The role of methyl radicals in the reduction of NO by CH_4 over a Ba/MgO catalyst

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Under conventional flow conditions at 760 Torr, 4 mol% Ba/MgO is an effective catalyst for the reduction of NO by CH_4. The conversion of NO at 700°C is increased ca. threefold when O_2 is added to the system. When reactions are carried out at 500 mTorr, $CH_3\cdot$ radicals are detected in the gas phase over the catalyst with O_2 as the oxidant, but not with NO as the oxidant. Moreover, $CH_3\cdot$ radicals appear to react with NO, presumably to form CH_3NO, which is believed to be an intermediate in the reduction reaction. The positive effect of O_2 can thus be explained by its role in the generation of $CH_3\cdot$ radicals.

Keywords: NO reduction, methane, barium oxides, methyl radicals

1. Introduction

The removal of NO_x from exhaust streams under lean-burn conditions continues to be a major challenge in heterogeneous catalysis. Vannice and coworkers [1–4] have demonstrated that many of the basic oxide catalysts which are effective in the oxidative coupling of CH_4 also are active for the reduction of NO by CH_4, particularly when O_2 is present as a reagent. These catalysts are capable of generating $CH_3\cdot$ radicals that enter the gas phase, and, in the absence of NO, the radicals couple to form C_2H_6 [5–7]. If NO is added under oxidative coupling conditions, the formation of C_2H_6 is greatly suppressed [1]. These observations led Vannice and coworkers to conclude that $CH_3\cdot$ radicals may be involved in the catalytic reduction of NO over this class of catalysts.

In an attempt to understand the importance of surface-generated gas-phase $CH_3\cdot$ radicals in the reduction of NO we have utilized a variable ionization energy mass spectrometer (VIEMS) system that enables us to detect the radicals in the presence of a very large excess of CH_4. The methodology was previously applied to detect radicals formed during the reduction of NO over Sr/La_2O_3 [8], which is one of the most active catalysts reported by Vannice and co-workers [3,4]. In our previous study it was concluded that O_2 is required for the formation of the $CH_3\cdot$ radicals; i.e., NO is not capable of generating active oxygen centers on the catalyst. More recently, we have shown that Ba/MgO, one of the better catalysts for the oxidative coupling of CH_4 [9], also is active for the reduction of NO. Preliminary catalytic results are given here; however, the major focus of this communication is on the formation and role of $CH_3\cdot$ radicals in the reduction reaction.

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2. Experimental

Appearance potentials for the radical intermediates and stable molecules of interest in this study differ sufficiently to allow selective ionization of certain species, particularly $CH_3\cdot$. Values (in eV) for the following species are given in parentheses: NO (9.2), $CH_3\cdot$ (9.8), C_2H_4 (10.5), C_2H_6 (11.5), O_2 (12.1), H_2O (12.6), CH_4 (12.8), N_2O (12.9), CO_2 (13.9), CO (14.1) and N_2 (17) [10]. Thus, by varying the nominal electron-impact energy in a mass spectrometer, it is possible to selectively ionize $CH_3\cdot$ radicals in the presence of a large excess of CH_4. In this case, the ability to selectively ionize the minor species is important because at higher electron-impact energies (e.g., 70 eV) the fragmentation peak at 15 amu from CH_4 would completely obscure the parent peak resulting from the ionization of $CH_3\cdot$. Stair and co-workers [11] demonstrated this principle with respect to the detection of $CH_3\cdot$ radicals. Gutman and co-workers [7] used a similar concept, but in their case selective ionization was carried out by photons instead of electrons.

The experiments to detect $CH_3\cdot$ radicals were carried out in the fused-quartz reactor described previously [8]. Approximately 200 mg of catalyst was placed on a quartz frit. The gases entered a UTI model 100 C quadrupole mass spectrometer via a leak that was placed approximately 2 mm downstream from the catalyst. Most of the gas flow exited through a valve to a vacuum pump. The pressure in the reactor was about 500 mTorr, while that in the mass spectrometer was about 3×10^{-6} Torr. Prior to reaction, the catalyst was pretreated in pure flowing O_2 for 1 h at a pressure of 125 mTorr and a temperature of 700°C.

