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Catalytic Reactions of NO over 0–7 mol% Ba/MgO Catalysts

II. Reduction with CH_4 and CO

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Barium oxide supported on magnesium oxide (Ba/MgO) is an effective catalyst at elevated temperatures for the selective catalytic reduction (SCR) of nitric oxide, with methane as the reductant. The rate of the SCR reaction is greater than either the rate of reduction with CH_4, in the absence of O_2, or the rate of decomposition of NO. At 650°C the rate of the SCR reaction over 1 mol% Ba/MgO was 0.19 μmol g^{-1} s^{-1} with 1% NO, 0.25% CH_4, and 0.5% O_2. The SCR reaction is believed to occur via gas-phase $CH_3\cdot$ radicals that are formed at the surface. First-order kinetics with respect to CH_4 is consistent with radical formation being the rate-determining step. The activities of the catalysts and the overall reaction order are influenced by CO_2, which is a product of the reaction, but also would be present in an exhaust stream. The inhibiting effect of CO_2 is much more significant for a catalyst containing 4 mol% Ba than for one containing 1 mol% Ba. In the latter case, the MgO support modifies the basicity of the BaO. In the absence of O_2, CO also is a reductant for NO, but if O_2 is present, the nonselective oxidation of CO occurs. That is, CO reacts preferentially with O_2 instead of NO.

Key Words: **nitric oxide; methane; barium oxide; selective catalytic reduction.**

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1. INTRODUCTION

Methane is one of the more desirable reductants for the removal of NO because of its abundance and availability; however, methane is difficult to activate. Nevertheless, a number of different catalysts, including cobalt-exchanged zeolites (1–3), gallium- and indium-loaded H–ZSM-5 (4), and Ce/Ag–ZSM-5 (5), have been reported to be active and selective for the selective catalytic reduction (SCR) of NO with CH_4 at moderate temperatures.

Among the various types of materials that have activity for the SCR of NO with CH_4, the alkaline earth and rare-earth oxides (e.g., Li/MgO and Sr/La_2O_3) are unique in that the mechanism of the reaction appears to involve surface-generated methyl radicals (6–8). Vannice and coworkers (6, 7), who were the first to study these catalysts for SCR of NO, noted that they also were active and selective for the oxidative coupling of methane, a reaction that is known to involve $CH_3\cdot$ radicals (9). Furthermore, they observed that the presence of NO strongly inhibited the formation of the coupling products, C_2H_4 and C_2H_6, which is consistent with the reaction of NO with the $CH_3\cdot$ radicals. Methyl radicals have also been postulated as intermediates in the SCR of NO with CH_4 over Co–ZSM-5; however, there is less direct evidence for formation of radicals over this catalyst (10–12). In fact, we have attempted without success to detect $CH_3\cdot$ radicals over Co–ZSM-5 by using a variable ionization energy mass spectrometer (13).

It was demonstrated in our laboratory that the reaction of CH_4 with O_2 indeed results in the formation of $CH_3\cdot$ radicals over Sr/La_2O_3 and Ba/MgO catalysts (8, 14). These radicals emanate into the gas phase, where they may couple or react with NO, if present. The concentration of radicals decreased when the argon diluent was replaced by nitric oxide. Moreover, when $CH_3\cdot$ radicals, derived from the thermal decomposition of azomethane, were allowed to react with NO in the gas phase, nitrosomethane, CH_3NO, was detected by mass spectrometry (8). This reaction occurred at 25°C, but CH_3NO was detected in decreasing amounts at temperatures up to 800°C.

In the study reported here, the more general properties of Ba/MgO catalysts containing up to 7 mol% Ba were determined, with emphasis on the kinetics of the reaction. The SCR reaction with CH_4 was investigated, as well as the reaction with CH_4 and CO in the absence of O_2. Particular attention was given to the negative effect that CO_2 has on these reactions, in part because of the role that CO_2 plays in the interpretation of kinetic results, but also because of the presence of large concentrations of CO_2 in any practical application of these catalysts for the removal of NO from combustion products. No attempt was made to determine the inhibiting effect of SO_2 or H_2O. The results of these reduction reactions are compared with those obtained during the direct decomposition of NO over the same set of catalysts, as described in Part I (15).

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TABLE 1

Activation Energies of NO Reduction by Methane over Ba/MgO Catalysts[a]

Catalysts	Surface area (m^2 g^{-1})[b]	Activation energy (kcal/mol)		
		$NO + CH_4$[c]	$NO + CH_4 + O_2$[d]	$NO + CO$[e]
MgO	38.3	31.7	23.7	28.2
1% Ba/MgO	27.8	32.2	31.8	31.2
4% Ba/MgO	13.3	30.8	36.8	27.2
7% Ba/MgO	4.6	30.7	29.4	24.7

[a] Kinetic data were obtained in the temperature range 600–800°C and with NO conversion less than 20%.

[b] After reaction of 1% NO with 0.25% CH_4 and 0.5% O_2 at 800°C for 1 hr.

