75 ml/min.

[a] Feed stream contained 0.21% NO + 0.28% CH_4 + 2.6% O_2 in He.

[b] SCR reaction.

[c] For CH_4 oxidation by O_2 alone (0.28% CH_4 + 2.6% O_2 in He were used).

n.d., no data available; because of low conversion of CH_4 rates could not be determined accurately.

The data presented above clearly demonstrate that the SCR process (coupled reactions of NO_x reduction into N_2 and of CH_4 oxidation by NO_x into CO_x) is initiated by reaction of CH_4 with NO_2. At the same time, Fig. 1 shows that not only NO_x but O_2 also may participate in CH_4 oxidation. The ratio of these rates is critical for the selectivity of the SCR process. Hence, it was of interest to compare quantitatively the rate of CH_4 oxidation by O_2 alone with the rate of CH_4 oxidation in the course of the SCR process, i.e., by the mixture of NO_x and O_2. Of course, it was also interesting to compare the rate of the latter reaction with the rate of NO_x reduction into N_2, since such a comparison will provide additional information about the relationship between transformations of NO_x into N_2 and of CH_4 into CO_x. The absolute rates of CH_4 oxidation by O_2 are compared with those occurring in the SCR process in Table 3. The rates of these reactions were determined under differential reaction conditions. Several points should be made in connection with these data. *First*, the Arrhenius dependence for the rate of NO reduction into N_2 is valid up to about 500°C, i.e., in the temperature range where thermodynamics favors NO_2 over NO (9, 21). At higher temperatures formation of NO_2 from NO and O_2 becomes less favorable and this explains the bending of the Arrhenius plot (not shown) at higher temperatures. *Second*, CH_4 oxidation into CO_x and NO reduction into N_2 proceed with the same activation energy and comparable rates showing that these two reactions are coupled and have the same rate limiting step. Moreover, the observed activation energies of the SCR process over CoZSM-5 and HZSM-5 catalysts (about 21 and 14 kcal/mol, respectively) coincide within experimental error with the activation energies observed over these two catalysts for the reaction of NO_2 with CH_4 (see Table 2). Based on this latter fact we can conclude that the SCR of NO with CH_4 in the presence of excess O_2 is initiated by the reaction of NO_2 with CH_4 and that this reaction is the rate limiting step of the overall process. *Third*, the activation energy of the SCR reaction is higher with CoZSM-5 catalyst than with HZSM-5, and reaction of CH_4 with O_2 has much the highest activation energy, explaining the decrease in selectivity for N_2 formation with increasing temperature (7). Interestingly, the value of the activation energy determined in this work for the SCR process over CoZSM-5 catalyst coincides with that (22 kcal/mol) reported by Li and Armor (22) for the SCR process over Co-ferrierite catalyst. *Finally*, Table 3 shows that at low temperatures the rates of CH_4 oxidation by O_2 alone are much lower than the rates of CH_4 oxidation during the SCR reaction, e.g., at 400°C with CoZSM-5 catalyst the difference between these rates is about 10 times. With increasing temperatures this difference diminishes. In considering Table 3 recall that the rate of CH_4 oxidation during the SCR process includes a contribution from CH_4 oxidation by O_2 alone. However, at low temperatures O_2 should not compete with NO_2 for CH_4; at high temperatures such a competition will exist and results in the observed decrease in the SCR selectivity (7).

The above statement is supported by the data of Fig. 5 which show the effect of temperature on the selectivity of the SCR process (given by the slope of the curves at any point). These data indicate that the highest selectivity of the SCR process is observed at low temperatures and low conversions of the two reactants (NO and CH_4). Interestingly, the selectivities do not differ greatly for CoZSM-5 and HZSM-5 catalysts when comparison is made at the same conversion levels. This fact is in agreement with the data in Table 3 which also show that under these conditions CH_4 should be oxidized mainly by NO_x. An increase in temperature or a decrease in NO_x concentration should lead to enhancement of the competition between NO_x and O_2 for CH_4, and, consequently, by a decrease of the SCR selectivity. Moreover, at any given temperature the difference between the rates of CH_4 oxidation by the mixture of $NO_x + O_2$ and by O_2 alone is higher for HZSM-5 catalyst than for CoZSM-5 (Table 3). Thus, the competition between NO_x and O_2 for CH_4 should be stronger in the case with CoZSM-5.