The mass spectrometer was modified to allow variation in the electron-impact energy. In the work reported here, the nominal electron-impact energy was set at either 19 or 70 eV. At the higher impact energy there

was, of course, no discrimination based on appearance potential.

More conventional catalytic results were obtained with a 4 mm i.d. fused-quartz, single-pass flow reactor operating at atmospheric pressure. Typically, 200 mg of catalyst was placed between two layers of quartz wool, and quartz chips were used to fill the space upstream from the catalyst. The reagent gases consisted of 4.14% NO in He, 1.10% CH_4 in He and 9.89% O_2 in He, all of which were obtained from Matheson. The gases were mixed with pure He in predetermined proportions to obtain a total flow rate of 40 ml/min. Analyses were carried out using gas chromatography. In the absence of added O_2, the mass balance for nitrogen and carbon was ±4%; however, when O_2 was present in the feed, part of the NO reacted to form NO_2. Moreover, the equilibrium reaction

$$NO + \tfrac{1}{2}O_2 \rightleftharpoons NO_2 \qquad (1)$$

is favored at low temperature, and no attempt was made to detect NO_2 at the temperature of the catalytic reaction. Since the amount of NO_2 was not determined, it was not possible to obtain an oxygen or a nitrogen balance. The fractional NO conversion is defined as the moles of N_2 plus N_2O formed, divided by one-half the moles of NO in the feed mixture.

The 4 mol% Ba/MgO catalyst was prepared by adding 30 ml of a $Ba(NO_3)_2$ (Baker) solution, containing the required amount of Ba, to a slurry consisting of 5.0 g MgO (Fisher-light) and 30 ml of deionized water. The $Ba(NO_3)_2$ solution was added dropwise at 25°C while vigorously stirring the MgO slurry. The slurry was stirred overnight and the water was evaporated at 100°C. The catalyst was then dried in air at 700°C for 2 h, pressed under 20 000 psi, crushed and sieved to 20–40 mesh size. Prior to carrying out the reaction, the catalyst was pretreated at 800°C for 1 h in 9.89% O_2 in He at a flow rate of 20 ml/min. A period of 45 min was allowed at each temperature for the reaction to reach steady state. After measurements at the highest temperature, the activities at several lower temperatures were measured again to ensure that no deactivation had occurred. The surface areas of the catalyst, obtained using a QuantaChrome system, decreased from 23 m^2/g after calcination in air to 13 m^2/g after reaction.

3. Results and discussion

3.1. Detection of methyl radicals during the reaction of methane with molecular oxygen

Previous studies have demonstrated that the 4 mol% Ba/MgO catalyst consists of a surface layer of BaO, BaO_2 and $BaCO_3$ on MgO [9,13]. It has been suggested that surface peroxide ions are responsible for the activation of CH_4 to form $CH_3\cdot$ radicals [9]. Typical mass spectra obtained at two different electron-impact energies during the reaction of CH_4 and O_2 at 775°C over the Ba/MgO catalyst are compared in fig. 1 with the background spectra and those obtained with only CH_4, O_2 and Ar in the gas phase at 25°C. Even though the apparent electron-impact energy of 19 eV was significantly larger than the appearance potential of 12.8 eV for CH_4, the parent peak at 16 amu and the fragmentation peak at 15 amu were small. The reaction resulted in the formation of $CH_3\cdot$ radicals, as indicated by the greatly enhanced peak at 15 amu in spectrum c for an electron-impact energy of 19 eV. In panel A, one can also observe large peaks at 18 amu from H_2O, at 28 amu from C_2H_6 and at 32 amu from O_2. Results obtained with pure ethane confirm that its largest peak is at 28 amu, rather than at 30 amu, as expected. The absolute pressure of $CH_3\cdot$ radicals was determined from a calibration curve obtained with radicals produced by the thermal decomposition of azomethane [12]. The typical mass spectrum of CH_4 at 70 eV is evident in fig. 1B; because of the large fragmentation peak at 15 amu, the presence of $CH_3\cdot$ radicals is not apparent at this impact energy. From the results of fig. 1, one may conclude that $CH_3\cdot$ radicals may be detected even though the CH_4 : $CH_3\cdot$ ratio was ca. 100 over the Ba/MgO catalyst.