[c] Reagent gas composition, 1% NO + 0.25% CH_4.

[d] Reagent gas composition, 1% NO + 0.25% CH_4 + 0.5% O_2.

[e] Reagent gas composition, 1% NO + 1% CO.

2. EXPERIMENTAL

The catalysts, reactor, and analytical methods were the same as those reported in Part I (15). Reactant gases were obtained by mixing 4% NO/He, 1% CH_4/He or 1% CO/He, and 5.4% O_2/He. Pure He was used as a makeup gas to keep the total flow rate at 40 ml/min. Typically 200 mg catalyst was used. The surface areas of the catalysts used are reported in Table 1.

The CH_4 conversion was based on either the disappearance of CH_4 or the formation of CO_2. Only trace amounts of CO were detected as products during NO reduction by CH_4. In the presence of O_2, there are two main reaction pathways that are responsible for the disappearance of CH_4,

$$CH_4 + 2NO + O_2 \rightarrow N_2 + CO_2 + 2H_2O \qquad [1]$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \qquad [2]$$

Reaction [1] is taken to be the selective oxidation reaction, which produced N_2, and in Reaction [2], only CO_2 and H_2O are formed. The selectivity of CH_4 is defined as the percentage of CH_4 reacted via reaction [1]; i.e., $S(CH_4) = [N_2]/([CO_2]_1 + [CO_2]_2) \times 100 = [N_2]/[CO_2]_{total} \times 100$. Selectivities defined in this manner are a factor of two larger than those obtained using the definition of Vannice and coworkers (16). Unless stated otherwise, rates were obtained by assuming differential conditions up to ca. 30% conversion, which is a reasonable approximation considering the apparent orders of reaction (see below).

3. RESULTS

3.1. Reduction of NO by CH_4 in the Absence of O_2

Even in the absence of added oxygen, the reduction of NO with CH_4 occurs at a moderate rate, as shown in Fig. 1A. Among the materials studied, the 7 mol% Ba/MgO catalyst exhibited the largest specific activity, in part because of its smaller surface area (Table 1). On a per gram basis, the 1 mol% Ba/MgO catalyst was the most active, as shown in Fig. 1B, and the NO conversion at 800°C was 40%, which is about six times the conversion for NO decomposition over the same catalyst.

With 0.25% CH_4 added to 1% NO, the N_2 formation rate at 800°C over the 7 mol% Ba/MgO catalyst was 0.040 μmol m^{-2} s^{-1}, which may be compared to a value of 0.015 μmol m^{-2} s^{-1} for the direct decomposition of NO over the same catalyst at 800°C (15). The rate for the direct decomposition is not negligible compared to the N_2 formation rate during the reaction of NO with CH_4; however, the direct decomposition of NO is strongly suppressed by the presence of CO_2 (see below), which is an inevitable product after CH_4 is introduced. Therefore, the reduction reaction is the primary pathway for the formation of N_2 when CH_4 is present.

3.2. Selective Catalytic Reduction of NO with CH_4 in the Presence of O_2

At temperatures <750°C, the presence of 0.5% O_2 in the reagent stream further enhanced the N_2 formation rate during NO reduction by CH_4, as shown in Fig. 2A. For example, with the 7 mol% Ba/MgO catalyst at 700°C, the N_2 formation rate increased from 0.008 μmol m^{-2} s^{-1} in the

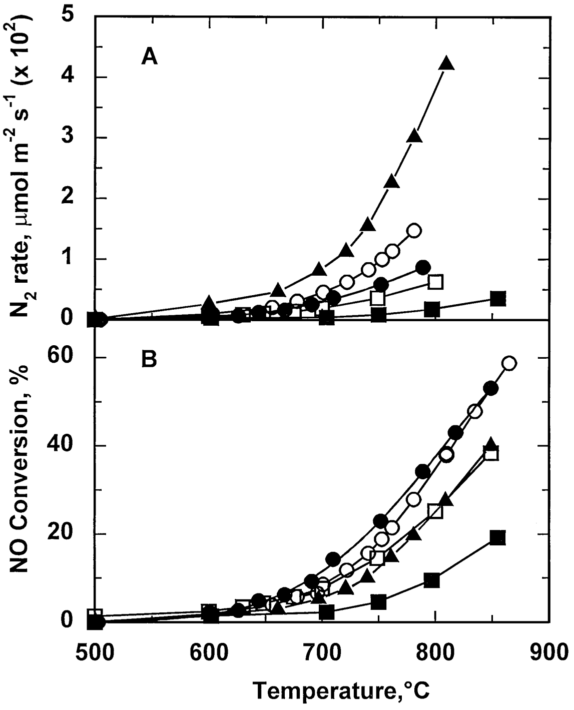

FIG. 1. Nitrogen formation rate (A) and NO conversion (B) as a function of temperature during the reaction of 1% NO + 0.25% CH_4 over MgO and Ba/MgO catalysts: (■) MgO, (□) 0.5 mol% Ba/MgO, (●) 1 mol% Ba/MgO, (○) 4 mol% Ba/MgO, (▲) 7 mol% Ba/MgO. Catalyst weight, 0.2 g; flow rate, 40 ml/min.

