NO reduction over La_2O_3 using methanol

Todd J. Toops [a], Arden B. Walters [b] and M. Albert Vannice [a,*]

[a] *Department of Chemical Engineering, 107 Fenske Laboratory, The Pennsylvania State University, University Park, PA 16802-4400, USA*
E-mail: mavche@engr.psu.edu
[b] *Advanced Energy Research, 13114 Bayfield Drive, Austin, TX 78727-3320, USA*

Received 5 October 1999; accepted 14 December 1999

Nitric oxide (NO) reduction by methanol was studied over La_2O_3 in the presence and absence of oxygen. In the absence of O_2, CH_3OH reduced NO to both N_2O and N_2, with selectivity to dinitrogen formation decreasing from around 85% at 623 K to 50–70% at 723 K. With 1% O_2 in the feed, rates were 4–8 times higher, but the selectivity to N_2 dropped from 50% at 623 K to 10% at 723 K. The specific activities with La_2O_3 for this reaction were higher than those for other reductants; for example, at 773 K with hydrogen a specific activity of 35 μmol NO/s m^2 was obtained whereas that for methanol was 600 μmol NO/s m^2. The Arrhenius plots were linear under differential reaction conditions, and the apparent activation energy was consistently near 14 kcal/mol with CH_3OH. Linear partial pressure dependencies based on a power rate law were obtained and showed a near-zero order in CH_3OH and a near-first order in H_2. In the absence of O_2, a Langmuir–Hinshelwood type model assuming a surface reaction between adsorbed CH_3OH and adsorbed NO as the slow step satisfactorily fitted the data, and the model invoking two types of sites provided the best fit and gave thermodynamically consistent rate constants. In the presence of O_2 a homogeneous gas-phase reaction between O_2, NO, and CH_3OH occurred to yield methyl nitrite. This reaction converted more than 30% of the methanol at 300 K and continued to occur up to temperatures where methanol was fully oxidized. Quantitative kinetic studies of the heterogeneous reaction with O_2 present were significantly complicated by this homogeneous reaction.

Keywords: NO reduction, CH_3OH, La_2O_3, methyl nitrite, kinetics

1. Introduction

Nitrogen oxides (NO_x) in the exhaust of both automobile and stationary sources are of critical concern because these by-products are toxic environmental pollutants that lead to acid rain and ozone formation [1]. Due to these effects, the Environmental Protection Agency established strict emission regulations in the 1970s that have become more rigorous with time [2], and heterogeneous catalysts are used to reduce the oxides to N_2 from both sources. The three-way catalysts containing Rh, Pd, and Pt that are utilized in automobile catalytic converters are effective at or below the stoichiometric air-to-fuel ratio [3]; however, under the lean-burn combustion conditions existing in diesel and future four-stroke automobile engines, the catalytic converter is considerably less effective for NO_x reduction [4]. Furthermore, long-term oxygen exposure inhibits catalytic activity. Stationary sources of NO_x typically employ a selective catalytic reduction process with ammonia as the reductant. This reaction occurs readily in the presence of O_2, but the process involves environmental, safety, and economic concerns related to ammonia emission, transportation, and storage [5]. A less expensive, environmentally benign method to reduce NO_x that is applicable in an oxidizing environment would be highly desirable.

A relatively recent breakthrough in catalysis related to this topic was the successful reduction of nitric oxide (NO) with methane over a Cu/ZSM-5 zeolite under oxidizing conditions [6]. Following this discovery various other systems, such as ion-exchanged zeolites, single and binary metal oxides, supported metal oxides, and noble metals, have been determined to be effective using hydrocarbons as the reductant [7–10]. Unlike the three-way catalyst system, these new processes are typically enhanced by O_2; however, problems have arisen due to loss of catalytic activity above 673 K and catalyst instability in the presence of water vapor [7,11].