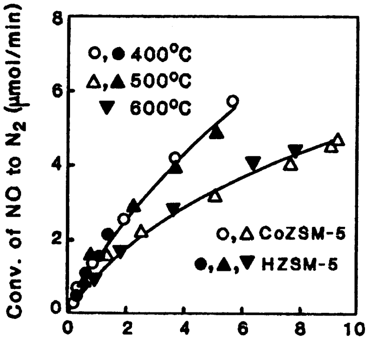

FIG. 5. Effect of temperature on the selectivity of the SCR reaction over CoZSM-5 (open symbols) and HZSM-5 (solid symbols) catalysts. Feed contained 0.28% CH_4, 0.21% NO and 2.6% O_2 in He at a flow rate of 75 ml/min (flow rates of CH_4 and NO were 9.375 and 7.03 micromol/min, respectively), and the different conversions of NO and CH_4 were obtained by changing the weight of the catalyst samples from 9 to 500 mg.

The detailed consideration of the data obtained over CoZSM-5 at 400°C indicates that the change in the SCR selectivity begins at very low NO conversions where the rate of CH_4 oxidation by NO_x is much higher than with O_2 (see Table 3, line D). Thus, a question arises concerning the possibility of a competitive reaction of NO_x vs O_2 with an intermediate species, e.g., $CH_3\cdot$. It is reasonable to think that such a competition may exist and be decisive in the control of the selectivity. For example, two separate reaction channels

$$CH_3\cdot + NO \text{ (or } NO_2) \xrightarrow{k_1} CH_3NO \text{ (or } CH_3NO_2) \rightarrow N_2 \text{ path (plus } CO_2 \text{ and } H_2O) \quad [1]$$

$$CH_3\cdot + O_2 \xrightarrow{k_2} CH_3OO\cdot \rightarrow CO_2 + H_2O \text{ path} \quad [2]$$

could control the formation of N_2 and CO_2, respectively. Pursuing this possibility an attempt has been made to describe quantitatively the rates of NO reduction to N_2 and of CH_4 oxidation to CO_2 over CoZSM-5 catalysts at 400°C. The empirical pressure dependencies of the rates on NO and CH_4 have been determined from the data shown in Fig. 6. These reaction orders are in good agreement with the results obtained over a CoZSM-5 catalyst by Li *et al.* (16). Interestingly, the dependence of the rate of NO reduction into N_2, r_{NO}, on NO pressure differs from that for CH_4 oxidation into CO_2, r_{CH_4}, but both reactions have the same dependence on CH_4 pressure. Thus the rates are expressed as

$$r_{NO} = k_3 P_{NO}^{0.45} P_{CH_4}^{0.62} \quad [3]$$

$$r_{CH_4} = k_4 P_{CH_4}^{0.62} \quad [4]$$

The fact that the two reactions have different kinetics is both interesting and significant. If Eq. [1] expresses the pathway for N_2 formation, a positive order in NO would be anticipated and if Eq. [2] describes the formation of CO_2, a zero order dependence in O_2 has been demonstrated in Fig. 4. Both reactions have the *same* dependence on CH_4 concentrations because this reflects the necessary rate determining step, viz., the formation of the common

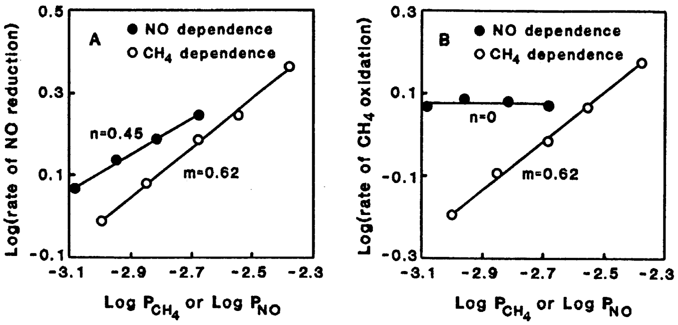

FIG. 6. Empirical orders for the rate of NO reduction into N_2 (A) and for the rate of CH_4 oxidation into CO_2 (B) with respect to NO and CH_4. Catalyst: 30 mg of CoZSM-5; GHSV = 75,000 h^{-1}; $T = 400°C$. For NO dependence the partial pressures of CH_4 and O_2 in feed were 0.0028 and 0.026 atm, respectively; for CH_4 dependence the partial pressures of NO and O_2 in feed were 0.0021 and 0.026 atm, respectively. The rates were calculated based on the conversions of the reactants in the range between 5 and 20%.