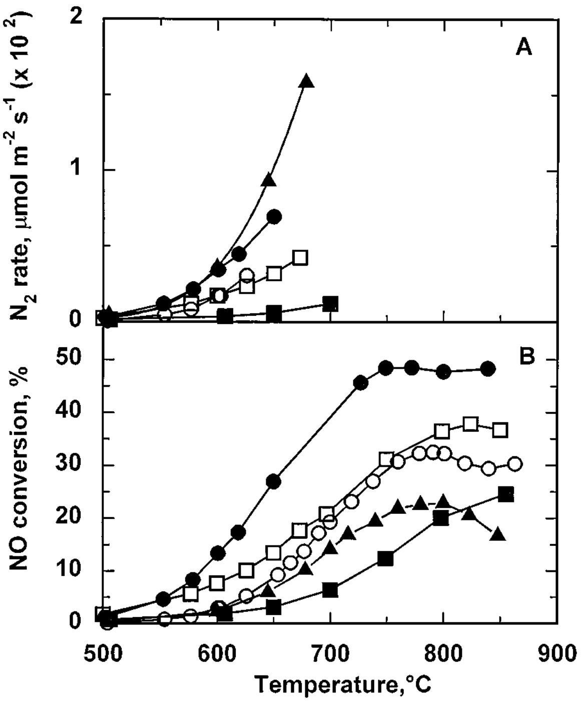

FIG. 2. Reaction rates (A) and NO conversions (B) as a function of temperature during the reaction of 1% NO + 0.25% CH_4 + 0.5% O_2 over MgO and Ba/MgO catalysts: (■) MgO, (□) 0.5 mol% Ba/MgO, (●) 1 mol% Ba/MgO, (○) 4 mol% Ba/MgO, (▲) 7 mol% Ba/MgO.

absence of O_2 to 0.022 μmol m^{-2} s^{-1} in the presence of O_2. Again, the specific activity was the largest for the 7 mol% Ba/MgO catalyst, but when the conversions were compared for a fixed mass of catalyst, as shown in Fig. 2B, the NO conversion was the largest over the 1 mol% Ba/MgO catalyst. At 650°C, the rate of reaction over this catalyst was 0.19 μmol g^{-1} s^{-1}.

As the temperature was increased above ca. 750°C, the NO conversion no longer increased continuously, and at a certain temperature it went through a maximum. With the 1 mol% Ba/MgO catalyst, the maximum was not as pronounced. A similar phenomenon has been reported for the SCR reaction over many other catalysts and is due to the fact that the CH_4 conversion approaches 100% at a particular temperature. For the Ba/MgO catalysts, this is made evident by comparing the results of Fig. 3A with the temperatures of the maxima, which were between 750 and 850°C, as shown in Fig. 2B. Obviously, the temperature at which the maximum NO conversion occurs depends on the catalytic activity and selectivity for CH_4 oxidation, as well as the loading of the catalyst. The maximum for the 1 mol% Ba/MgO catalyst was at a lower temperature, which is consistent with the fact that the CH_4 conversion approached 100% at a lower temperature (Fig. 3A). Since the reaction is CH_4 limited, the concentration of CH_4 and O_2 may affect the temperature maximum as well. With an excess of methane (25%), no maximum in NO conversion was observed at temperatures up to 875°C. At temperatures that are higher than the maximum, other reactions occur, such as the direct decomposition of NO, and the relative rates of these reactions also will define the maximum.

In the selective catalytic reduction of NO by CH_4, two reactions compete for methane, with Reaction [1] being desirable and Reaction [2] being undesirable. The CH_4 selectivity as a function of reaction temperature is shown in Fig. 3B. For the 4 mol% Ba/MgO catalyst the carbon balance was within 95% of the theoretical value. The 1 mol% Ba/MgO sample had exceptionally high CH_4 selectivity (>80%) over the entire temperature range that was studied, and the selectivity approached 100% at temperatures >700°C. This high selectivity provides a significant advantage for the practical utilization of such a catalyst. At both larger and smaller barium loadings, and for temperatures corresponding to a reasonable level of NO conversion (>700°C), the selectivities were less, with 7 mol% Ba/MgO being the least selective.