The results of fig. 2 provide definitive evidence that these radicals are formed at temperatures as low as 600°C when CH_4 and O_2 react over the catalyst. As the catalyst temperature was increased, the concentration of radicals and the formation of C_2 products increased up

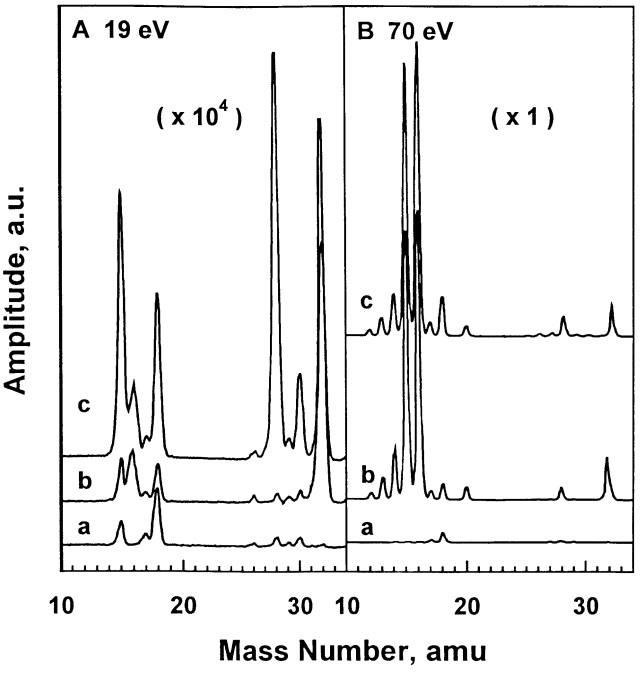

Fig. 1. Mass spectra obtained at different electron-impact energies: (a) background; (b) CH_4 and O_2 at 25°C; (c) after passing CH_4 and O_2 over a 4 mol% Ba/MgO catalyst at 775°C. The CH_4/O_2 ratio was 10 : 1.

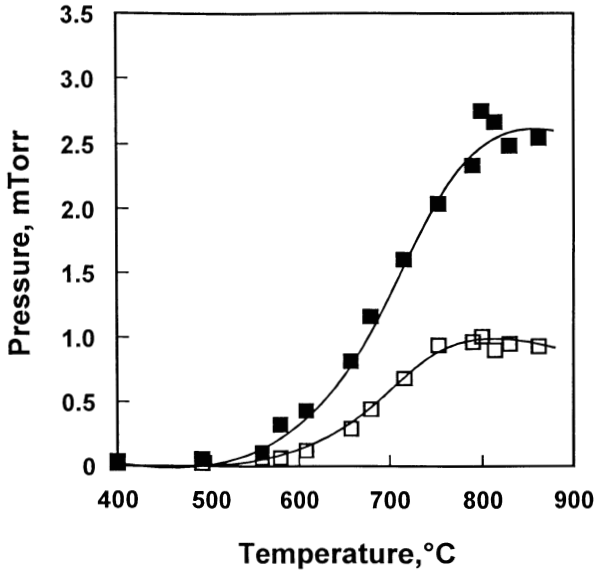

Fig. 2. Effect of temperature on product distribution when passing Ar, CH_4 and O_2 in a 10 : 10 : 1 ratio over 4 mol% Ba/MgO: (■) CH_3· radicals; (□) C_2H_6. The total pressure was 500 mTorr, mass spectra were obtained at 19 eV electron-impact energy.