Several studies have shown that alcohols are promising reductants of NO. Of the alcohols studied, Hamada et al. found methanol to display excellent reducing capabilities in the presence of oxygen, especially at lower temperatures below 673 K [12]. Although methanol has shown little or no activity over Cu/ZSM-5, varying degrees of success have been obtained with the pure alumina [12–16], alumina promoted with different elements [3,12,14–16], and certain zeolite systems [3,12]. These metal/alumina catalysts have shown stability, activity, and selectivity in the presence of water vapor and oxygen; however, there has been little progress in determining the heterogeneous reaction mechanism that governs reduction of NO by methanol. Hamada et al. suggested the formation of NO_2 is important in the presence of O_2 due to its high reactivity with methanol [12], and their data indicated that NO cannot be significantly reduced by methanol on Al_2O_3 below 873 K in the absence of oxygen, but NO_2 showed significant activity at 573 K. Regarding the role of metal impregnation, Tabata et al. determined the metal was not active by itself, but it was an

---

[*] To whom correspondence should be addressed.

interaction between the added metal and the alumina surface that increased effectiveness [16]. Studies by Vannice and coworkers have shown the ability of La_2O_3 to selectively reduce NO with methane [9,10,17,18]; in addition, CO and H_2 are good reductants for NO although La_2O_3 is not especially selective when excess O_2 is present [19]. Thus, it is reasonable to anticipate that methanol would also be an effective reductant using La_2O_3 as a catalyst, and it is of interest to explore the kinetic behavior of NO reduction by methanol over La_2O_3. This study examines catalytic behavior of this reaction in both the presence and the absence of O_2, and a reaction model is proposed for the latter situation.

2. Experimental

The La_2O_3 (Molycorp, 99.9%) samples were first calcined at 1023 K in O_2 for 10 h, and the specific surface area of the catalyst was then determined by N_2 physisorption using a Quantasorb system (Quantachrome Company) described previously [19]. The kinetic experiments were conducted at 1 atm in a microreactor system described previously [17]. The effluent gas stream was analyzed with a Perkin–Elmer Sigma 2B gas chromatograph combined with a Perkin–Elmer Sigma 1 integrator. The $8' \times 1/8''$ Chromosorb 102 GC column was conditioned in 30 cm^3 (STP)/min He at 453 K for 1 h before gas analysis. The temperature program varied slightly over the range of experiments performed, but was essentially as follows: hold at 232 K for 2–2.5 min, ramp temperature at 35–40 K/min to 453 K and hold 3–5 min for a total run time of 11–14 min. This allowed for good separation of H_2, N_2, O_2, NO, CO, CO_2, N_2O, and CH_3OH peaks, with the H_2O peak observable but not quantifiable. Methylnitrite (CH_3ONO) and formaldehyde (CH_2O) were also observable species of interest. CH_3ONO eluted just before the methanol peak and was difficult to quantify; however, a distinct valley existed which was used as the separation point between the two peaks. CH_2O eluted on the tail of the water peak and was also difficult to quantify, but the area was determined by skimming the peak off the tail. These methods allowed full analysis of the effluent stream except for H_2O, although greater uncertainty existed for the CH_2O and CH_3ONO for the by-products.

Before beginning experimentation the catalyst was pretreated *in situ* at 973 K in 9.80% O_2 in He (20 cm^3/min) for 1 h to remove any carbonaceous deposits. The gases used in the experiments were: 4.03% NO in He, 9.80% O_2 in He, and 100% He (99.999%). All gases were UHP from MG Industries except for the NO, which was 99.0+% with 99.999% He as the balance. Pure He was fed through a bubble impinger inserted in methanol (VWR, 99.9%) stabilized at 273 K in an ice water bath, and the line from the methanol holder to the reactor was heated to 323 K to prevent methanol condensation. About 25 mg catalyst was used for each experiment.