3.3. Reduction of NO by CO

Carbon monoxide is an active reductant for NO over Pt–Rh–Pd three-way catalysts (17). With Ba/MgO as the catalyst, CO was not observed as a product during the SCR of NO by CH_4. The absence of CO may result from the fact

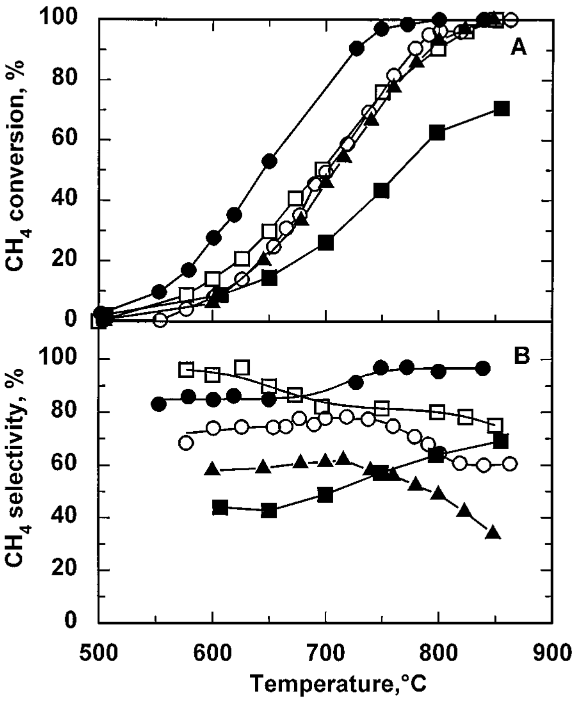

FIG. 3. Nitric oxide and methane conversions during the reaction of 1% NO + 0.25% CH_4 + 0.5% O_2 over MgO and Ba/MgO catalysts: (■) MgO, (□) 0.5 mol% Ba/MgO, (●) 1 mol% Ba/MgO, (○) 4 mol% Ba/MgO, (▲) 7 mol% Ba/MgO. Catalyst weight, 0.2 g; flow rate, 40 ml/min.

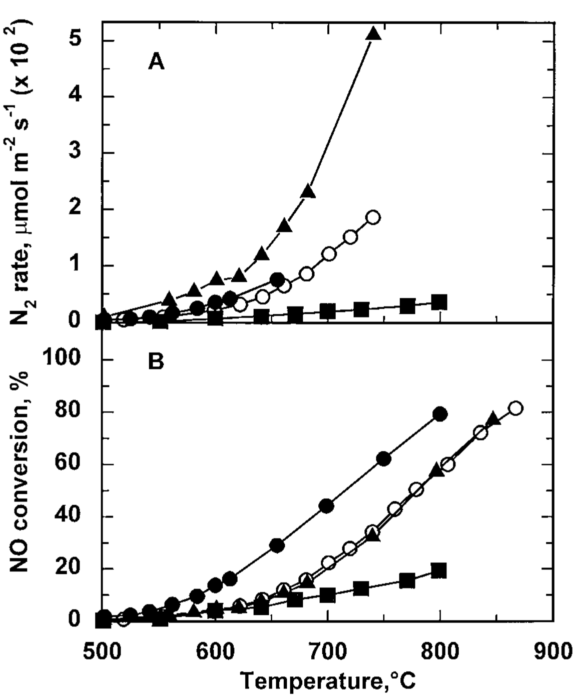

FIG. 4. Reaction rates (A) and NO conversions (B) as a function of temperature during the reaction of 1% NO + 1% CO over MgO and Ba/MgO catalysts: (■) MgO, (●) 1 mol% Ba/MgO, (○) 4 mol% Ba/MgO, (▲) 7 mol% Ba/MgO. Catalyst weight, 0.2 g; flow rate, 40 ml/min.

that no CO was formed, or that CO rapidly reacted with NO or O_2 so that it existed only in trace amounts. To clarify the role of CO in the SCR reaction over Ba/MgO catalysts, the reaction of NO with CO was also studied. The overall reaction of NO with CO is

$$2CO + 2NO \rightarrow N_2 + 2CO_2. \qquad [3]$$

With a stoichiometric mixture containing 1% NO and 1% CO, the results shown in Fig. 4 were obtained over MgO and the Ba/MgO catalysts. Again, the 7 mol% Ba/MgO catalyst had the largest specific rate for N_2 formation, but the 1 mol% Ba/MgO was the most active on a per gram basis, and resulted in the largest NO conversion (Fig. 4B). A comparison of the results of Figs. 1 and 4 indicates that for the larger amount of CO (1% CO versus 0.25% CH_4), the N_2 formation rates were greater with CO than with CH_4. However, when the same amounts of CO and CH_4 (0.25%) were employed, the rate of NO reduction was larger with CH_4 as the reductant (see below).

The NO conversions obtained with several different gas mixtures are compared in Fig. 5A for a 4 mol% Ba/MgO catalyst. The highest conversion was obtained for the standard mixture of 1% NO + 0.25% CH_4 + 0.5% O_2. Addition of 0.25% CO to this mixture actually caused a slight decrease in conversion at $T < 800°C$. With the deletion of CH_4 from the mixture, almost no nitric oxide was reduced. This result, together with the observation that the CO conversion was nearly 100% for $T > 700°C$ (Fig. 5B), confirms that CO reacts preferentially with O_2, rather than with NO. This is supported by the fact that the CO conversion was less when only NO and CO were present as reagents (i.e., no O_2). In summary, the small decrease in NO conversion that resulted from the addition of CO to the standard SCR mixture with CH_4 (Fig. 5A) is a result of the poisoning effect of CO_2. The rapid reaction of CO with O_2 led to a higher concentration of CO_2 in the gas stream. Similarly, with the mixture of 1% NO + 0.25% CO + 0.5% O_2, all of the CO rapidly reacted to form CO_2, and even the direct decomposition of NO to form N_2 and O_2 was poisoned. This set of experiments establishes that CO is not a primary intermediate in the SCR of NO with CH_4.