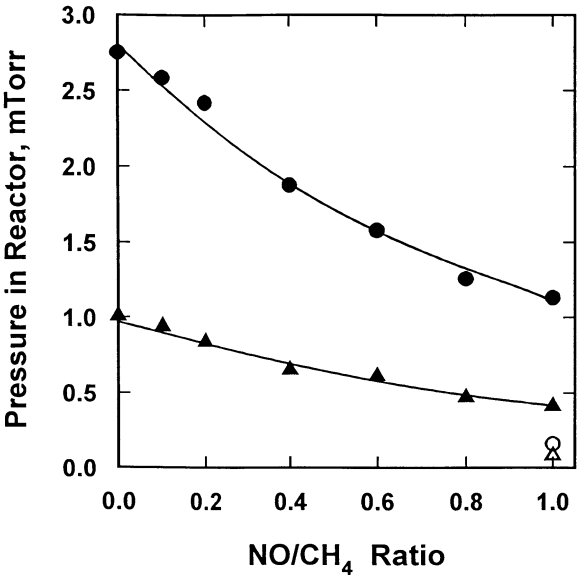

Fig. 3. Effect of adding NO to a $CH_4 + O_2$ reaction mixture ($P_{CH_4} = 238$ mTorr, $P_{O_2} = 24$ mTorr) over a 4 mol% Ba/MgO catalyst at 800°C and a total pressure of 500 mTorr: (●) CH_3· radicals; (▲) C_2H_6. In the absence of O_2: (○) CH_3· radicals; (△) C_2H_6. Mass spectra were obtained at 19 eV electron-impact energy.

to ca. 800°C. The shallow maxima may be related to the depletion of O_2 and to secondary reactions of CH_3· radicals other than coupling. The apparent activation energy for CH_3· radical formation is ca. 18 kcal/mol, although this value is somewhat less than the actual activation energy because of the coupling reaction which partially removes CH_3· radicals [6].

As noted above, the principal C_2 product observed was C_2H_6, which is expected because the secondary dehydrogenation reaction to form C_2H_4 would be limited under these conditions. The VIEMS system has an advantage over the matrix isolation electron spin resonance (MIESR) system, which was previously used, in that nonradical products can simultaneously be detected.

3.2. Effect of nitric oxide on methyl radical formation

When NO was added in increasing amounts to the CH_4/O_2 mixture, and the Ar flow rate was correspondingly decreased, there was a monotonic decrease in the pressures of CH_3· radicals and C_2 products, as shown in fig. 3. The pressures of CH_3· radicals and C_2 products decreased proportionally. The decrease in CH_3· radicals is consistent with our previous observation that the radicals react with NO to form nitrosomethane, CH_3NO [8]. This reaction, of course, competes with the coupling reaction. There is evidence that CH_3NO may react further with NO in the gas phase to form N_2O and CH_3O· [14], which provides one pathway for the formation of N–N bonds.

In the absence of O_2, there was a large decrease in the concentration of CH_3· radicals and C_2 products, as indicated by the open symbols in fig. 3. These results are more clearly depicted in fig. 4, which shows the effect of various gas compositions on the intensities of mass spectral peaks that are related to CH_3· radicals and stable products. Here, the intensities of the 15 amu peak, corresponding to CH_3· radicals, were those obtained at an electron-impact energy of 19 eV, and those of the other three peaks were obtained at 70 eV. The peaks at 26 and 27 amu are due only to C_2H_6 fragmentation, while that