NO reduction in the absence of oxygen was studied between 623 and 823 K to obtain Arrhenius plots, and the feed stream (45 cm^3 (STP)/min) had a standard composition of 0.6% methanol and 1.8% NO, which is stoichiometric based on equation (1), with He composing the balance of the flow. When the reaction was studied in the presence of oxygen, the feed had similar inlet reactant conditions but 1.2% O_2 was also present in the 45 sccm feed stream. A wider temperature range of 298–773 K was used in the presence of oxygen to examine the homogeneous gas-phase reaction that was observed between NO and CH_3OH. The partial pressure studies for the NO/methanol reaction were performed in the absence of oxygen at four different temperatures between 723 and 798 K by varying the inlet partial pressure of one reactant while keeping the other reactant concentration and the flow rate constant. Generally, four different partial pressures were used for each run. Conversions were kept below 20% to approximate differential conditions, and a power rate law was used to determine apparent reaction orders. The average of the inlet and exit concentrations was used to calculate the relative partial pressures. The methanol concentration was varied from 2.3 to 16 Torr (0.3–2.1%) while maintaining NO at 14 Torr (1.8%), and NO was varied from 3.6 to 19 Torr (0.5–2.5%) while keeping methanol at 12 Torr (1.5%). A new catalyst was used for each test, which caused minor variations in the rates; however, all runs were normalized to the Arrhenius plot at standard conditions to eliminate this complication during the data-fitting optimization procedures. Experiments in the presence of O_2 were not performed due to the previously-mentioned gas-phase reaction to form methyl nitrite.

3. Results

After calcination, the BET surface area of the La_2O_3 was 2.2 m^2/g. The feed stream concentrations of 0.6% methanol and 1.8% NO in He give the stoichiometric ratio for complete reduction of NO according to the following equation:

$$3NO + CH_3OH \rightarrow N_2 + 2H_2O + CO_2 \qquad (1)$$

although N_2O formation can occur via

$$NO + CH_3OH \rightarrow 2N_2O + 2H_2O + CO \qquad (2)$$

Two different catalyst samples were used to determine an average activation energy near 14 kcal/mol for NO conversion to both N_2 and N_2O, as shown in figure 1(a). Only data obtained at conversions of methanol and NO below 20% were used in the calculation of the activation energies. There was significant nitrous oxide (N_2O) formed, so the activities for N_2 and N_2O formation are also displayed in figure 1 (b) and (c), and the activation energies for each of the latter two products are also provided in table 1 along with the selectivity to N_2, which is defined as

$$\text{selectivity} = \frac{\text{moles } N_2}{\text{moles } N_2 + \text{moles } N_2O} \times 100\%.$$