3.4. Inhibition by CO_2

Carbon dioxide strongly inhibits the oxidative coupling of methane over basic catalysts due to the formation of inactive surface carbonates (18). The effect of CO_2 on NO decomposition and reduction by CH_4 was studied by varying the flow rate of a 10% CO_2/He mixture while keeping the total flow rate of the reagents at 40 ml min^{-1}. From the results shown in Fig. 6A, it is evident that CO_2 had a negative effect on the N_2 formation rate for the

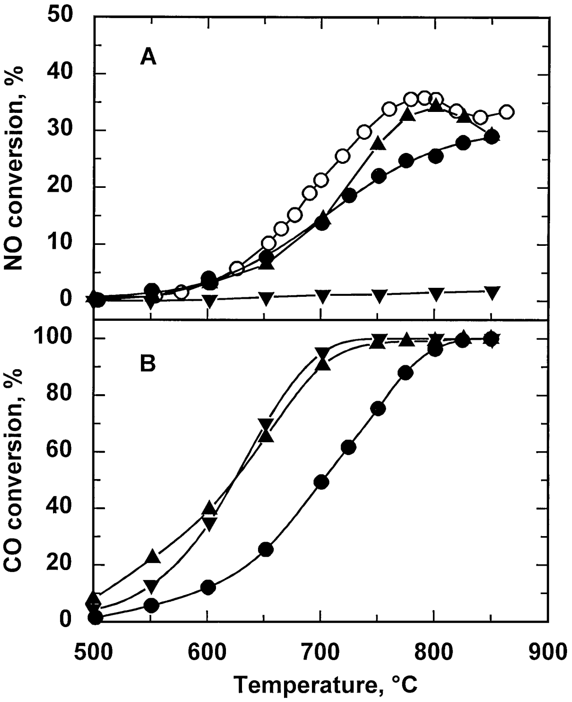

FIG. 5. Comparison of NO and CO conversions with different reagent gases over 200 mg of 4 mol% Ba/MgO catalyst. Gas composition: (○) 1% NO + 0.25% CH_4 + 0.5% O_2, (●) 1% NO + 0.25% CO, (▲) 1% NO + 0.25% CH_4 + 0.25% CO + 0.5% O_2, (▼) 1% NO + 0.25% CO + 0.5% O_2. Catalyst, 0.2 g 4 mol% Ba/MgO.

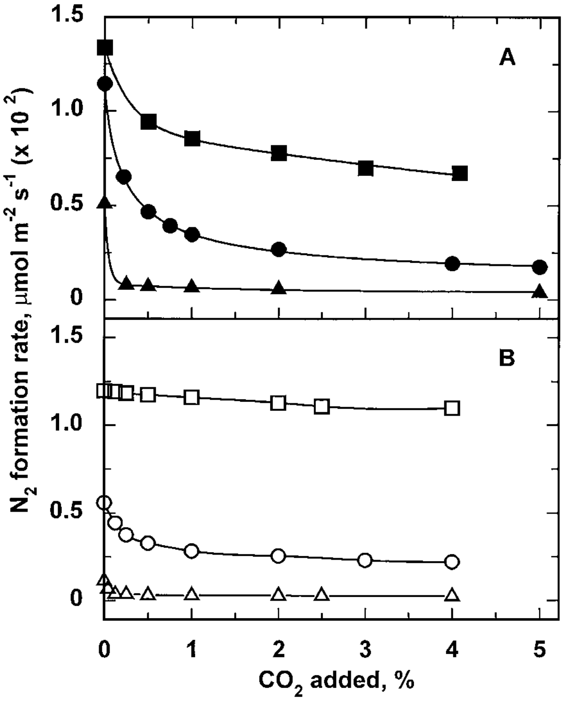

FIG. 6. The effect of added CO_2 on the reaction rates of NO decomposition and reduction with CH_4. (A) 4 mol% Ba/MgO catalyst (0.3 g): (▲) 1% NO, (●) 1% NO + 0.25% CH_4, (■) 1% NO + 0.25% CH_4 + 0.5% O_2. (B) 1 mol% Ba/MgO catalyst (0.2 g): (△) 1% NO, (○) 1% NO + 0.25% CH_4, (□) 1% NO + 0.25% CH_4 + 0.5% O_2. $T = 750°C$.

reagent gas compositions 1% NO, 1% NO + 0.25% CH_4, and 1% NO + 0.25% CH_4 + 0.5% O_2, but the decrease was much more dramatic for the direct decomposition of NO over the 4 mol% Ba/MgO catalyst. In this case, the N_2 formation rate at 750°C decreased from 5.1×10^{-3} μmol m^{-2} s^{-1} to 0.8×10^{-3} μmol m^{-2} s^{-1} upon the addition of 0.25% CO_2 to the reagent gas.