intermediate, $CH_3\cdot$, i.e.,

$$CH_4\ (g) + NO_2\ (ads) \xrightarrow{k_5} CH_3\cdot\ (g) + NO\ (ads) + HO\cdot\ (g)\ [\text{or HONO}] \quad [5]$$

Because both NO and NO_2 are stable free radicals present in relatively high concentration, methane coupling was not observed. Instead, Eqs. [1] and [2] dominate leading ultimately to the formation of N_2 and CO_2. The $HO\cdot$ formed in Eq. [5] may also attack CH_4 forming a second $CH_3\cdot$, i.e.,

$$HO\cdot + CH_4 \xrightarrow{k_6} H_2O + CH_3\cdot \quad [6]$$

Obviously, the $CH_3\cdot$ free radical can react with O_2 or with NO or with NO_2 present in the system. Moreover, the rates of these reactions may be comparable in contrast to the corresponding rates of reaction with CH_4 (Fig. 1). However, for CH_4 oxidation the ratio of the rates of reactions of $CH_3\cdot$ with different oxidizing compounds is not important, since every reaction must ultimately result in the oxidation of every $CH_3\cdot$ into CO_2 and H_2O. The situation is different for NO reduction into N_2. In this case the ratios between reactions of $CH_3\cdot$ with NO, NO_2 and O_2 are very important, since reactions of NO_x will result in N_2 formation, while the reaction with O_2 can produce CO_2 and H_2O only. Thus, it may be suggested that even at low temperatures (400°C) a competition exists between NO_x and O_2 for the $CH_3\cdot$ radicals.

Equations [3] and [4] were numerically integrated to simulate the conversions of NO into N_2 and of CH_4 into CO_2. The result of this calculation is shown as the solid line in Fig. 7. Agreement with the experimental points is satisfactory. Thus, not only the differential reaction kinetics but the kinetics in the integral reactor are adequately described by these equations.

To further simplify the kinetic analysis reactions [1] and [2] may be considered irreversible. Thus, two reaction channels are opened. One leads to N_2 as well as $CO_2 + H_2O$ and the other to only CO_2 and H_2O. We suppose (see discussion below) that N_2 is formed by NO_x reactions with the products of CH_3NO_x transformations. Thus, oxidation of one CH_4 can lead to the formation of one N_2 molecule and to the reduction of two NO molecules, i.e.,

$$CH_4 + 2NO + O_2 = CO_2 + 2H_2O + N_2 \quad [7]$$

Equation [7] shows that the selectivity when where is no contribution from Eq. [2] will be $N_2/CO_2 = 1.0$. This is the limiting slope of Fig. 7. Lower values indicate contribution from direct oxidation of CH_4 with O_2.

Before pursuing a microscopic treatment of the kinetics the physical picture must be clarified. It is known that over CoZSM-5 (18) and HZSM-5 (14) the oxidation of NO to NO_2 occurs at temperatures as low as 200–300°C. At 400°C and low conversions this means that comparable concentrations of NO and NO_2 are present in the gas phase. The NO_2/NO ratio will of course depend on the experimental conditions. However, it is well known that NO_2 is more strongly adsorbed than NO and therefore its site coverage may be assumed to be higher than that of NO, and in the steady state be effectively constant. However, Li *et al.* (16) have shown that H_2O is a strong reversible poison and hence this may limit the site coverage with NO_2. Taking these facts into account, the following relationships may be written:

$$NO_2\ (g) + S = NO_2\ (ads); \quad \theta_{NO_2} = K_{NO_2}P_{NO_2}(1-\theta) \quad [8]$$

and

$$H_2O\ (g) + S = H_2O\ (ads); \quad \theta_W = K_W P_W\,(1-\theta), \quad [9]$$

where $(1-\theta)$ is the fraction of *all* the sites that are empty and θ_{NO_2} and θ_W are the fractions covered by NO_2 (ads) and H_2O (ads), respectively, (S simply indicates an available site). Since the infrared data indicate that NO is not strongly

