JOURNAL OF CATALYSIS 146, 568–578 (1994)

Catalytic Reduction of NO by CH_4 over Li-Promoted MgO

Xiankuan Zhang, Arden B. Walters, and M. Albert Vannice[1]

Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802-4400

Received October 5, 1993; revised November 23, 1993

NO reduction by CH_4 was conducted in a quartz microreactor from 773 to 953 K over a series of nonmetallic catalysts typically used for CH_4 oxidative coupling—MgO, 1 wt% Li/MgO, 4 wt% Li/MgO, and 16 wt% Li/MgO. This represents a new family of catalysts for NO reduction by CH_4 which has not previously been investigated. All four catalysts were active for NO reduction in the absence of molecular O_2, but the specific activities of N_2 formation (μmol $N_2/s \cdot m^2$) over the Li/MgO samples were almost five times higher than that over pure MgO, indicating that lithium promotes NO reduction; however, NO reduction was not a strong function of lithium loading. No direct NO decomposition occurred over any sample in the absence of CH_4. The apparent activation energy for NO reduction to N_2 by CH_4 over all four catalysts was 29.0 ± 1.1 kcal/mol; thus, there was no correlation between activation energies and lithium loadings. For these four catalysts at 923 K in the absence of oxygen, reaction orders in CH_4 and NO were approximately 0.73 ± 0.11 and 0.43 ± 0.05, respectively. Over all the samples, N_2, CO_2, and smaller amounts of N_2O were observed as products with our GC column; little or no NO_2 formation occurred based on N_2 balances. Selectivity to N_2 increased and that to N_2O decreased with increasing reaction temperature. These catalysts were also active with O_2 in the feed but NO conversion decreased and CH_4 conversion increased, although the inhibiting effect of O_2 on NO reduction to N_2 was less at a higher temperature. The apparent activation energy in the presence of 1.0% O_2 shifted to a higher value of 35.0 ± 1.0 kcal/mol with all four catalysts, and a negative reaction order in O_2 of −0.54 ± 0.13 was determined at 923 K. Over the three Li/MgO catalysts, the apparent activation energy for N_2O formation was 19.7 ± 1.8 kcal/mol. © 1994 Academic Press, Inc.

INTRODUCTION

The reduction of NO_x (NO and NO_2) to N_2 is an important air emission control challenge for the electric utilities and other process industries, as well as for motor vehicles (1, 2). Industrial processes emit NO_x from fuel-burning reactions used to meet large electrical and thermal requirements, as well as from more process-specific NO_x sources such as NO in the tail gas from nitric acid plants. Current technology for NO_x reduction typically requires the use of ammonia (3), which creates problems of its own, or other fixed-nitrogen reducing reagents with or without a solid catalyst in back-end, flue gas cleanup equipment. The use of these reagents involves costs and hazards of transporting, storing, and handling, especially for small, customer-located, and transportation NO_x sources (1). A major advance in NO_x control would result if fuel gases already present and in use at the process site could be substituted for the special NO_x reducing reagents (for example, using natural gas rather than ammonia) while still attaining significant NO_x reduction with low-cost catalysts (1, 4, 5).

Since the pioneering work of Iwamoto *et al.* (6), much attention has been focused on zeolite-based catalysts, in particular Cu/ZSM-5 (7–11) and Co/ZSM-5 (4, 5, 12), for the selective reduction of NO_x with hydrocarbons. However, the following important questions remain: (a) do reaction intermediates such as NO_2, N_2O, or C_xH_yO exist; (b) is there a promoting effect of oxygen; (c) what is the role of different reductants; and (d) what kinetic models are applicable? It has been found that the degree of NO reduction very much depends on the reductants used, and they have been classified into either a "selective" group (C_2H_4, C_3H_6, C_3H_8, C_4H_8) or a "nonselective" group (H_2, CO, CH_4, C_2H_6) for NO reduction over Cu/ZSM-5 in the presence of oxygen (7). The natural gas fuel used at most cogeneration and combined-cycle electrical power plants is comprised mainly of CH_4; therefore, it would be desirable for NO_x emission reduction at these facilities to develop a catalyst which is active for the selective reduction of NO by CH_4 in oxygen-rich (fuel-lean) atmospheres. Recently, Li and Armor have reported the interesting result that NO reduction by CH_4 can effectively proceed on Co/ZSM-5 in the presence of excess oxygen (4, 5). However, as observed with other zeolite catalysts, the activity of Co/ZSM-5 also showed a volcano-like activity dependence on temperature, with the maximum rate achieved around 710 K. At higher temperatures NO reduction is severely decreased, which could limit the suitability of these zeolite catalysts for some applications, such as in power plant duct burner

---

[1] To whom correspondence should be addressed.

0021-9517/94 $6.00

sections of heat recovery steam generators at temperatures typically over 800 K (13). It is obvious that further investigations are needed not only to explore new catalyst systems which can effectively reduce NO with CH_4 at high temperature, but also to understand more of the fundamental chemistry associated with this reaction.

Natural gas injected into the exit gas stream from boiler furnaces at concentrations high enough to provide a slightly fuel-rich zone in a reburning process can significantly reduce NO_x levels via homogenous reactions presumably involving methyl radicals (14). Consequently, enhanced reduction of NO_x might be expected if the concentration of methyl radicals were increased by an additional generation reaction on a catalyst surface, analogous to the CH_4 oxidative coupling reaction (15). Lunsford and co-workers have clearly shown that appropriate heterogeneous catalysts enhance oxidative coupling rates at temperatures between 800 to 1000 K by generating gas-phase methyl radicals (16–18); mechanistic studies have implied that O_2 is essential in generating $CH_3\cdot$ radicals on some of these catalysts by forming active centers which remove H abstracted from CH_4. Our study is focused on testing a new concept—could CH_4 be activated on these oxidative coupling catalysts to effectively reduce NO_x? These oxide catalysts do not contain expensive metals and they should operate in a temperature regime high enough for certain important applications. Our first investigation deals with NO reduction by CH_4 over Li/MgO catalysts in the presence and absence of gas-phase O_2. A family of MgO and Li/MgO catalysts was prepared by reported methods (17, 18), and the specific activities, activation energies, and observed reaction kinetics are discussed in this paper.

EXPERIMENTAL

Li/MgO samples were prepared by following the recipe of Lunsford and co-workers (17, 18). Appropriate amounts of MgO (Aldrich, 99.99%) and Li_2CO_3 (Aldrich, 99.997%) were added to deionized water, and the resulting slurry was then stirred and heated until only a thick paste remained. To ensure that a completely homogeneous catalyst was obtained, a fresh portion of deionized water was added to the paste; this procedure was repeated two more times. The resulting paste was dried in air at 400 K overnight, ground into powder, and then calcined at 973 K (rather than 1023 K, as used by Lunsford) for 10 h under flowing dry air (50 cm^3/min). By this method, three samples of Li/MgO were prepared containing 1.0, 4.0, and 16 wt% Li. A MgO sample was prepared by calcining MgO powder (Aldrich, 99.99%) at 973 K for 10 h under flowing dry air (50 cm^3/min). BET surface area measurements were carried out with a Quantasorb system using three premixed gases containing 10, 20, and 30% N_2 in He (99.999%). Table 1 shows the BET surface areas of fresh and used samples. A calcination time of 1 hr was used at the four lower temperatures, and 10 h at the three higher temperatures (see Fig. 2).