Thus, compared to the direct decomposition of NO, the reduction of NO by CH_4 was less susceptible to the CO_2 poisoning, especially when O_2 was present. For the reduction of NO by CH_4 in the absence of O_2, the reaction rate was sensitive to the presence of CO_2 for concentrations up to 1%, but the CO_2 poisoning effect was less significant when the CO_2 concentration was greater than 1%. In the presence of O_2, even with 4% CO_2 in the feed gas, the N_2 formation rate over the 4 mol% Ba/MgO catalyst remained at a relatively high value of 6.7×10^{-3} μmol m^{-2} s^{-1}, which is about half of the N_2 formation rate without the addition of CO_2. Even when CO_2 was not added to the reagents, it was, of course, present as a product when CH_4 was introduced as the reductant. In the absence and presence of O_2 at 750°C, the products contained ca. 0.08 and 0.22% CO_2, respectively, at the normal flow rate of 40 ml min^{-1}. The activity for N_2 formation increased by nearly a factor of 4.5 to 4.2×10^{-2} μmol m^{-2} s^{-1} when the flow rate was 480 ml min^{-1}, at which point the product gas contained only 0.07% CO_2. The existence of CO_2 as the product of NO reduction by CH_4 may explain why the reaction rates of NO with CH_4 and NO with CH_4 and O_2 were reduced to a smaller extent when CO_2 was added to the gases. As shown in Fig. 6B, the 1 mol% Ba/MgO catalyst was much less susceptible to CO_2 poisoning during the reduction of NO with CH_4 in the presence of O_2 than was the 4 mol% Ba/MgO catalyst, which is consistent with a decrease in basicity of the material (see below).

3.5. Kinetic Parameters for NO Reduction by CH_4

The activation energies for N_2 formation with mixtures consisting of 1% NO + 0.5% CH_4, 1% NO + 0.25% CH_4 + 0.5% O_2, and 1% NO + 0.25% CO over MgO and Ba/MgO catalysts were determined and the results are given in Table 1. For the simple reduction with CH_4 the activation energy was 31 ± 1 kcal mol^{-1} for MgO and the three Ba/MgO catalysts. When O_2 was added, the variation was greater, with a maximum of 36.8 kcal mol^{-1} occurring for the 4 mol% Ba/MgO catalyst. A similar activation energy of 39 kcal mol^{-1} was observed for CH_4 oxidation coupling over this catalyst (18), which is consistent with the common role of $CH_3\cdot$ radicals in the coupling and the SCR reactions. Agreement in activation energies for the two reactions also was found for the 1 mol% Ba/MgO catalyst. The activation energy of 29.4 kcal mol^{-1} for the SCR reaction over the 7 mol% Ba/MgO, however, was unexpectedly low when compared to a value of 43 kcal mol^{-1} (18) for the coupling reaction over 8 mol% Ba/MgO catalyst. The difference could have resulted, in part, from the temperature-dependent poisoning effect of CO_2. In the coupling reaction, the amount of CO_2 formed was much larger and the effect was more significant at the higher Ba loadings. With CO as the reductant, one might have expected a significantly different activation energy because of a different mechanism. Such was the case for the 4 mol% Ba/MgO catalysts, but not for the 1 mol% Ba/MgO catalyst.

To determine the reaction orders during NO reduction over the 4 mol% Ba/MgO catalyst, it was necessary to account for the CO_2 poisoning effect on the activity. The amount of CO_2 formed during NO reduction by CH_4 varied with reaction conditions such as the reaction temperature and the concentrations of oxygen and methane. Larger amounts of CO_2 are expected when the CH_4 concentration is increased, if the conversion of CH_4 is constant. In order to overcome the effects that result from a variation in the amount of CO_2, an excess of CO_2 (2.5%) was introduced into the feed gas to minimize the effect of CO_2 produced during the reaction. Thus the reaction became pseudo zero order with respect to CO_2 (Fig. 6). Another advantage in determining the reaction orders for NO reduction in an excess amount of CO_2 is that the NO decomposition is almost completely suppressed with 2.5% CO_2 added. That is, the contribution of N_2 formation from the direct decomposition of NO is minimized.

In these experiments, the concentration of CH_4 was kept constant at 0.25% while the concentration of NO was varied between 0.5 and 3.5%. When the reaction order with respect to CH_4 was determined, the NO concentration was 1% and the CH_4 concentration was varied between 0.075 and 0.75%. The initial concentration of O_2, when present, was 0.5%. The conversions for NO and CH_4 were kept less than 20% in experiments determining the kinetic orders. The experimental results are summarized in Table 2.