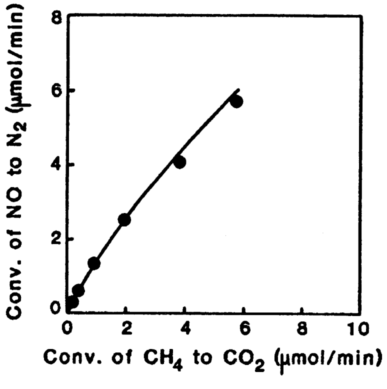

FIG. 7. Comparison of experimental (points) and simulated (curve) selectivities of the SCR reaction over CoZSM-5 at 400°C. Experimental data were derived from Fig. 5. The solid line was obtained by numerical integration of Eqs. [3] and [4].

adsorbed at 400°C (18), it will be assumed that $\theta_{\mathrm{NO}} \rightarrow$ O under our experimental conditions. It follows from Eq. [1] that

$$-r_{\mathrm{NO}} = 2r_{\mathrm{N_2}} = 2k_1\theta_{\mathrm{NO_2}}P_{\mathrm{CH_3}\cdot}. \qquad [10]$$

Li *et al.* (16) have shown that $r_{\mathrm{N_2}}$ is strongly poisoned (reversibly) by H_2O. Assuming the Langmuir description for competitive adsorption of the two strongly adsorbed species, NO_2 (ads) and H_2O (ads), we may write

$$\theta_{\mathrm{NO_2}} + \theta_{\mathrm{W}} = \frac{K_{\mathrm{W}}P_{\mathrm{W}} + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}}{1 + K_{\mathrm{W}}P_{\mathrm{W}} + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}}, \qquad [11]$$

where the subscript W stands for H_2O. Thus the $(1-\theta)$ term of Eqs. [8] and [9] can be evaluated, i.e.,

$$(1-\theta) = 1 - \frac{K_{\mathrm{W}}P_{\mathrm{W}} + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}}{1 + K_{\mathrm{W}}P_{\mathrm{W}} + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}} = \frac{1}{1 + K_{\mathrm{W}}P_{\mathrm{W}} + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}} \qquad [12]$$

It follows from Eq. [10] that

$$-r_{\mathrm{NO}} = 2r_{\mathrm{N_2}} = 2k_1\theta_{\mathrm{NO_2}}P_{\mathrm{CH_3}\cdot} = \frac{2k_1K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}P_{\mathrm{CH_3}\cdot}}{1 + K_{\mathrm{W}}P_{\mathrm{W}} + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}} \qquad [13]$$

Applying the steady state approximation to the methyl radical,

$$k_5P_{\mathrm{CH_4}}\theta_{\mathrm{NO_2}} = k_1\theta_{\mathrm{NO_2}}P_{\mathrm{CH_3}\cdot} + k_2P_{\mathrm{O_2}}P_{\mathrm{CH_3}\cdot}$$

or

$$P_{\mathrm{CH_3}\cdot} = \frac{k_5P_{\mathrm{CH_4}}\theta_{\mathrm{NO_2}}}{k_1\theta_{\mathrm{NO_2}} + k_2P_{\mathrm{O_2}}} \qquad [14]$$

Inspection of Eq. [14] shows that the problem can be greatly simplified if the second term of the denominator can be neglected, i.e., when the selectivity for N_2 formation is high. Recalling that the CO_2 and H_2O produced concomitant with N_2 formation (1 CO_2 for each N_2) should not be counted as stemming from reaction of $CH_3\cdot$ with O_2, the neglect of this term should not introduce much error. The data suggest that this should be permissible at low conversion, particularly at low temperatures, although it obviously will not be true in general. Hence, for the present purposes it will be assumed that

$$P_{\mathrm{CH_3}\cdot} \approx (k_5/k_1)P_{\mathrm{CH_4}} \qquad [15]$$

This approximation is in agreement with our observation (Fig. 5) that at 400°C and low conversion the selectivity for forming N_2 rather than CO_2 is high, i.e., most of the reaction of $CH_3\cdot$ goes via Eq. [1], not by Eq. [2]. Inserting Eq. [15] into Eq. [13] yields

$$-r_{\mathrm{NO}} = 2r_{\mathrm{N_2}} = \frac{2k_5K_{\mathrm{NO_2}}}{1 + K_{\mathrm{W}}P_{\mathrm{W}} + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}}(P_{\mathrm{NO_2}}P_{\mathrm{CH_4}}) \qquad [16]$$

This result is formally very similar to that obtained by Li *et al.* (16, 22) except that we focus on NO_2 as the key and dominant reaction intermediate leading to a free radical mechanism rather than NO.