TABLE 1
BET Surface Areas of MgO and Li/MgO Catalysts

Catalyst	Fresh sample (m^2/g)[a]	Used sample (m^2/g)[b]
MgO	10.9	9.0
1% Li/MgO	2.6	2.7
4% Li/MgO	3.7	3.5
16% Li/MgO	2.0	1.8

[a] All samples were calcined at 973 K.
[b] Highest reaction temperature was 953 K.

Activity measurements and kinetic studies were made at atmospheric pressure in a microreactor under steady-state reaction conditions. A reactor made from 4-mm-I.D. quartz tubing was used, and the diameter in the middle of the reactor was constricted to ~2.5 mm to support quartz wool on which catalyst samples were loaded. A typical gas mixture, unless otherwise specified, of 4.04% NO/He and 1.01% CH_4/He at a stoichiometric ratio of NO : CH_4 = 4 : 1 and a total flow rate of 10 cm^3 STP/min was passed through the reactor which contained ~200 mg catalyst (GHSV ≅ 3000 h^{-1}). The reactor was inserted into a tube furnace (Hoskins Electric Furnace FD-303-A) containing a solid brass insert to increase thermal conductivity and improve temperature uniformity. A gold-plated K-type thermocouple was inserted directly into the catalyst bed to obtain accurate temperature measurements. Except for the top and bottom 3 cm (total tube furnace length was 44.5 cm), temperature variations in the reactor were ± 1.5 K; thus, temperature gradients in the catalyst bed (typically 1.5 cm in height) were negligible. Before any data were taken, the samples were pretreated in 10% O_2/He at 973 K at a flow rate of 20 cm^3/min until no CO_2 was detected. At temperatures above 923 K, it was found that a residual white material (possibly Li_2CO_3 or Li_2O) was found in the reactor which showed slight activity toward NO reduction; however, this material was easily removed with aqua regia and the cleaned reactor again showed no blank reaction. All the gases used were from MG Ind., UHP Grade, except for the NO mixed with the He, which was 99.0^+% with major impurities of N_2 (<1%), N_2O (<0.5%), and some CO_2.

During the Arrhenius runs, a period of 30 min on stream was allowed at each temperature before any gas sample was taken. An ascending-temperature sequence from 773 to 953 K was usually followed by a descending-temperature sequence in order to detect any deactivation during these measurements. The conversions were generally kept below 20% to ensure differential reactor operation. The kinetic studies in the presence of gas-phase oxygen

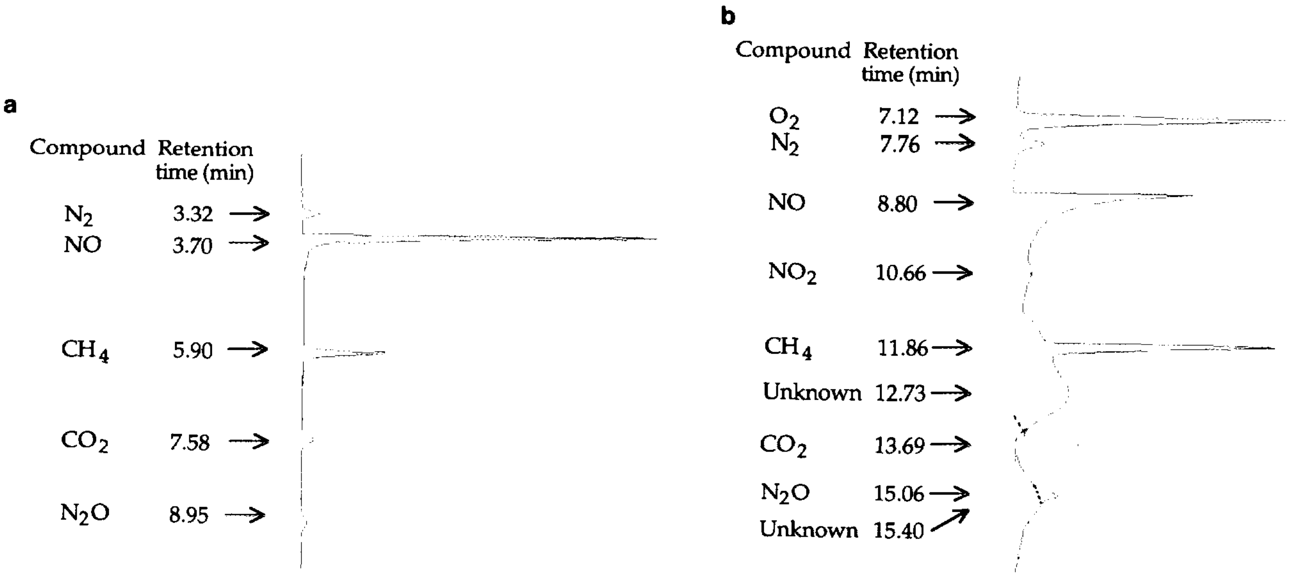

FIG. 1. (a) Gas chromatogram for analysis of N_2, NO, CH_4, and CO_2, and N_2O in the absence of O_2 (4% Li/MgO at 873 K); GC conditions–1 min at 373 K, 30 K/min to 498 K, hold. (b) Gas chromatogram for analysis of N_2, NO, NO_2, CH_4, CO_2, and N_2O in the presence of O_2. The two unknown peaks are noted (4% Li/MgO at 873 K, 1% O_2); GC conditions–5 min at 308 K, 30 K/min to 498 K, hold.

were carried out by adding a mixture of 10% O_2/He at a flow rate of 1.0 cm^3/min to the feed containing NO and CH_4 while maintaining a constant GHSV for the total flow. The effect of O_2 on NO and CH_4 conversion over these Li/MgO catalysts was also examined from 773 to 953 K by varying the O_2 concentration between 0 and 3.0%.

Partial pressure dependency measurements were made with all four samples at 923 K with constant $P_{NO} = 15$ Torr (1 Torr = 133.3 N/m^2) while the partial pressure of CH_4 was varied and with constant $P_{CH_4} = 3.8$ Torr while the NO partial pressure was varied. These pressures for NO and CH_4 were also used when the O_2 pressure was varied. For determination of reaction orders, a power rate law of the following form was utilized:

$$r = k P_{NO}^{a} P_{CH_4}^{b} P_{O_2}^{c}. \qquad [1]$$

P_{NO}, P_{CH_4}, and P_{O_2} are the partial pressures of NO, CH_4, and O_2, respectively, in the feed and a, b, and c are the respective reaction orders on NO, CH_4, and O_2.