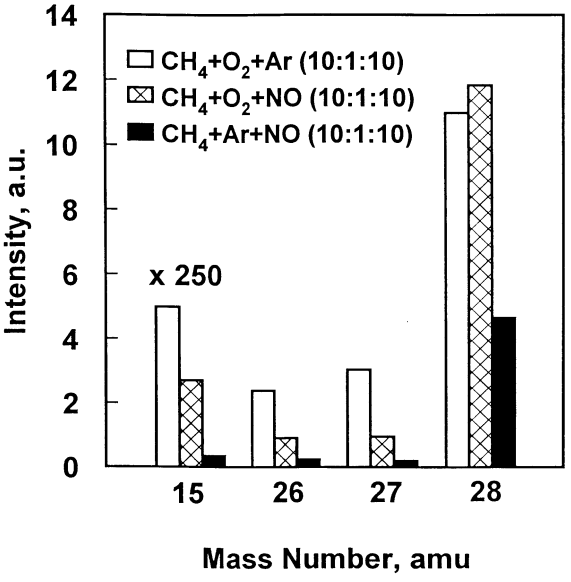

Fig. 4. Effect of reactant gas composition on concentration of products over 4 mol% Ba/MgO. Results were obtained at 19 eV for CH_3· radicals (15 amu) and at 70 eV for stable products (26, 27, 28 amu): P(total) = 500 mTorr, T = 775°C.

at 28 amu is due to both the parent peak of N_2 and the principal fragment of C_2H_6. The N_2 component of this peak can be separately determined, since the C_2H_6 component varies proportionately with the peaks at 26 and 27 amu. Again, when Ar was replaced by NO, the concentration of $CH_3\cdot$ radicals decreased by about 50%. But when O_2 was removed from the system and the NO concentration remained the same, the $CH_3\cdot$ radical signal decreased to almost background level. The mass spectrum at 70 eV is consistent with the decrease in C_2 products as the methyl radical concentration decreased, since the signals at 26 and 27 amu decreased in amplitude. Based on the latter decreases, it is apparent that more than 50% of the intensity of the peak at 28 amu is due to N_2 when NO was added to the CH_4/O_2 mixture. With only CH_4 and NO present (solid bars), the 28 amu peak is almost totally due to the formation of N_2.

As with the Sr/La_2O_3 catalyst, the results of fig. 4 suggest that NO itself is not capable of forming active centers that can generate $CH_3\cdot$ radicals. Previous results obtained with Ba/MgO indicated that surface peroxide ions are responsible for the activation of CH_4 during the oxidative coupling reaction [9]. It is anticipated that the concentration of such peroxide ions would be much greater when the catalyst is in the presence of O_2, rather than NO. When NO and O_2 were both present, one could argue that the negative effect of NO on $CH_3\cdot$ radical formation was a result of surface poisoning, instead of the gas phase reaction between $CH_3\cdot$ and NO; however, the latter explanation appears to be more reasonable since it can be shown that $CH_3\cdot$ and NO react extensively in the gas phase during the residence time in the reactor [15].

3.3. Catalytic reactions at atmospheric pressure

The behavior of the Ba/MgO catalyst at atmospheric pressure is consistent with the results obtained at 500 mTorr. As shown in fig. 5, the conversion of NO in the presence of CH_4 increased significantly when O_2 was added as a reagent, over the temperature range from 600 to 800°C. At 700°C, the effect of adding CH_4 was to increase the NO conversion twofold, while the effect of adding CH_4 + O_2 was to increase the NO conversion fivefold. The results are comparable to those that Vannice and co-workers [4] reported previously over Sr/La_2O_3 at temperatures up to 700°C. We have extended the study of Sr/La_2O_3 to 870°C [8]. Rates of reaction and activation energies are summarized in table 1 for the Ba/MgO catalyst and two Sr/La_2O_3 catalysts. On a per gram basis the rates of NO reduction over the 4 wt% Sr/La_2O_3 and the 4 mol% Ba/MgO catalysts were essentially the same at 700°C; however, the specific rate, based on surface area, was considerably greater over the 4 wt%