Inverting Eq. [16] yields

$$\frac{1}{r_{\mathrm{NO}}} = \frac{1 + K_{\mathrm{W}}P_{\mathrm{W}} + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}}{2k_5K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}P_{\mathrm{CH_4}}} \qquad [17]$$

and when $P_{\mathrm{CH_4}}$ is held constant

$$\frac{1}{r_{\mathrm{NO}}} = \frac{1}{2k_5P_{\mathrm{CH_4}}} + \frac{1 + K_{\mathrm{W}}P_{\mathrm{W}}}{2k_5K_{\mathrm{NO_2}}P_{\mathrm{CH_4}}}\frac{1}{P_{\mathrm{NO_2}}} \qquad [18]$$

This equation is of the Langmuir–Hinshelwood type. It is verified by the data in Fig. 8A. When $P_{\mathrm{CH_4}}$ is held constant, P_{W} cannot vary much under differential reaction conditions. Note that the intercept is dependent on the value of $P_{\mathrm{CH_4}}$ selected to be constant.

If P_{NO} is held constant while $P_{\mathrm{CH_4}}$ is varied, the relation becomes

$$\frac{P_{\mathrm{CH_4}}}{r_{\mathrm{NO}}} = \frac{1 + K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}}{2k_5K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}} + \frac{K_{\mathrm{W}}}{2k_5K_{\mathrm{NO_2}}P_{\mathrm{NO_2}}}P_{\mathrm{W}} \qquad [19]$$

This relationship is confirmed by the linear plot shown as Fig. 8B. Here the P_{W} present was calculated from the H_2O produced in the reaction using a dry feed. It shows the effect of P_{W} on the left hand member as both the rate and H_2O formed are increased by increasing $P_{\mathrm{CH_4}}$. Shown also are related data taken from Li *et al.* (16). Both sets of data show the predicted linear dependence.

Shelef *et al.* (12) have shown that when ratios of NO_2/NO ∼40 are fed and reduced with C_3H_8 at 410°C in the presence of excess O_2, these ratios in the tail gas dropped to ∼0.04, i.e., by three orders of magnitude. These same data showed that NO_2 was selectively removed from the gas leading to a substantial increase in [NO]. Thus, in the steady state in the gas phase $[NO_x] \approx [NO]$. This conclusion is further supported by the data of Yokoyama and Misono (13) who have found that over a number of ZSM-5 catalysts the steady state $[NO_2]$ is much lower than [NO]. Thus it may be inferred that the catalytic sites are preferentially populated with NO_2 which is then preferentially reacted whether it is being made *in situ* or is initially present in the gas phase. This proposal is strongly supported by the experiments reported in Figs. 1 and 3.

The $CH_3\cdot$ radicals may be more or less free inside the pore systems of the MFI zeolites but, as shown by IR spectra taken at reaction temperatures (23, 24), adsorbed NO_y $(y \geq 2)$ are stable. If it is assumed that the reaction sites are populated with NO_2, Eq. [5] may be interpreted as an Eley–Rideal reaction of gaseous CH_4 with chemisorbed NO_x within the pore system, i.e.,

$$r_{\mathrm{CH_3}\cdot} = k_5\theta_{\mathrm{NO_2}}P_{\mathrm{CH_4}} \qquad [20]$$