The reactor effluent was analyzed with a Perkin–Elmer gas chromatograph (Sigma-2B) equipped with a Carboxen^{1000} column (Supelco) and a P–E Nelson 1020S integrator. This recently available column nicely separates N_2, NO, CH_4, CO_2, and N_2O using a single GC oven program with an initial hold at 373 K for 1 min, then heating to 498 K at 30 K/min and holding at 498 K for 5 min, as shown in Fig. 1a, but a sharp peak for H_2O is not observed and NO_2 gives a broad peak that is difficult to quantify. Good nitrogen and carbon mass balances (±2.5%) were obtained in the absence of O_2 in the feed, thus indicating little or no NO_2 formation. In the presence of oxygen, two broad, unknown peaks in addition to the broad NO_2 peak were observed, and a typical chromatogram is provided in Fig. 1b. Subambient temperature programming was also used to enhance the separation of these three peaks. Using mass spectroscopy, one of these two additional peaks was confirmed to be N_2O_4 while the other appears to be N_2O_5 formed by gas-phase reactions of NO_2 during analysis. The highest possible concentration of H_2O as a reaction product is 1%, and at concentrations below 3%, H_2O gives rise to a very broad feature. Even in the absence of O_2 in the feed, NO consumption is not an accurate measure of the degree of NO reduction to N_2 because N_2O can also be formed. Therefore, specific activities for NO reduction to N_2 are expressed as the number of N_2 molecules produced per second per square meter of catalyst, while NO conversion (%) is defined as NO converted to N_2 and N_2O (the only two nitrogen-containing products observed) divided by total NO fed. Background impurity levels of N_2 and N_2O in the cylinder gas (4.04% NO/He) were subtracted from the total amounts of N_2 and N_2O detected.

RESULTS

Catalyst Stability

Catalyst stability for NO reduction by CH_4 was tested at 953 K over 4% Li/MgO. It was initially found that activity for NO reduction by CH_4 continuously decreased with reaction time and temperature over a higher surface area sample of 4% Li/MgO calcined at 870 K (ca. 35 m^2/g), but a simultaneous decrease in BET surface area of the sample also occurred. The BET surface area variation

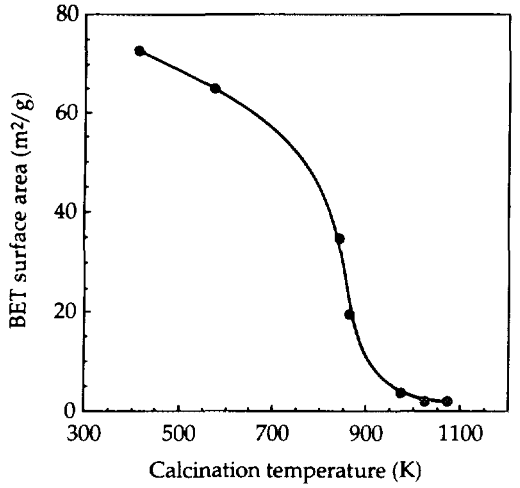

FIG. 2. BET surface area variation of 4% Li/MgO as a function of calcination temperature.

as a function of calcination time and temperature was subsequently examined with this catalyst, and the dependence is shown in Fig. 2. The BET surface area is high (>50 m^2/g) at calcination temperatures below 750 K, but it decreases rapidly with increasing calcination temperature and finally stabilizes below 5 m^2/g at temperatures above 950 K. Consequently, each sample used in the following kinetic experiments was calcined at 973 K for 10 h. The results for NO reduction by CH_4 over 4% Li/MgO at 953 K showed a constant production of N_2 (μmol $N_2/s \cdot m^2$) over a period of 30 h and no significant changes were observed in BET surface area with any of the samples after a period of 30 h on stream, as shown in Table 1.

Activity and Selectivity

NO reduction by CH_4 from 773 to 953 K was performed over four samples—MgO, 1.0% Li/MgO, 4.0% Li/MgO, and 16% Li/MgO. In these experiments N_2, CO_2, and N_2O were observed as products, and the N and C mass balances were each within ±2.5%. Thermal response factors of 37 and 48 were determined for NO and N_2O, respectively, for our thermal conductivity detector. With all the samples, NO conversion increased with reaction temperature up to 953 K. Unlike zeolite-based catalysts, no activity maximum with increasing temperature was observed with the Li/MgO catalysts. Below 893 K, respective selectivities to N_2 and N_2O were typically ~60 and ~40%, but selectivity to N_2 rapidly increased at higher temperatures, while that to N_2O simultaneously fell. As an example, Fig. 3 shows both NO conversions and selectivities to N_2 and N_2O as a function of temperature over 4% Li/MgO. It should be pointed out that over MgO, selectivity to N_2O fell to almost zero above 873 K, while that to N_2 increased to ~100%, although overall rates of N_2 formation were lower.

Table 2 lists NO conversions, rates of NO disappearance, and rates of N_2 formation obtained over all four catalysts. The specific activities for N_2 formation in terms of μmol $N_2/s \cdot m^2$ on the Li/MgO catalysts are almost five times higher than for pure MgO. Clearly the presence of lithium promotes NO reduction to N_2; however, rates of N_2 formation are not a strong function of lithium loadings over the range tested. In fact, very similar results were observed with all three Li/MgO samples. Under the standard conditions used in this work, i.e., 2% NO/0.5% CH_4/97.5% He and 3000 h^{-1} GHSV, the rates of N_2 formation at 953 K (μmol $N_2/s \cdot$ gcat) are comparable to or higher than the maximum activities reported over zeolite-based catalysts at lower temperatures. When the experiments were performed at the same concentrations of NO and CH_4 as those over Co/ZSM-5 in the absence of O_2 (10), similar rates of N_2 formation over 4% Li/MgO were obtained but a higher temperature was required. It should also be noted in this comparison that the presence of oxygen (≥0.5%) greatly enhanced N_2 formation over Co/ZSM-5, while it had little effect on Li/MgO catalysts when the NO and CH_4 concentrations were low and it decreased activity noticeably at higher NO and CH_4 pressures (Table 3).

Kinetic Studies

After calcination at 973 K, all the Arrhenius plots showed reproducible rates of N_2 formation in ascending- and descending-temperature sequences, and the rates of N_2 formation vs reciprocal temperature in the absence of oxygen are shown in Fig. 4, while the relevant kinetic parameters are summarized in Table 4. The apparent activation energies at concentrations of 0.5% CH_4 and 2% NO are 29.0 ± 1.1 kcal/mol, including that obtained over

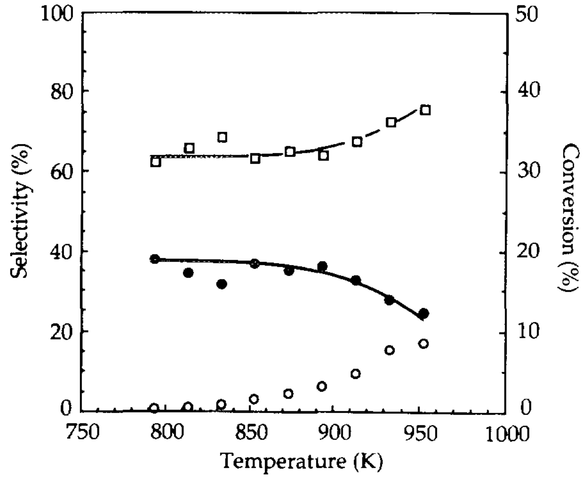

FIG. 3. NO conversion (○) and selectivities to N_2 (□) and N_2O (●) over 4% Li/MgO. Reaction conditions: 2% NO, 0.5% CH_4, balance He, 1 atm total pressure, and GHSV = 3000 h^{-1}.