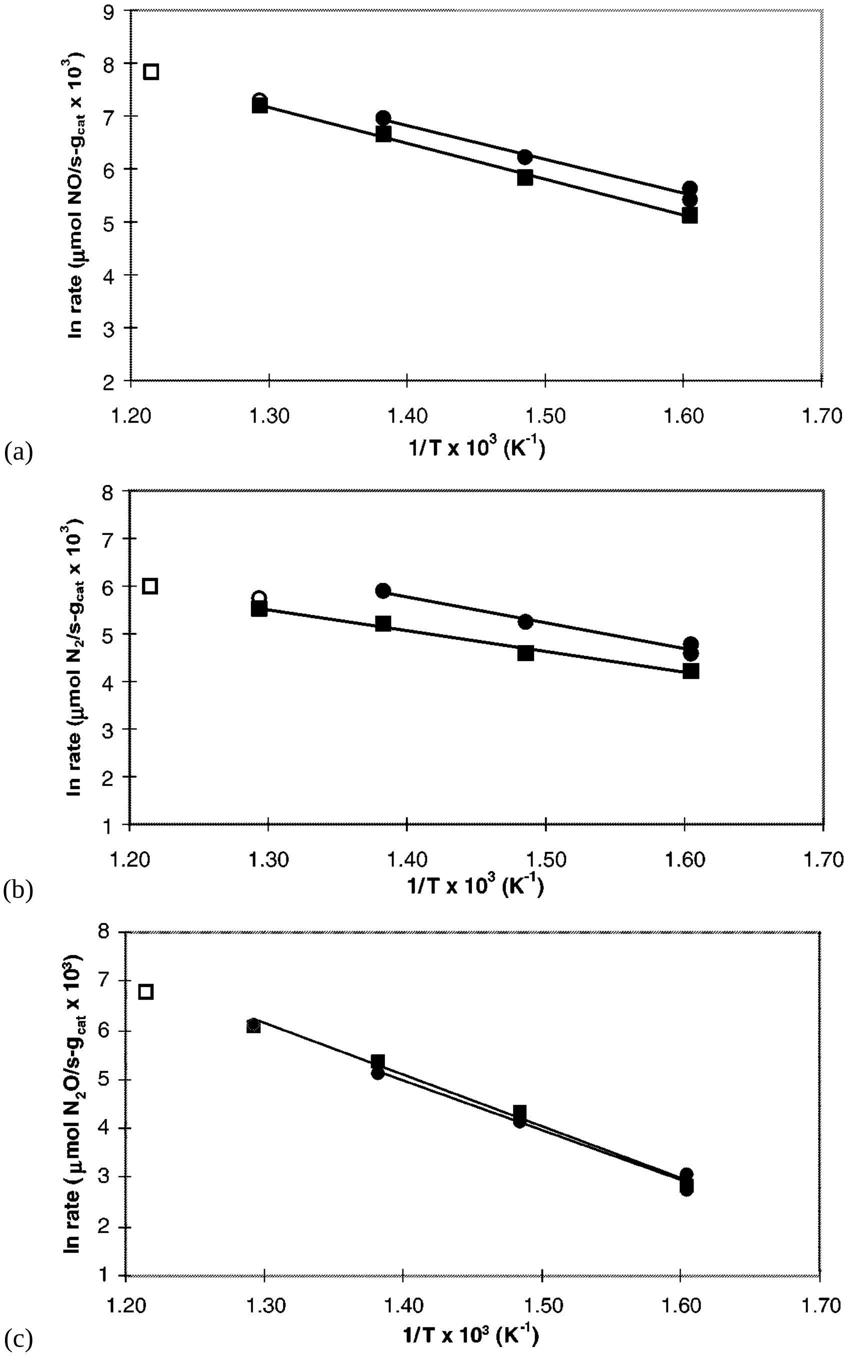


Figure 1. Arrhenius runs for (a) NO disappearance, (b) N_2 formation, and (c) N_2O formation. Reaction conditions: 1.8% NO, 0.6% CH_3OH in He, $P_T = 1$ atm. The solid points were used for activation energy determination.

This is because the only nitrogen-based products detected were N_2 and nitrous oxide (N_2O).

Methanol was oxidized to CO_2 or CO, and the formation of CO appears to be linked to the formation of N_2O, whereas CO_2 is the primary product with N_2, which is stoichiometrically consistent. As an example, a representative product concentration profile is shown in figure 2. Longer-term experiments showed a 45% decrease in NO reduction with activity stabilizing after 2 h on stream. A blank run with no catalyst was conducted to observe the role of gas-phase reactions (figure 3). The plots show that homogeneous reactions play a small role in the reduction of NO above 673 K, and La_2O_3 inhibits the net formation of formaldehyde, which is a common pollutant in methanol-fueled vehicles [20–22].

To determine the effect of dioxygen on the above reactions, a similar study was performed in the presence of 1.2% O_2 with the flow rate and the concentrations of methanol and NO remaining the same. In contrast to NO reduction in the absence of O_2, homogeneous reactions now play a principal role in the presence of oxygen, and figure 4 shows the gas-phase product distributions for both

Table 1
Arrhenius runs for NO reduction by methanol.[a]

Run	NO	N_2 formation			N_2O formation			Selectivity to N_2 (%)	
	E_a (kcal/mol)	E_a (kcal/mol)	Activity (μmol/s m^2 × 10^3)		E_a (kcal/mol)	Activity (μmol/s m^2 × 10^3)		623 K	723 K
			623 K	723 K		623 K	723 K		
1[b]	13	9	49	183	21	6.7	73	88	71
2[b]	14	11	31	82	20	7.1	94	81	47
3[c]	17	8	30	58	21	30	608	50	9
3[d]	19	(−6)	28	15	28	10	597	74	2

[a] Reaction conditions: 1.8% NO, 0.6% CH_3OH, balance He, $P_{total} = 1$ atm.