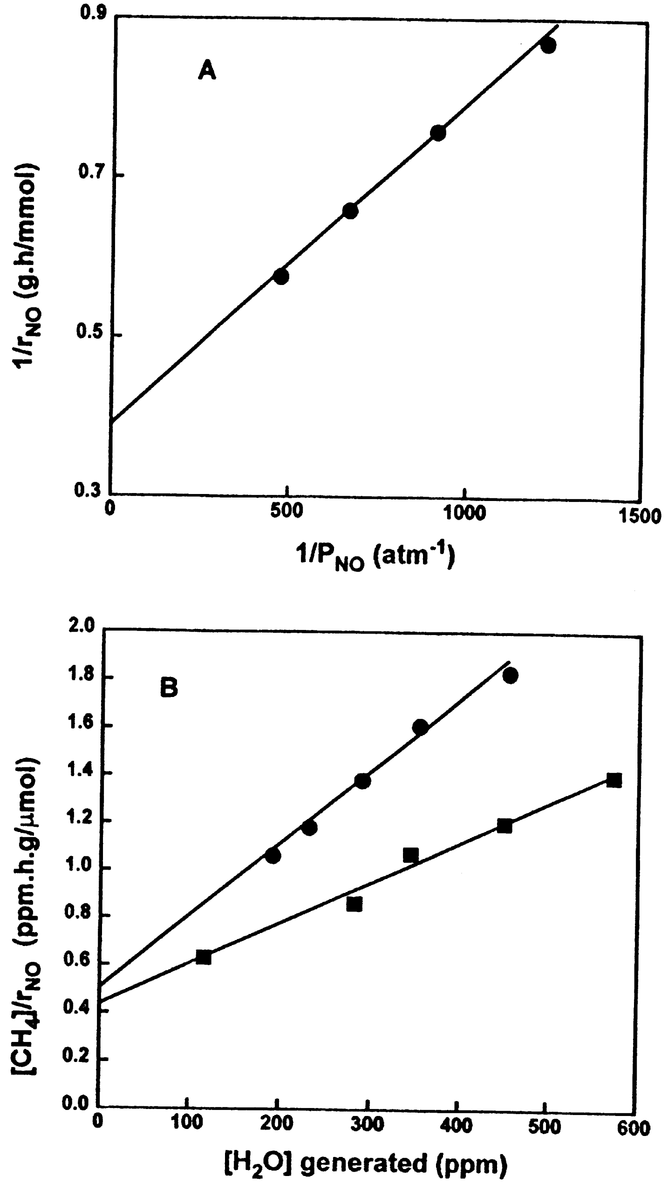

FIG. 8. (A) Langmuir–Hinshelwood plots of $1/r_{NO}$ vs $1/P_{NO}$, and (B) P_{CH_4}/r_{NO} vs P_W for constant P_{NO}. ●, present work; ■, data taken from Ref. 16.

This is the rate determining step as required by the experiments of Cant and co-workers (19, 20).

Pathways of the SCR of NO$_x$

Our data suggest that the catalytic reduction of NO_x into N_2 and, consequently, the oxidation of CH_4 into CO_x are initiated by CH_4 interaction with adsorbed NO_2. With CoZSM-5 and HZSM-5 catalysts the "light-off" occurs at 350°C (Fig. 1) at a GHSV of 45,000 and 9,000 h^{-1}, respectively. In the empty tube the "light-off" of CH_4 combustion with NO_2 occurs about 450°C (Fig. 3D). Under these conditions (homogeneous oxidation), the conversion of NO_2 into NO increased sharply with temperature and achieved 100% at 600°C. Formation of N_2 was not observed. With NaZSM-5 the same result was obtained (Fig. 3D). The chief difference, aside from temperature, between the catalytic and homogeneous reaction was this difference in the products obtained. In the presence of the NaZSM-5, CH_4 was oxidized into CO and CO_2 (the CO/CO_2 ratio was about 2) and the carbon balance was complete at all temperatures. In the empty tube the carbon balance did not close at 500°and 550°C, possibly due to the formation of formaldehyde (15). The suggestion of formaldehyde formation in the course of the homogeneous oxidation of CH_4 by NO_2 (15) is supported by the data of Irusta *et al.* (25) who showed that NO enhances formaldehyde yield during the homogeneous oxidation of CH_4 at the temperatures of interest (450–600°C). Also over NaZSM-5, N_2 did not form, and a rapid oxidation of methane and partial oxidation products occurred. It is interesting that Yokoyama and Misono reported that NaZSM-5 produced N_2 when NO_2 was substituted for NO in the SCR stream when C_3H_6 was the reducing gas (13).