In the absence of O_2, the reaction order with respect to CH_4 in the reaction of NO with CH_4 was almost the same in the absence and presence of added CO_2, with values of 0.25 and 0.24, respectively. When the NO concentration was fixed and the CH_4 concentration was varied, the change in the concentration of CO_2 formed varied only slightly in the absence of added CO_2. There is, however, a difference in reaction orders with respect to NO, with and without added CO_2. The NO order was higher (0.88 vs. 0.52) in the presence of added 2.5% CO_2. When the CH_4 concentration was fixed and the NO concentration was increased, more CO_2 was formed, and the increase in reaction rate was offset by a larger inhibiting effect of CO_2. The results in Table 2 also suggest that the N_2 formation rate during the reaction of NO with CH_4 is less sensitive to the change in the CH_4 concentration than that in the NO concentration.

With the reaction mixture consisting of NO, CH_4, and O_2, the reaction orders with respect to NO and CH_4, determined in the presence of added CO_2, were significantly higher than those obtained in the absence of added CO_2 (Table 2). In contrast to the reaction of NO with CH_4 in the absence of O_2, the reaction orders for both NO and CH_4 were affected by the presence of added CO_2. The reaction orders with respect to CH_4 were 0.68 in the absence of added CO_2 and 1.02 with 2.5% CO_2 added in the feed gas. The reaction orders with respect to NO were 0.21 and 0.36, respectively, without and with the added CO_2. The different reaction orders with and without O_2 suggest that the reaction mechanisms may be different for these two reactions.

No attempt has been made to determine quantitatively the reaction order with respect to O_2 since the effect of O_2 on the N_2 formation rate depends on the concentration used. The order with respect to O_2 may be either positive or negative, as shown in Fig. 7. The addition of small amounts of O_2 to a mixture of $1\%\ NO + 0.25\%\ CH_4$ increased the NO conversion up to a maximum with 0.5% O_2, which was the amount used in the experiments described above. Larger O_2 concentrations resulted in a decrease in the NO conversion, largely because the conversion of CH_4 approached 100%. When the added O_2 was greater than 2%, the NO conversion was even less than that observed with $1\%\ NO + 0.5\%\ CH_4$ in the absence of O_2. Therefore, a positive reaction order with O_2 during the reaction of NO with CH_4 and O_2 would be obtained if the O_2 concentration were kept lower than 0.5%, while a negative value would be observed if larger O_2 concentrations were employed.

TABLE 2

Reaction Orders of NO and CH_4 over a 4 mol% Ba/MgO Catalyst[a]

	$NO + CH_4$		$NO + CH_4 + O_2$	
	NO	CH_4	NO	CH_4
Without added CO_2	0.52 ± 0.02	0.25 ± 0.01	0.21 ± 0.07	0.68 ± 0.03
With 2.5% CO_2 added	0.88 ± 0.03	0.24 ± 0.01	0.36 ± 0.01	1.02 ± 0.04

[a] Reaction orders were obtained with conversions for NO and CH_4 less than 20%.

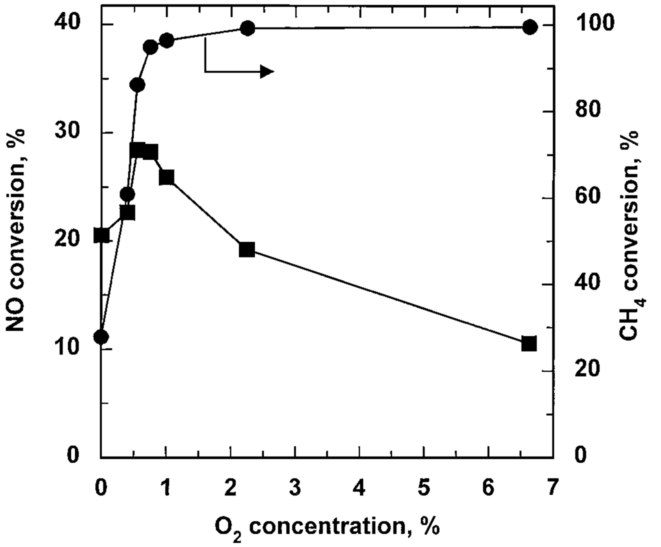

FIG. 7. Nitrogen formation rates as a function of O_2 concentration during the reaction of 1% NO with 0.25% CH_4 and different concentrations of O_2: (■) N_2 formation rate, (●) CH_4 conversion. Catalyst, 0.2 g 4 mol% Ba/MgO; $T = 750°C$.