[b] No O_2 in feed.

[c] 1.2% O_2 in feed, no correction for homogeneous reaction.

[d] 1.2% O_2 in feed, contribution from homogeneous reaction subtracted.

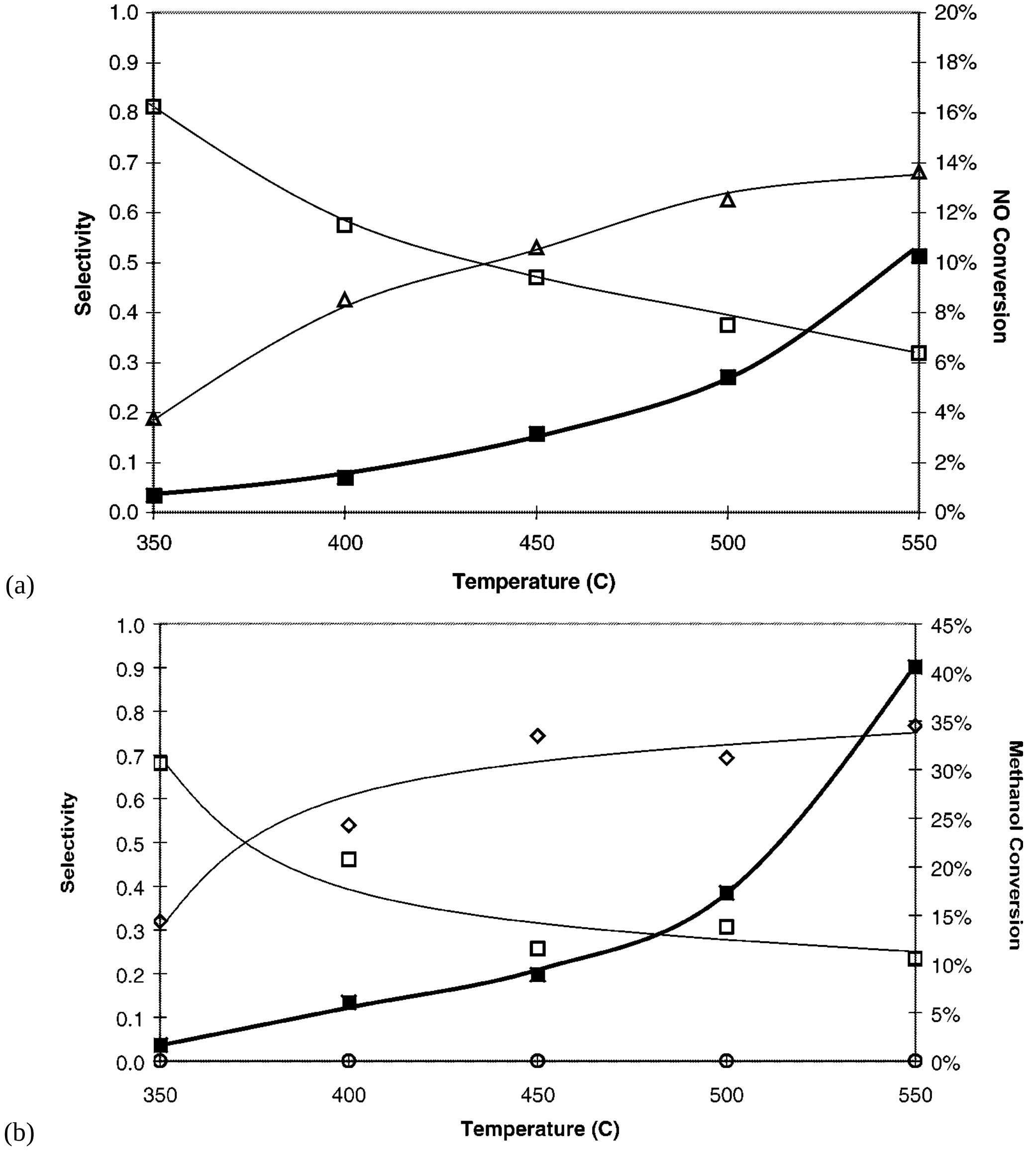


Figure 2. Product formation during NO reduction by CH_3OH over La_2O_3 in the absence of O_2. (a) N-based products: (□) dinitrogen, (△) nitrous oxide, (■) nitric oxide conversion; and (b) C-based products: (◇) carbon monoxide, (□) carbon dioxide, (○) formaldehyde, (■) methanol conversion. Reaction conditions: 1.8% NO, 0.6% CH_3OH, in He, $P = 1$ atm.