Many years ago Wojciechowski and Laidler (26) studied the homogeneous decomposition of CH_4 and C_2H_6 in the presence of NO and concluded that the stable free radical NO could abstract an H atom from a paraffin molecule. Since NO_2 is also a stable free radical and a much stronger oxidizing agent than NO, we suggest that NO_2 abstracts an H atom from CH_4 forming $CH_3\cdot$ radical via reaction (5). Because of their relatively high concentrations, either NO_2 or NO could play a role of radical trap. Therefore coupling of $CH_3\cdot$ radicals would not be expected and was not observed. The formation of CH_3NO_2 and/or CH_3NO (reaction [4]) seems much more likely and have been found in the products (27).

A number of products other than CO, CO_2, N_2 and H_2O have been reported for various catalysts and a variety of hydrocarbons. The rule is that just because certain unusual products appear with one system does not necessarily mean that they will occur with others. Nevertheless, they must be considered as potential reaction intermediates. They include HNCO (7, 31), HCOO· (27), $CH_3\cdot$ (27), CH_2O (15), HCN (13, 30), C_2N_2 (13, 30), and oximes (32). Interestingly, free radical chemistry provides feasible routes by which these products may be formed and reacted.

The "light-off" temperature shift observed with CoZSM-5 and HZSM-5 may be explained by the catalytic formation of NO_2 or by the activation of an oxygen atom in NO_2 molecules adsorbed on the active sites. The existence of such molecules on Co-containing ferrierites at temperatures of interest (~300°C) has been confirmed by the IR data obtained by Li *et al.* (18). The reaction of CH_4 with an oxygen atom of adsorbed NO_2 should occur faster, and consequently at the lower temperatures, than with the oxygen atom of the gaseous NO_2 molecule. The activation of an oxygen atom in the NO_2 molecule by the HZSM-5 catalyst is confirmed by occurrence of the decomposition reaction of NO_2 into $NO + \frac{1}{2}O_2$ and by the downward shift of the "light-off" temperature of reactions with NO_2 in comparison with the homogeneous case (7, 15).

Vannice and co-workers (28, 29) found that typical methane coupling catalysts were effective for the SCR reaction with CH_4. Recently reported (32) calculations on CH_4 activation with an O atom adsorbed on the surface of a catalyst demonstrated that the abstraction of an H atom from CH_4 molecules with formation of $CH_3\cdot$ free radicals should be energetically favorable compared with the other possible mechanisms of CH_4 activation. Thus, the chemistry of Eq. [5] seems plausible and free radical chemistry can occur within the zeolite pore system, just as it can in solution. However, the lack of molecular sieving effects with larger hydrocarbons (7) has led us to think that part of the reaction may occur homogeneously in the gas phase.

The idea that CH_3NO_2 may be involved in the process of N_2 formation is strongly supported by the experiments on CH_3NO_2 transformation reported by Yokoyama and Misono (13). At the present time it is not possible to define with certainty the reaction steps involved in N_2 formation but it is clear that N_2 can be produced by reaction of NO_2 with CH_3NO_2.

On the Possible Role of Homogeneous Reactions in the SCR Process

The possibility exists that a part of the reactions occurring during the SCR process may proceed homogeneously in the gas phase. Two observations strongly support this view.

First, the analysis of the literature data, performed by Sinev *et al.* (32), shows that the release of the catalytically formed intermediate species (i.e., free radicals) into gas phase has been detected in a wide variety of oxidation reactions of different hydrocarbons including CH_4. Thus, a conclusion can be drawn that the presence of a homogeneous component in catalytic oxidation reactions is a common phenomenon. Methane coupling reaction is a good example. A homogeneous step is essential for formation of C_2 hydrocarbons (33–37). In the SCR process the formation of $CH_3\cdot$ free radicals seems plausible, although the release of these radicals from the zeolite channels into gas phase has not been proved. Nevertheless, a part of the catalyzed reactions that produce $CH_3\cdot$ radicals may occur on the exterior surface of the zeolite particles or at the pore mouths. If so, then the emanation of the reaction into gas phase becomes probable.

Second, it has been established (15) that formation of N_2 requires a catalyst, while oxidation of CH_4 by NO_x may occur at relatively high rate (at temperatures higher than 450°C) in the empty reactor. Thus, a part of CH_4 may be oxidized homogeneously.