4. DISCUSSION

As described in the Introduction, there is evidence that $CH_3\cdot$ radicals, formed on the surface of Ba/MgO, may be involved in the SCR of NO (14). The $CH_3\cdot$ radicals subsequently react with NO in the gas phase to produce N_2O, and ultimately N_2. The following mechanism appears to be consistent with the evidence obtained for these catalysts:

$$O_2 + 2s \rightleftarrows 2O_s \qquad [4]$$

$$CH_4 + O_s \rightarrow CH_3\cdot + OH_s\ (RDS) \qquad [5]$$

$$2OH_s \rightarrow H_2O + O_s \qquad [6]$$

$$CH_3\cdot + NO \rightarrow CH_3NO \qquad [7]$$

$$CH_3NO + NO \rightarrow\rightarrow N_2O + CH_3O\cdot \qquad [8]$$

$$N_2O + s \rightarrow N_2 + O_s \qquad [9]$$

$$CH_3O\cdot + O_2 \rightarrow\rightarrow CO_2 + H_2O \qquad [10]$$

$$CH_3\cdot + O_2 \rightarrow\rightarrow CO_2 + H_2O. \qquad [11]$$

The surface species, O_s and OH_s, are probably present as ions (i.e., O_s^- and OH_s^-). If the active form of oxygen is a peroxide ion, as might be the case for Ba/MgO (19), one could write an analogous reaction mechanism. The formation of $CH_3\cdot$ radicals is suggested to be the rate-determining step (RDS), which is consistent with the reaction being first order with respect to CH_4. The reaction of $CH_3\cdot$ radicals with NO to form CH_3NO must be rapid since C_2H_6 and C_2H_4, the products of methyl radical coupling, were not detected. Nitrosomethane may react with NO through a series of steps to form N_2O (20). Another possible pathway for the formation of N_2 may be through a bimolecular reaction of CH_3NO; however, this is probably a minor pathway, considering the fact that the concentration of NO is much larger than that of CH_3NO. The 0.36 order with respect to NO may be the result of several reactions. As shown previously, NO had a negative effect on $CH_3\cdot$ radical formation (8), which could result from the competitive reactions of NO with the O_s species. But subsequent reactions (e.g., Reactions [7] and [8]) would require the presence of NO in the formation of N_2.

It was demonstrated that N_2O is a reaction intermediate during NO decomposition over Ba/MgO catalysts (15). In the SCR of NO with CH_4, the role of N_2O as an intermediate is uncertain, although it was detected in small amounts in the product stream at reaction temperatures $<700^\circ C$. The presence of CH_4 inhibited the decomposition of N_2O. One could replace Reaction [8] by

$$CH_3NO + NO \rightarrow\rightarrow N_2 + CH_3O_2\cdot, \qquad [8a]$$

which would not lead to the formation of N_2O.

Since the formation of $CH_3\cdot$ radicals is believed to be a common feature in both the SCR of NO and the oxidative coupling of CH_4, it is of interest to compare a common feature of the Ba/MgO catalysts for these reactions, namely, the resistance of the 1 mol% Ba/MgO catalyst to poisoning by CO_2. This resistance to poisoning is of practical significance since CO_2 is a major product of combustion. At low BaO loadings (<2 mol%), the basicity of the Ba/MgO catalysts, as determined by the temperature-programmed desorption of CO_2, decreased as a result of interaction with the much less basic MgO support (18). Hence, the 1 mol% Ba/MgO catalyst was much less susceptible to CO_2 poisoning than the 4 mol% Ba/MgO catalyst.

The mechanism for the reduction of NO with CH_4, in the absence of O_2, is less certain because $CH_3\cdot$ radicals were detected only in very small concentrations over Ba/MgO and Sr/La_2O_3 catalysts when O_2 was replaced by NO (8, 14). Vannice *et al.* (21) tentatively adopted a mechanism that agreed with their kinetic results over La_2O_3 and Sr/La_2O_3. In this mechanism it was proposed that adsorbed NO and CH_4 reacted in the rate-determining step to form adsorbed HNO and $CH_3\cdot$ radicals. Based on results obtained with CH_4 and O_2 (8, 14), it was expected that the $CH_3\cdot$ radicals would desorb, yet almost none were detected. In addition, NO and CH_4 would be only weakly adsorbed on these closed shell oxides at the reaction temperatures employed. Considering the fact that Ba/MgO reacts with NO to form nitrate and nitrite ions that exist at elevated temperatures (15), we propose that gas-phase CH_4 reacts with these polyatomic anions to reduce the nitrogen. The reactions through which N_2 is formed are not known, but they probably involve ionic intermediates. One cannot exclude the possibility that, even in the presence of O_2, a nonradical mechanism accounts for part of the NO conversion.

5. CONCLUSIONS

The SCR of NO with CH_4 over a series of Ba/MgO catalysts occurs at a significantly higher rate than either the direct decomposition of NO or the reduction of NO in the absence of O_2. The SCR reaction is partially poisoned by CO_2, which would be present as a product of combustion. This poisoning effect is less on the catalyst containing 1 mol% Ba than on the one containing 4 mol% Ba because at low loadings the basicity of the barium oxide is moderated by the less basic MgO support. When the effect of CO_2 is taken into account, the reaction becomes first order with respect to CH_4, which is consistent with $CH_3\cdot$ radicals being formed in the rate-determining step. In the absence of O_2, the order with respect to methane decreased to 0.24, which suggested a change in the reaction mechanism. The details of this mechanism are not known, but it probably involves the reaction of CH_4 with ionic NO_x species, rather than adsorbed NO.

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