TABLE 2
Comparison of Rates of N_2 Formation over Different Catalysts

	Reaction conditions (1 atm)					Rate of NO disappearance	N_2 formation		
Catalyst	NO (%)	CH_4 (%)	O_2 (%)	Temp (K)	NO conv. (%)	(μmol NO/s · gcat × 10^2)	Rate(μmol/s · gcat × 10^2)	Specific activity (μmol/s · m^2 × 10^3)	Ref.
MgO	2.02	0.505	0	773	0.462	0.346	0.112	0.113	[a]
	2.02	0.505	0	953	12.1	9.04	4.52	4.54	[a]
1% Li/MgO	2.02	0.505	0	773	0.582	0.436	0.120	0.453	[a]
	2.02	0.505	0	953	18.5	13.9	5.01	18.9	[a]
4% Li/MgO	2.02	0.505	0	773	0.775	0.581	0.180	0.500	[a]
	2.02	0.505	0	953	27.2	20.4	7.70	21.4	[a]
	0.0820	0.0820	0	773	1.15	0.0926	0.0347	0.0965	[a]
	0.0820	0.0820	0	953	39.3	3.15	1.18	3.29	[a]
	0.0820	0.0820	0.5	773	—	—	0.0199	0.0553	[a]
	0.0820	0.0820	0.5	953	—	—	1.02	2.83	
16% Li/MgO	2.02	0.505	0	773	0.582	0.436	0.120	0.453	[a]
	2.02	0.505	0	953	14.8	11.1	4.16	21.9	[a]
Co/ZSM-5	0.0820	0.0820	0	673	17	2.58	1.29[b]	[c]	(10)
	0.0820	0.0820	>0.5	673	60	9.12	4.56[b]	[c]	(10)
H-zeolites	0.1000	0.0300[d]	0	673	65	2.90	1.45[e]	[c]	(19)
Cu/ZSM-5	0.1000	0.0250[f]	2	523	40	8.92	4.46[b]	[c]	(20)
Cu/ZSM-5	0.0230	0.0800[g]	7	620	335	1.19	0.595[b]	[c]	(21)

[a] This work.
[b] Assuming selectivities to N_2 are 100%.
[c] Surface areas are unknown.
[d] Reductant is C_3H_8.
[e] Assuming catalyst density is 1 g/ml.
[f] Reductant is C_2H_4.
[g] Reductant is C_3H_6.

TABLE 3
Effect of O_2 on Rates of N_2 Formation

		N_2 activity[a] (μmol/s · m^2 × 10^3)		
Catalyst	Temp (K)	$O_2 = 0$	$O_2 = 1.0\%$	$[N_2(O_2 = 1\%)/N_2(O_2 = 0\%)]$
1% Li/MgO	823	9.80	0.67	0.068
	873	15.5	2.45	0.158
	923	17.7	5.56	0.315
4% Li/MgO	823	11.6	1.89	0.163
	873	17.4	7.47	0.429
	923	25.6	14.2	0.555
16% Li/MgO	823	11.4	1.81	0.159
	873	21.7	8.09	0.373
	923	26.8	16.2	0.606

[a] $P_{NO} = 15$ Torr, $P_{CH_4} = 3.8$ Torr.

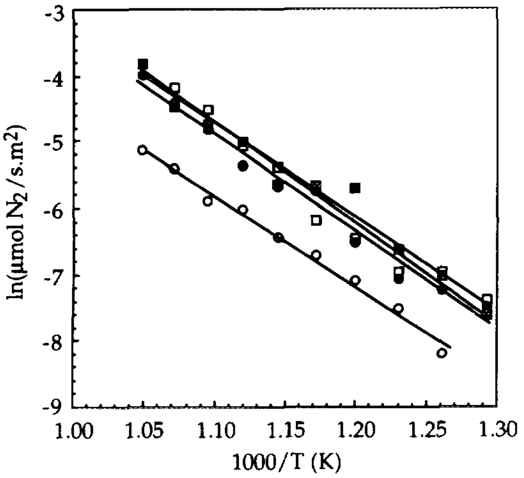

FIG. 4. Temperature dependencies of NO reduction to N_2 by CH_4 over (○) MgO, (●) 1% Li/MgO, (□) 4% Li/MgO, and (■) 16% Li/MgO. Reaction conditions: 2% NO, 0.5% CH_4, balance He, 1 atm total pressure, and GHSV = 3000 h^{-1}.

pure MgO, and no correlation between activation energies and lithium loadings was observed. For comparison, kinetic studies were also carried out at lower NO and higher CH_4 concentrations and the corresponding activation energies, all presented in Table 4, are not significantly different, although the absolute concentration of NO was 10 times lower and that of CH_4 was 10 times higher. For the experiments at low NO concentrations, including the partial pressure studies described below, NO conversions were sometimes as high as ~40% in order to accurately measure products. Figure 4 shows that rates of N_2 formation over the three Li/MgO samples are significantly higher than for pure MgO; however, N_2 formation is not a strong function of lithium loading. In fact, specific activities for N_2 formation over 4 and 16% Li/MgO are almost the same, and they are both only slightly higher than that over 1% Li/MgO. It is interesting to note that pure MgO has a very similar apparent activation energy although its activity is lower than those of the Li/MgO samples. It should be pointed out that those data points taken at low temperatures (see Fig. 4) and low partial pressures (see Fig. 5) have the greatest uncertainties because GC peak areas were the smallest. Arrhenius plots for the rates of N_2O formation are shown in Fig. 6. The activation energies for N_2O formation over 1% Li/MgO, 4% Li/MgO, and 16% MgO were 18.0, 22.1, and 18.9 kcal/mol, respectively, giving an average value of 19.7 ± 1.8. Thus, this reaction has a much lower activation energy than that for N_2 formation.

The reaction orders with respect to CH_4 and NO in the absence of O_2 were determined by first keeping NO at 15.4 Torr and then by keeping P_{CH_4} at 3.8 Torr; typical sets of data are shown in Fig. 5. As summarized in Table 4, the average empirical reaction orders, with their standard

TABLE 4

Kinetic Behavior of Li/MgO Catalysts for NO Reduction to N_2 by CH_4

Catalyst	O_2 (%)	E_a (kcal/mol)	Reaction order in CH_4	Reaction order in NO	Reaction order in O_2[a]
MgO	0	27.6	0.60	0.44	—
	1.0	33.9	—	—	—
1% Li/MgO	0	29.4	0.73	0.41	—
	1.0	36.6	—	—	−0.73
4% Li/MgO	0	30.5	0.70	0.35	—
	0	28.7[b]	0.73[c]	0.48	—
	0	24.9[d]	—	—	—
	1.0	35.0	—	—	−0.43
16% Li/MgO	0	28.4	0.91	0.45	—
	1.0	34.5	—	—	−0.47

[a] O_2 concentration was below 2%. At higher O_2 concentration, the reaction order approaches zero.