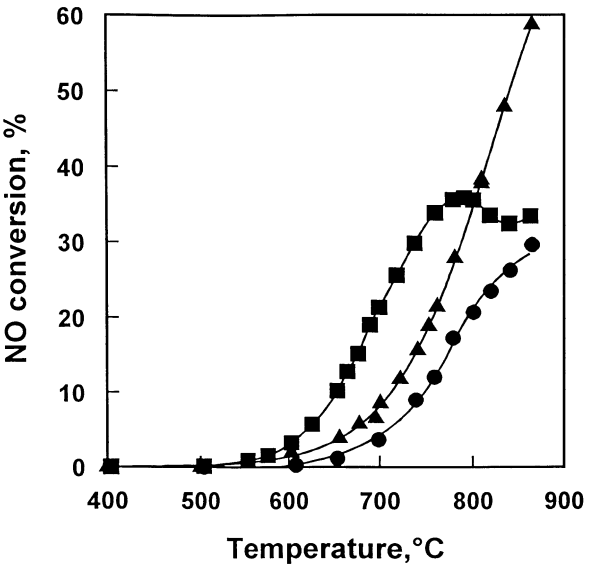

Fig. 5. Conversion of NO over 4 mol% Ba/MgO in a conventional catalytic reactor with the following reagent gases: (●) 1% NO; (▲) 1% NO + 0.25% CH_4; (■) 1% NO + 0.25% CH_4 + 0.5% O_2. The total pressure was 760 Torr.

Table 1
Comparison of N_2 formation rates and activation energies over different catalysts

Catalyst	Reaction conditions[a]			Rate of N_2 formation		E_a	Ref.
	NO (%)	CH_4 (%)	O_2 (%)	(μmol/(s gcat)) $\times 10^2$	(μmol/(s m^2)) $\times 10^2$	(kcal/mol)	
4 wt% Sr/La_2O_3 [b]	1.0	0	0	3.6	2.1	28	[4]
	1.0	0.25	0	15.0	8.9	26	
	1.0	0.25	0.5	19.6	11.5	26	
1 wt% Sr/La_2O_3	1.0	0	0	2.9	0.54	38	[8]
	1.0	0.25	0	5.9	1.09	28	
	1.0	0.25	0.5	13.4	2.48	–	
4 mol% Ba/MgO	1.0	0	0	3.1	0.23	40	this
	1.0	0.25	0	6.0	0.45	31	work
	1.0	0.25	0.5	15.0	1.13	37	

[a] Rate data were obtained with the catalysts at 700°C. NO conversions were less than 20%.
[b] The N_2 formation rate has been normalized to 1% NO, 0.25% CH_4 and 0.5% O_2 using the kinetic parameters obtained from ref. [4].

Sr/La_2O_3 catalyst. The apparent activation energies over the 4 mol% Ba/MgO catalyst were larger than those over the 4 wt% Sr/La_2O_3 catalyst. These observations suggest that the distribution of active centers and, perhaps, the nature of the active centers may be different for the two catalysts.

At temperatures near 780°C, the conversion of NO went through a maximum when NO, CH_4 and O_2 were the reagents (fig. 5). The conversion of CH_4 approached nearly 100% at this temperature. Although it is not possible to measure directly the amount of O_2 under reaction conditions, one may conclude that some remained since the initial O_2/CH_4 ratio was two, which is the stoichiometric ratio if all of the CH_4 reacted only with O_2. But we know that part of the CH_4 was consumed in the reduction of NO. The maximum, therefore, probably results from the change in selectivity at the higher temperatures. That is, because the reaction of CH_4 with O_2 has a larger activation energy than the reaction with NO, more of the CH_4 will be consumed in the former reaction and less will be available for the reduction of NO.

In the absence of O_2, the conversion of NO continued to increase with temperature, both in the presence and absence of CH_4. The change in the slope of the conversion curve for pure NO at $T > 800$°C may result from the decomposition of a surface NO_x intermediate that reacts with gas phase or weakly bound NO. As the temperature increases the concentration of this intermediate decreases because of an unfavorable equilibrium effect.

4. Conclusions

The results confirm that $CH_3\cdot$ radicals are formed over a 4 mol% Ba/MgO catalyst during the reaction of CH_4 with O_2; however, when O_2 is replaced by NO almost no radicals are produced. It appears that NO is not capable of generating the active centers on the catalyst that are responsible for abstracting a hydrogen atom from CH_4. The positive effect of O_2 during the reduction of NO by CH_4 over this catalyst may be attributed to the role of $CH_3\cdot$ radicals as an intermediate. Presumably, $CH_3\cdot$ radicals react with NO in the gas phase to form nitrosomethane.

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