nitrogen-containing and carbon-containing compounds in the absence of any catalyst. The biggest difference is the high methanol conversion at all temperatures, even at 573 K (40% conversion), with methyl nitrite being produced. This reaction can also occur near room temperature, and it can be attributed to a multi-step homogeneous reaction involv-

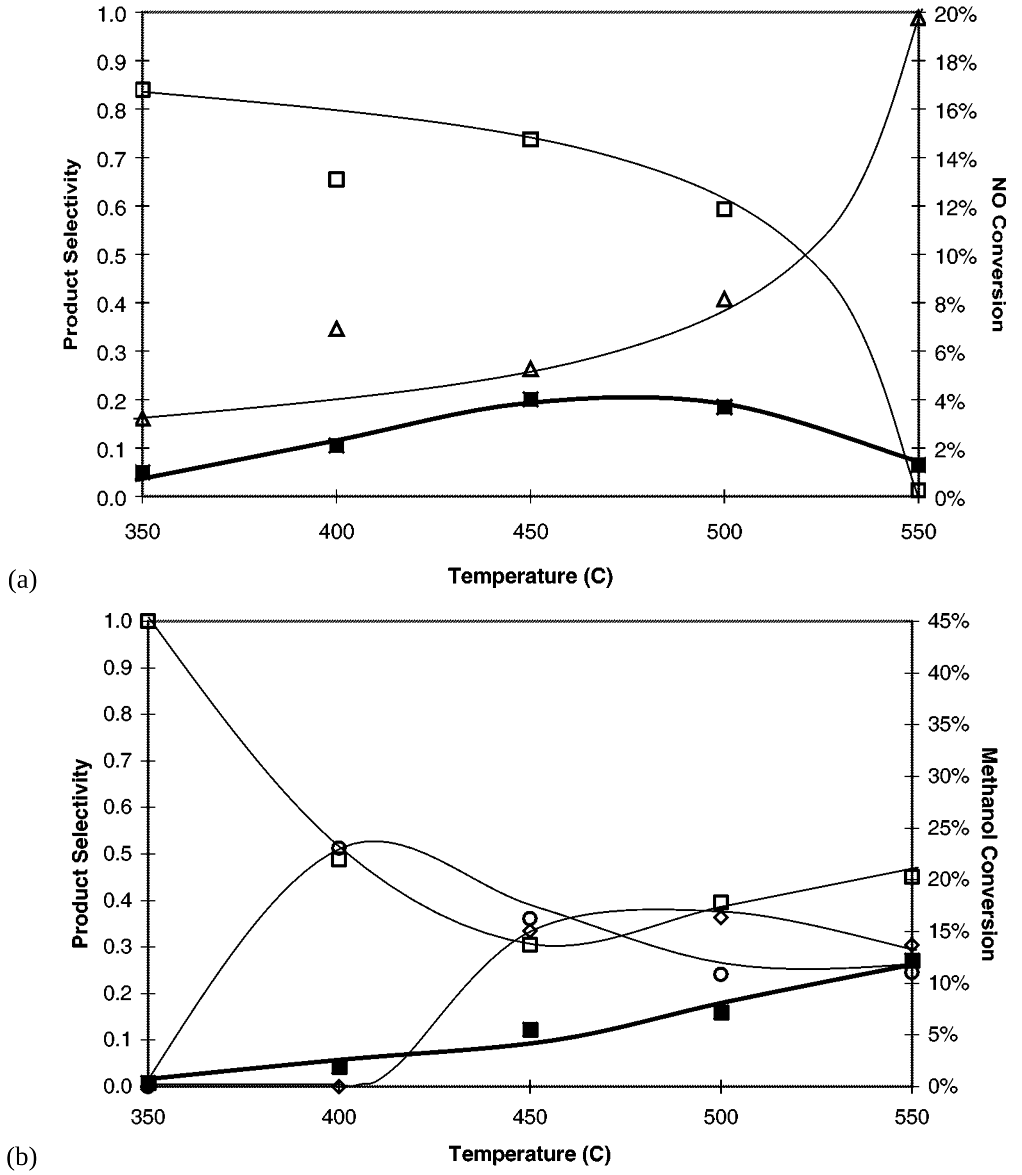


Figure 3. NO reduction by CH_3OH in the absence of O_2 in empty reactor. (a) N-based products: (□) dinitrogen, (△) nitrous oxide, (■) nitric oxide conversion; and (b) C-based products: (◇) carbon monoxide, (□) carbon dioxide, (○) formaldehyde, (■) methanol conversion. Reaction conditions: 1.8% NO, 0.6% CH_3OH, in He, $P = 1$ atm.

ing NO, O_2, and methanol which leads to the formation of methyl nitrite (CH_3ONO) [23–26]. Methyl nitrite is prevalent in the product stream until temperatures above 673 K are attained, and N_2 and N_2O formation appears to be inhibited until methyl nitrite is no longer a significant product.

The effect of La_2O_3 on the reactions among NO, CH_3OH and O_2 can be seen in figure 5. Homogeneous reactions dominate, the catalyst does not appear to play a significant role below 673 K, and methyl nitrite is again the predominant product below 700 K. At 673 K and above, La_2O_3 enhances the removal of NO, suppresses formaldehyde formation, and gives higher yields of CO. The partial-pressure dependencies obtained from the data in figure 6 based on a power rate law were slightly less than zero on methanol and near-first order on H_2, as shown in table 2. The lines fitting the data in this figure are those provided by equation (11).

Methanol decomposition over La_2O_3 in the absence of O_2 and NO was studied between 723 and 923 K using a gas feed of 3.0% methanol in He flowing at 45 cm^3 (STP)/min over 75–90 mg catalyst. Severe deactivation of the catalyst was observed at all temperatures, but product profiles developed from initial rates (after approximately 20 min on stream) showed that CO and H_2 were the principal products with the molar production rate of H_2 roughly double that of CO. There was no significant reaction below 923 K in an empty reactor. The effect of O_2 on methanol decomposition over La_2O_3 was also studied at these temperatures using a feed of 3.0% O_2 and 1.5% CH_3OH in He with the same space velocity. No deactivation was observed and nearly 100% of the methanol was reacted above 773 K. At