[b] Reaction conditions: 0.2% NO, 0.5% CH_4, He balance, and 1 atm total pressure.

[c] NO was kept at 1.6 Torr (0.2%).

[d] Reaction conditions: 0.2% NO, 5% CH_4, He balance, and 1 atm total pressure.

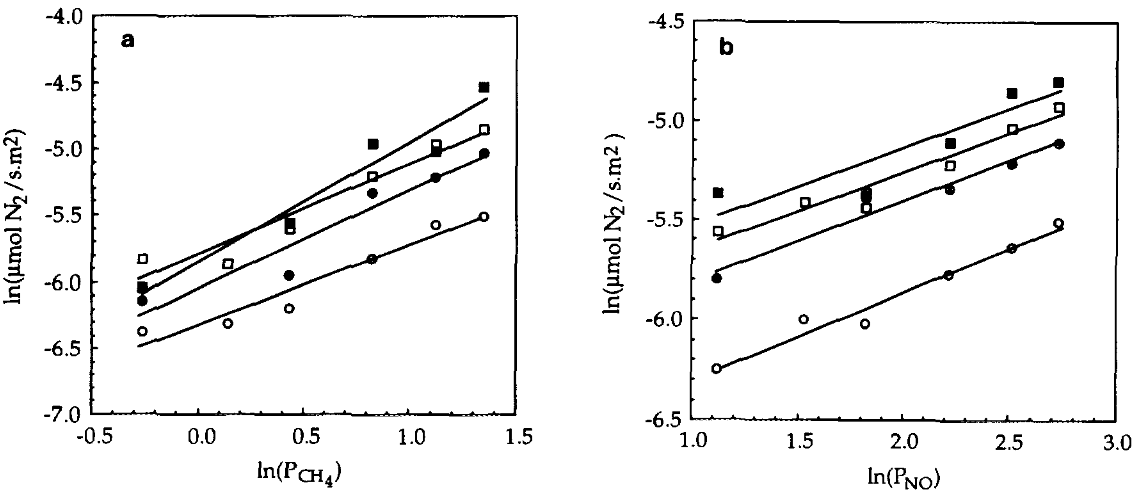

FIG. 5. Pressure dependencies of NO reduction to N_2 by CH_4 at 923 K: (a) rate vs P_{CH_4} at P_{NO} = 15.4 Torr, over (○) MgO, (●) 1% Li/MgO, (□) 4% Li/MgO, and (■) 16% Li/MgO and (b) rate vs P_{NO} at P_{CH_4} = 3.8 Torr.

deviations, are 0.73 ± 0.11 for CH_4 and 0.43 ± 0.05 for NO. The lithium loading seems to have no significant effect on the NO partial pressure dependency, but it may increase the CH_4 dependency somewhat compared to pure MgO. The partial pressure dependency studies were also extended to low NO concentrations over the 4% Li/MgO catalyst (down to 200 ppm) and the corresponding NO and CH_4 reaction orders were determined at P_{CH_4} = 33.8 Torr and P_{NO} = 1.6 Torr, respectively. The reaction orders thus obtained (0.73 for CH_4 and 0.48 for NO) are very close to those at higher NO concentration, making Eq. [1] valid for NO concentrations over a range of two orders of magnitude (200–20,000 ppm).

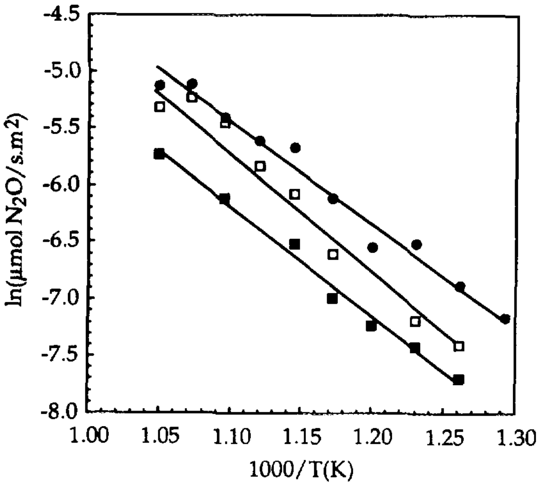

FIG. 6. Temperature dependencies of N_2O formation over: (●) 1% Li/MgO, (□) 4% Li/MgO, and (■) 16% Li/MgO. Reaction conditions: 2% NO, 0.5% CH_4, balance He, 1 atm total pressure, and GHSV = 3000 h^{-1}.

O_2 Effect on NO Conversion

The effect of O_2 on NO reduction was investigated over the three Li/MgO catalysts. The experiments were conducted at three temperatures—823, 873, and 923 K—using a GHSV of 3000 h^{-1} and a gas mixture of 2% NO and 0.5% CH_4, which is the stoichiometric ratio. The O_2 concentration was varied between 1 and 2.8% while a total feed flow rate of 10 ml/min was maintained. Similar results were observed over all three Li/MgO samples, and Fig. 7 shows representative results of the effect of O_2 on NO reduction and CH_4 conversion over 4% Li/MgO. As seen in Fig. 7a, NO conversion rapidly decreases with increasing oxygen concentration but begins to level off at about 0.7% O_2 and becomes independent of O_2 concentration at high O_2 levels. The corresponding CH_4 conversion shows an opposite trend as a function of O_2 concentration. Table 3 compares NO conversion over the Li/MgO catalysts at the different temperatures, and it is clear that the effect of O_2 on NO conversion depends strongly on temperature as well as the lithium loading. The inhibiting effect of O_2 on the activity becomes less pronounced at high temperature and high lithium loading. The conversion of CH_4 is also a strong function of temperature, as shown in Fig. 7b. At temperatures below 823 K, CH_4 conversion varies little over the entire range of O_2 concentration; however, at temperatures above 873 K, CH_4 conversion dramatically increases as the O_2 concentration approaches 1%; it then levels off. The 1% O_2 level represents the stoichiometric ratio for deep oxidation of CH_4(at 0.5%), i.e., $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. No C_2H_4 and C_2H_6 and no C_xH_yO compounds were detected in the presence of gas-phase oxygen under these reaction conditions, although in a separate set of experi-