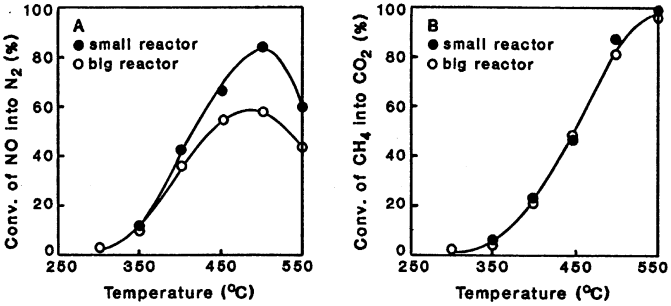

FIG. 9. Conversion of NO into N_2 (A) and conversion of CH_4 into CO_2 (B) over CoZSM-5 catalyst at various temperatures in different reactors. Volume of hot zone was about 7 and 2 ml in big and small reactors, respectively. Catalyst weight was 100 mg, feed contained 0.28% CH_4, 0.21% NO and 2.6% O_2 in He at a flow rate of 75 ml/min (GHSV = 22,500 h^{-1}).

Both processes considered above (emanation of $CH_3\cdot$ free radicals into the gas phase and homogeneous oxidation of CH_4 by NO_x) should result in a decrease in the SCR selectivity since a catalyst is essential for N_2 formation. The magnitude of this decrease should depend on the ratio between the free volume of the hot zone in the reactor and the volume occupied by a catalyst. A test was made by carrying out the SCR reaction in two very different reactors under otherwise identical conditions. Both contained the same weight of catalyst (100 mg), but one had a free volume of 7 ml in the "hot zone" while the other had only 2 ml. The results are reported in Fig. 9. They show that while the same amounts of methane are burned at every temperature, less N_2 is produced with the larger free volume. These data suggest that above 400°C an important fraction of the combustion reaction is homogeneous. Probably, these reactions took place in the reactor used by Cho (38), who found that a decrease in space velocity was followed by a decrease in the conversion of NO into N_2 during the SCR of NO with ethene and propene over CuZSM-5 catalyst.

The above results strongly suggest that the SCR of NO_x into N_2 with hydrocarbons in the presence of O_2 may be accompanied by reactions of hydrocarbon oxidation in the gas phase. This item is very important from both the scientific and practical point of view and, in our opinion, requires further serious investigation.

CONCLUSIONS

1. The SCR of NO with CH_4 in the presence of O_2 over CoZSM-5 and HZSM-5 catalysts is a complex catalytic reaction that proceeds via steps of competitive oxidation of CH_4 and intermediate species by NO_x and O_2.

2. The pathways of the SCR process over the two catalysts studied are the same and may include: (i) the step of catalytic oxidation of NO by O_2 into NO_2; (ii) the step of NO_2 interaction with CH_4 that results in formation of $CH_3\cdot$ free radicals; and (iii) the steps of interaction of $CH_3\cdot$ with NO_x and O_2 followed by the subsequent transformation of the products formed in these steps. In addition, at high

temperatures (above about 450°C) the direct oxidation of CH_4 by O_2 occurs.

3. NO reduction into N_2 and CH_4 oxidation into CO_x are coupled and initiated by the reaction of CH_4 with NO_2. The results suggest that this reaction may be considered as a limiting reaction step of the SCR reaction for the mixture of $CH_4 + NO + O_2$ when O_2 is present in large amounts. With this mixture when O_2 concentration is relatively low (up to about 1.5%) another reaction step, namely, the step of catalytic oxidation of NO by O_2 into NO_2 appears to control the rate of the SCR process. Thus, an important role of O_2 is to convert NO into NO_2.

4. At low temperatures (below 400°C) O_2 does not compete with NO_x for CH_4, but even at these temperatures O_2 participates in oxidation of the intermediate reaction species decreasing in this way the selectivity of the SCR process. At higher temperatures (above 450°C) a strong competition between O_2 and NO_x for CH_4 is observed and this results in a further decrease in the process selectivity. It is shown that the higher SCR selectivity of HZSM-5 catalyst in comparison with CoZSM-5 is due to the stronger competition between O_2 and NO_2 for CH_4 over the latter catalyst.

5. The formation of $CH_3\cdot$ free radical is postulated and possible reactions of this radical with NO_x, that form the pathways of the SCR process, are considered. Finally, the possible role of the gas phase reactions in the SCR process is discussed.

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