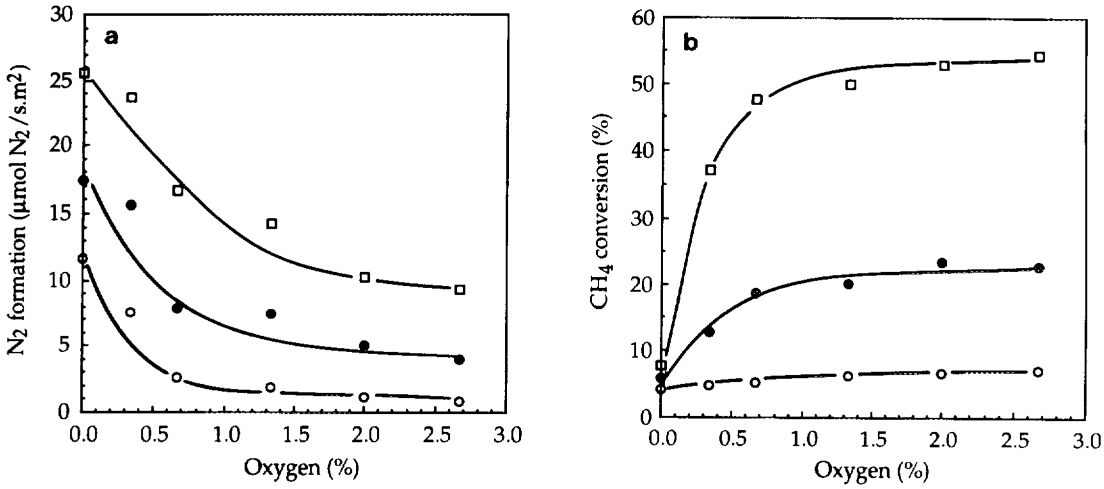

FIG. 7. Effect of O_2 on (a) N_2 formation and (b) CH_4 conversion over 4% Li/MgO at (○) 823 K, (●) 873 K, and (□) 923 K. Reaction conditions: 2% NO, 0.5% CH_4, balance He, 1 atm total pressure, and GHSV = 3000 h^{-1}.

ments employing oxidative coupling conditions of 0.99% CH_4 and 0.20% O_2 at 1 atm, C_2 hydrocarbons were produced at a rate of 0.033 μmol $C_2/\text{sec}\cdot\text{m}^2$ (30.7% CH_4 conversion) with a selectivity of 66.5% to C_2 hydrocarbons.

Kinetic studies of NO reduction by CH_4 in the presence of 1.0% O_2 were then performed over all four samples. Again, all the Arrhenius plots showed reproducible rates of N_2 formation in ascending- and descending-temperature sequences. Figure 8 shows rates of N_2 formation versus reciprocal temperature, while the corresponding kinetic parameters are summarized in Table 4. The apparent activation energies of 34.9 ± 1.8 kcal/mol are significantly higher than those in the absence of oxygen. Again, no correlation existed between activation energies and lithium loadings. For all catalysts, the empirical reaction orders in O_2 at 923 K determined at P_{CH_4} = 3.8 Torr and P_{NO} = 15.4 Torr were negative (average value of −0.54) for O_2 concentrations below 2%, as presented in Table 4, but the pressure dependence on O_2 approaches zero order for O_2 pressures greater than 15 Torr.

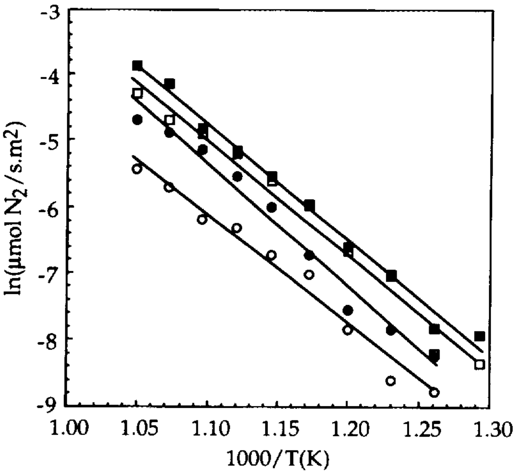

FIG. 8. Temperature dependence of NO reduction to N_2 by CH_4 at 15.4 Torr NO, 3.8 Torr CH_4, 7.5 Torr O_2, (balance He) over (○) MgO, (●) 1% Li/MgO, (□) 4% Li/MgO, and (■) 16% Li/MgO.

DISCUSSION

The concept of this study arose from two engineering studies which examined the influence on overall thermal efficiency of a reburn step to generate steam following a combustion gas turbine (14, 19). It was observed that NO_x concentrations were decreased during the homogeneous reaction between natural gas and oxygen. It was then demonstrated by Walters *et al.* that additional NO_x reduction by CH_4 could be achieved under similar conditions using Na or Ca sulfates as heterogeneous catalysts (20). We hypothesized at this point that methyl radicals were responsible for the decrease in NO_x concentration as the reactivity of $CH_3\cdot$ radicals with NO and NO_2 was well established in homogeneous gas-phase reactions (21–24). Furthermore, the gas-phase rate constant for the reaction between $CH_3\cdot$ and NO has been reported to be 15–20 times greater than that for the $CH_3\cdot + O_2$ reaction (25, 26). Consequently, our hypothesis was that an increase in methyl radical concentration would enhance the overall reaction between CH_4 and NO (i.e., NO_x), and to test this idea we chose several oxidative coupling catalyst systems which had been shown to produce these radicals by Lunsford and co-workers (16–18). We discuss here our initial results using a family of Li/MgO catalysts.

This study has shown that Li/MgO catalysts, as well as pure MgO, are indeed active for NO reduction by CH_4 and, depending on the surface area of the catalyst, the reaction can be observed at 723 K, although NO conversions were very low. The catalysts precalcined at 973 K for 10 h showed very stable performance for NO reduction over a period of 30 h, and the activity continuously increased with temperature up to 953 K, which was the highest temperature employed in this work. Both N_2 and N_2O as nitrogen-containing products were observed, and selectivity to N_2 (the N_2/N_2O ratio) increased with temperature. N_2 mass balances as well as gas chromatograms showed that little or no NO_2 formation occurred. With stable catalysts, even higher NO conversions and higher selectivity to N_2 are expected at temperatures above 953 K. Control experiments demonstrated that there was no reaction of either NO or CH_4 in an empty quartz tube reactor or with quartz wool inserted. Further experiments in the absence of co-fed CH_4 showed that there was no direct NO decomposition over these catalysts. The interaction of CH_4 only with 4.0% Li/MgO was investigated from 773 to 953 K at a GHSV of 3000 h^{-1} using a 1.01% CH_4/He mixture at a flow rate of 10 cm^3/min. No reaction occurred below 873 K, and at temperatures above 873 K a small amount of CO_2 was initially observed, but it decreased rapidly with time and temperature. The rapid decrease in CO_2 production is totally predictable because of continuing consumption of surface oxygen on the Li/MgO catalyst in the absence of co-fed, gas-phase oxygen (15). After a reaction period of 30 min at the higher temperatures, no detectable CO_2 was found. All these results suggest that NO reduction can proceed only in the presence of gaseous CH_4. In general, hydrocarbons have a certain degree of selectivity for promoting NO reduction vs their reaction with O_2 in the presence of excess oxygen. This relative reactivity is high for "selective" reductants like C_2H_4, C_3H_6, C_3H_8, and C_4H_8, while it is typically low for "nonselective" reductants like CH_4 and C_2H_6 (7). It is anticipated that NO reduction over Li/MgO using a selective hydrocarbon will result in higher activity for NO reduction and higher selectivity to N_2 formation; however, we have not yet tried any of these reactions.

These Li/MgO catalysts exhibit stable, long-term activity as long as no loss of surface area occurs. Initial studies of higher surface area catalysts (ca. 35 m^2/g) produced higher activities per gram but a continuous loss of activity occurred due to decreasing surface area under continuous operation at 863 K. Even though the surface area of the used catalyst sample decreased to about 10 m^2/g, the initial and final specific activities were almost the same. Therefore, to obtain reproducible kinetic data, all catalyst samples discussed here had been pretreated at 973 K to give stable surfaces near 3 m^2/g. A high Li loading seemed to facilitate sintering, as indicated in Table 1.

Rather high NO concentrations of around 2% along with a stoichiometric ratio of CH_4 (0.5%) were utilized in most of the runs conducted in this study. By operating the system as a differential reactor under these conditions, quite high rates per unit surface area were attained in the absence of O_2, as shown in Table 2. Varying the lithium loadings from 1 to 16% had little effect on specific activity, but the absence of lithium resulted in an approximate fivefold decrease, as shown in Table 2. Despite this decline in specific activity, neither the activation energy nor the partial pressure dependencies were strongly dependent on the lithium loading, thus suggesting a similar reaction path on all four catalyst surfaces. For all catalysts, the apparent E_{act} values were near 29 kcal/mol and the NO pressure dependence was around 0.43. The pressure dependence on CH_4 appeared to increase somewhat from 0.6 on pure MgO to 0.9 at a high lithium loading of 16%, while the negative dependence on O_2 seemed to decrease slightly (Table 4). The same rate equation holds at much lower NO concentrations, and Eq. [1] is thus applicable for NO pressures from 0.015 to 15 Torr. A substantial amount of N_2O is produced at high NO concentrations, and at temperatures below 900 K, the selectivity to N_2 is about 65%, giving a N_2/N_2O ratio of about 1.9; however, at higher temperatures and conversions, this ratio increases significantly to 3.0 at 953 K with the 4% Li/MgO catalyst, as shown in Fig. 3. Over pure MgO, the amount of N_2O formed approaches zero at these higher temperatures; thus, the presence of lithium may facilitate N_2O formation (this could imply a slightly different reaction path for N_2O formation over lithium-doped MgO vs undoped MgO).

The presence of molecular O_2 significantly inhibits N_2 formation at higher NO concentration, especially as the O_2 concentration increases to the stoichiometric ratio for CH_4 combustion (1% under our standard conditions) and the extent of CH_4 combustion increases markedly, especially at higher temperatures, as shown in Fig. 7. However, the relative decrease in the rate of N_2 formation caused by O_2 is much less at higher temperatures; for example, the N_2 formation rate on 4% Li/MgO with 1% O_2 at 823 K is only 16.3% of that in the absence of O_2, whereas at 923 K the relative rate is 55.5% (Table 3). This relative decrease in the N_2 formation rate with O_2 declines as lithium loadings increase.

It is well known that Li/MgO is one of the most active catalysts, and certainly the most studied catalyst system, for methane oxidative coupling (15). A widely accepted overall reaction mechanism involves methyl radicals generated on $[La^+O^-]$ sites of Li/MgO; two methyl radicals then couple into C_2H_6 in the gas phase, and C_2H_6 can be subsequently dehydrogenated into C_2H_4 on the catalyst surface (16–18). In order to look for any possible involvement of methyl radicals in NO reduction by CH_4, the methane oxidative coupling reaction was performed over 4% Li/MgO. Under similar conditions, e.g., at 923 K, a GHSV of 9000 h^{-1} and a $CH_4 : O_2$ ratio of 5 (a typical ratio in methane coupling), CH_4 conversion was 30.7% and selectivity to C_2H_4 plus C_2H_6 was 66.5%, which favorably compares with results reported by Lunsford *et al.*; i.e., their CH_4 conversion was ~20% and their C_2 selectivity was ~70% at 923 K (16–18). These results verify that the catalysts prepared in this study are truly methane oxidative coupling catalysts, which implies that they can generate methyl radicals under appropriate conditions; however, we cannot verify at this time that methyl radicals are directly involved in NO reduction by CH_4. We could detect no C_2 hydrocarbons under any circumstances during NO reduction by CH_4, even at a CH_4 : NO ratio of 5 : 2 and in the presence of O_2. These results indicate either that methyl radicals cannot be generated during NO reduction by CH_4 over Li/MgO catalysts, or that methyl radicals generated on the catalyst surface react with NO before they can desorb into the gas phase, or that if they do desorb, the reaction probability with gas-phase NO is much greater than with another methyl radical and no coupling is observed. The fact that the Li/MgO catalysts were active for NO reduction by CH_4 at 723 K and lower, while methyl radicals have been detected only at temperatures above 773 K on Li/MgO (15, 16), is consistent with the second possibility. Lunsford and co-workers have recently reported that N_2O can replace O_2 in its role to facilitate the generation of methyl radicals (27); thus, N_2O may play a similar role in this reaction. Finally, the similar, although lower, activity of pure MgO in this reaction is consistent with the recent study of Goodman *et al.* which indicated that oxygen vacancies present in MgO as well as Li-promoted MgO are involved in CH_4 activation (28).

It is important to compare these nonmetallic catalysts with the performance of zeolite catalysts because few catalysts have been able to successfully activate CH_4 for NO_x reduction to N_2. Among the zeolite catalysts tested, Cu/ZSM-5 is particularly good for direct NO decomposition (10) while Co/ZSM-5 is the best catalyst for reduction by CH_4 in the presence of oxygen (4). One obvious difference between the zeolites and these Li/MgO catalysts is that all the zeolite catalysts have shown a volcano-like activity dependence on temperature, with the activity maximum falling between 670 and 720 K, depending on the system (5). Li and Armor believe that the decrease in NO conversion at high temperature, to a large extent, may be the result of a significantly lowered CH_4 concentration due to combustion (5). The two reactions

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

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad [3]$$

are competitive, and if reaction [3] is favored at higher temperatures, CH_4 can be completely burned (15). However, Hall *et al.* have suggested that this decrease at higher temperatures for either direct NO decomposition or NO reduction by hydrocarbons is due to a decrease in NO_2 formation from NO and O_2, because NO_2 is known to form as an intermediate during NO decomposition (29, 30). The rate of NO reduction by CH_4 over Li/MgO catalyts continuously increases up to 953 K with or without oxygen; however, substantial CH_4 remains even at the highest temperature. In the absence of oxygen, no NO_2 was detected; thus, we cannot confirm that NO_2 may be a stable intermediate in NO reduction over these catalysts. In the presence of oxygen, no decrease in NO conversion with temperature was observed even though CH_4 conversions were above 50% at temperatures above 923 K. Li and Armor observed a decline in NO conversion at 700–725 K over Co/ZSM-5, at which point CH_4 conversions were 70–93% (5). Another significant difference between these two catalyst systems was that the presence of oxygen greatly enhanced NO conversion over the zeolite catalysts at low concentrations (ca. 1000 ppm), while it had little effect on the Li/MgO catalysts at low NO concentrations and it strongly inhibited NO conversion at high concentrations over Li/MgO at temperatures below 873 K. This effect became less significant at temperatures above 923 K, however. The baseline behavior of the gas chromatograms taken in the presence of oxygen provides some evidence for the presence of NO_2 (Fig. 1b), but the amounts cannot yet be quantified.

The only previous work on NO reduction by CH_4 available for comparison to our work is that of Li and Armor (4, 5). Over Mn/ZSM-5 and Co/ZSM-5, the CH_4 pressure dependencies were near 0.6 and the NO pressure dependencies were around 0.5 (5); thus, our reaction orders are similar. However, the major differences are that the addition of O_2 up to 0.5% increased NO conversion over Co/ZSM-5 (4), and the apparent activation energy calculated from their results for Co/ZSM-5 is about 12 kcal/mol (5); thus, the reaction mechanisms over metal-loaded ZSM-5 and Li-promoted MgO may be different. The efficient reduction of NO by CH_4 in the absence of molecular O_2 for our Li/MgO catalysts argues strongly against a NO_2 intermediate, as proposed by Hall and co-workers for zeolite systems (29, 30), and our experimental evidence that little or no NO_2 is formed is also consistent with this. Current studies are underway to gain more information about the sequence of elementary steps describing not only N_2 formation but also N_2O production over these MgO and Li/MgO catalysts. We hope to obtain a reasonable reaction mechanism which will allow the derivation of a rate expression consistent with that in Eq. [1]. In addition, the influence of H_2O and CO_2 on catalytic behavior will be examined.

SUMMARY

Nonmetallic catalysts known to produce methyl radicals during the methane oxidative coupling reaction have been shown to be active for NO reduction by CH_4. This reaction proceeds above 773 K over low surface area, Li-promoted MgO in the absence of O_2 to produce N_2 and N_2O with a (N_2/N_2O) selectivity below 2 at low temperature but which increases to 3 or more at higher temperatures. Unpromoted MgO is less active but produces almost 100% N_2. Little or no NO_2 is formed with no O_2 in the feed. The addition of O_2 decreases N_2 formation rates at higher NO concentrations (ca. 2%), but has little effect at levels around 1000 ppm; however, the relative inhibition decreases at higher temperatures. Operation at even higher temperatures with stable catalysts should favor N_2 selectivity and decrease the inhibition by O_2; thus, such catalysts may have applications in a catalytic reburn step conducted in a waste heat boiler which would not only reduce NO_x emissions but also increase the thermal efficiency of the overall process.

ACKNOWLEDGMENTS

This study was supported by the National Science Foundation under Grant CTS-9211552 and by the Florida Power and Light Company.

REFERENCES

1. Armor, J. N., *Appl. Catal. B* **1,** 221 (1992).
2. Truex, T. J., Searles, R. A., and Sun, D. C., *Platinum Met. Rev.* **36,** 2 (1992).
3. Beechman, J. W., and Hegedus, L. L., *Ind. Eng. Chem. Res.* **30,** 969 (1991).
4. Li, Y., and Armor, J. N., *Appl. Catal. B* **1,** L31 (1992).
5. Li, Y., and Armor, J. N., *Appl. Catal. B* **2,** 239 (1993).
6. Iwamoto, M., Yokoo, S., Sakai, K., and Kagawa, S., *J. Chem. Soc. Faraday Trans. 1* **77,** 1629 (1981).
7. Iwamoto, M., and Hamada, H., *Catal. Today* **10,** 57 (1991).
8. Iwamoto, M., and Yahiro, H., Yu-u, Y., Shundo, S., and Mizuno, N., *Shokubai* **32,** 430 (1990).
9. Burch, R., and Millington, P. J., *Appl. Catal. B* **2,** 101 (1993).
10. Li, Y., and Hall, W. K., *J. Phys. Chem.* **94,** 6145 (1990).
11. Ansell, G. P., Diwell, A. F., Golunski, S. E., Hayes, J. W., Rajaram, R. R., Truex, T. J., and Walker, A. P., *Appl. Catal. B* **2,** 81 (1993).
12. Li, Y., and Armor, J. N., U.S. Patent 5, 149, 512 (1992).
13. Walters, A. B., Craig, J. R., Culley, R. J., Herbster, R. E., and VanLaar, J. A. Paper 87-JPGC-Pwr-8, Joint ASME/IEEE Power Generation Conference, Miami Beach, FL, 1987.
14. Moller, E. C., Chen, S. L., Pershing, D. W., and Walters, A. B., Paper 88-73, Fall Meeting, The Combustion Institute, Western States Section, Dana Pt., CA, 1988.
15. Hutchings, G. J., Scurrell, M. S., and Woodhouse, J. R., *Chem. Soc. Rev.* **18,** 251 (1989).
16. Ito, T., and Lunsford, J. H., *Nature* **314,** 721 (1985).
17. Ito, T., Wang, J.-X., Lin, C.-H., and Lunsford, J. H., *J. Am. Chem. Soc.* **107,** 5062 (1985).
18. Xu, M., Shi, C., Yang, X., Rosynek, M. P., and Lunsford, J. H., *J. Phys. Chem.* **96,** 6395 (1992).
19. Chen, S. L., McCarthy, J. M., Clark, W. D., Heap, M. P., Seeker, W. R., and Pershing, D. W., 21st Symp. (International) on Comb., The Comb. Inst., 1159, 1986.
20. Walters, A. B., Maly, P. M., Cheng, F. W., Sanford, R. C., Cole, J. A., and Chen, S. L., Final Report to Florida Power & Light Company, the Energy and Environmental Research Corporation, May, 1991.
21. Miller, J. A., and Bowman, C. T., *Prog. Energy Combust. Sci.* **15,** 287 (1989).
22. Yamada, F., Slafle, I. R., and Gutman, D., *Chem. Phys. Lett.* **83,** 409 (1981).
23. Davies, J. W., Grant, N. J. B., and Pilling, M. J., *J. Chem. Soc. Faraday Trans.* **87,** 2317 (1991).
24. Thorne, L. R., Branch, M. C., Chandler, D. W., Kee, R. J., and Miller, J. A., 21st Symp. (International) on Comb., The Comb. Inst., 965, 1986.
25. Laufer, A. H., and Bass, A. M., *Int. J. Chem. Kinet.* **7,** 639 (1975).
26. Washida, N., *J. Chem. Phys.* **73,** 1665 (1980).
27. Yamamoto, H., Chu, H. Y., Xu, M., Shi, C., and Lunsford, J. H., *J. Catal.* **142,** 325 (1993).
28. Wu, M-C., Truong, C. M., Coulter, K., and Goodman, D. W., *J. Catal.* **140,** 344 (1993).
29. Li, Y., and Hall, W. K., *J. Catal.* **129,** 202 (1991).
30. Petunchi, J. O., and Hall, W. K., *Appl. Catal. B* **2,** L17 (1993).