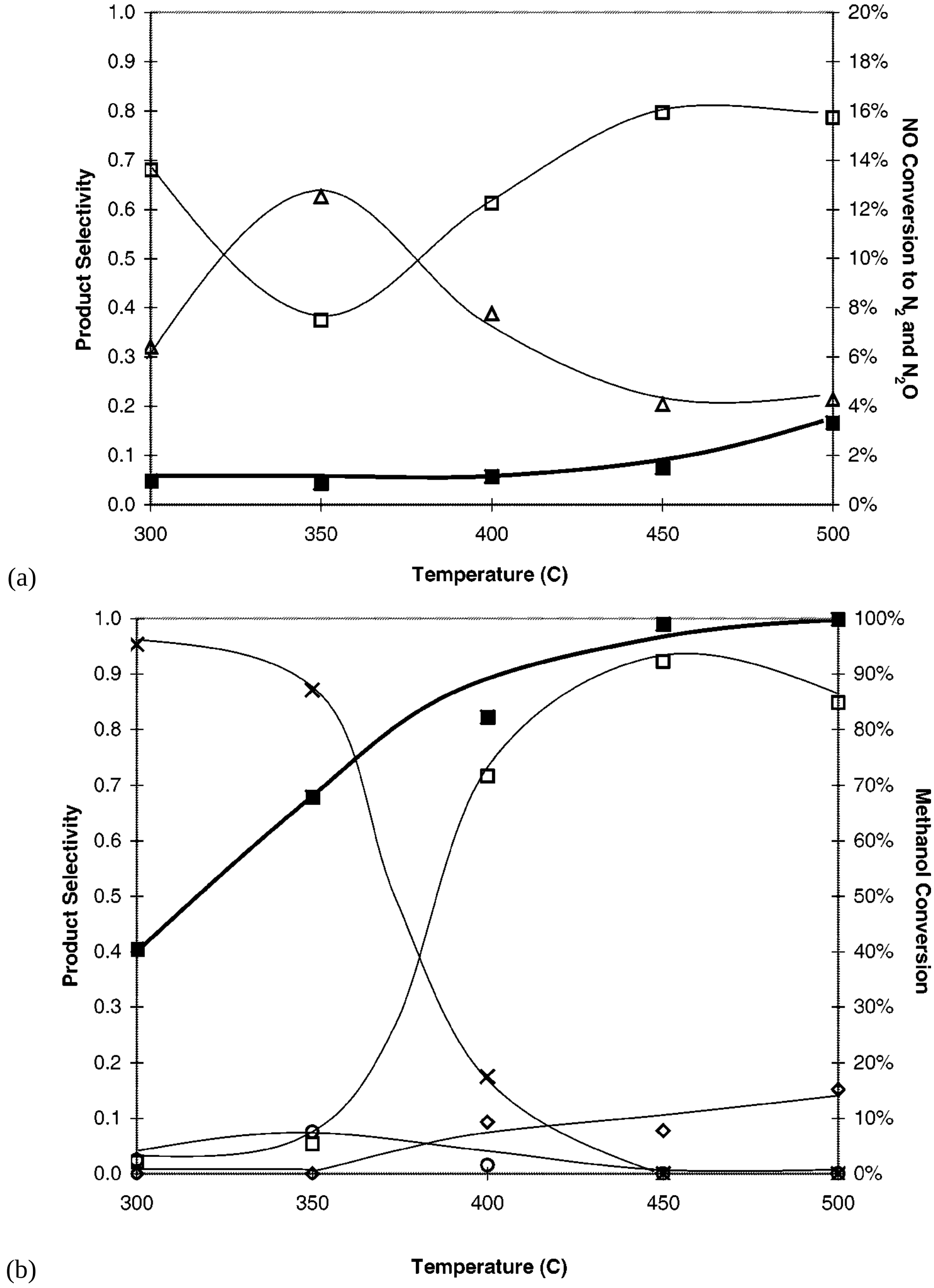


Figure 4. Reduction of NO by CH_3OH in empty reactor in the presence of O_2. (a) N-based products: (□) dinitrogen, (△) nitrous oxide, (■) nitric oxide conversion; and (b) C-based products: (◇) carbon monoxide, (□) carbon dioxide, (○) formaldehyde, (×) methyl nitrite, (■) methanol conversion. Reaction conditions: 1.8% NO, 0.6% CH_3OH, 1.2% O_2, in He, $P = 1$ atm.

723 K the activity increased slowly and complete conversion was observed after 3 h on stream. Both CO and H_2 were now present at significantly lower effluent concentrations as complete oxidation to CO_2 and H_2O was favored.

4. Discussion

As mentioned earlier, a number of alumina and promoted alumina catalysts as well as certain zeolite systems have been examined. It is difficult to determine the most effective catalyst because reaction conditions vary significantly, but Al_2O_3 impregnated with a metal, especially Sn, offers good activity for NO reduction with CH_3OH [16]. La_2O_3 is already a proven catalyst for reducing NO with CH_4, CO, or H_2, and this study shows it has even higher activity when methanol is used as the reductant. Table 3 compares the activities and activation energies with methanol to those for CH_4, H_2 and CO, as reported by Huang et al. [19]. Similar to CO and H_2, methanol provided significant formation of N_2O as well as N_2; however, the activation energy for N_2 formation is markedly lower when methanol is used, and the specific activity is about 20-fold greater than that with H_2 and 40-fold than that with CO. This dramatically higher

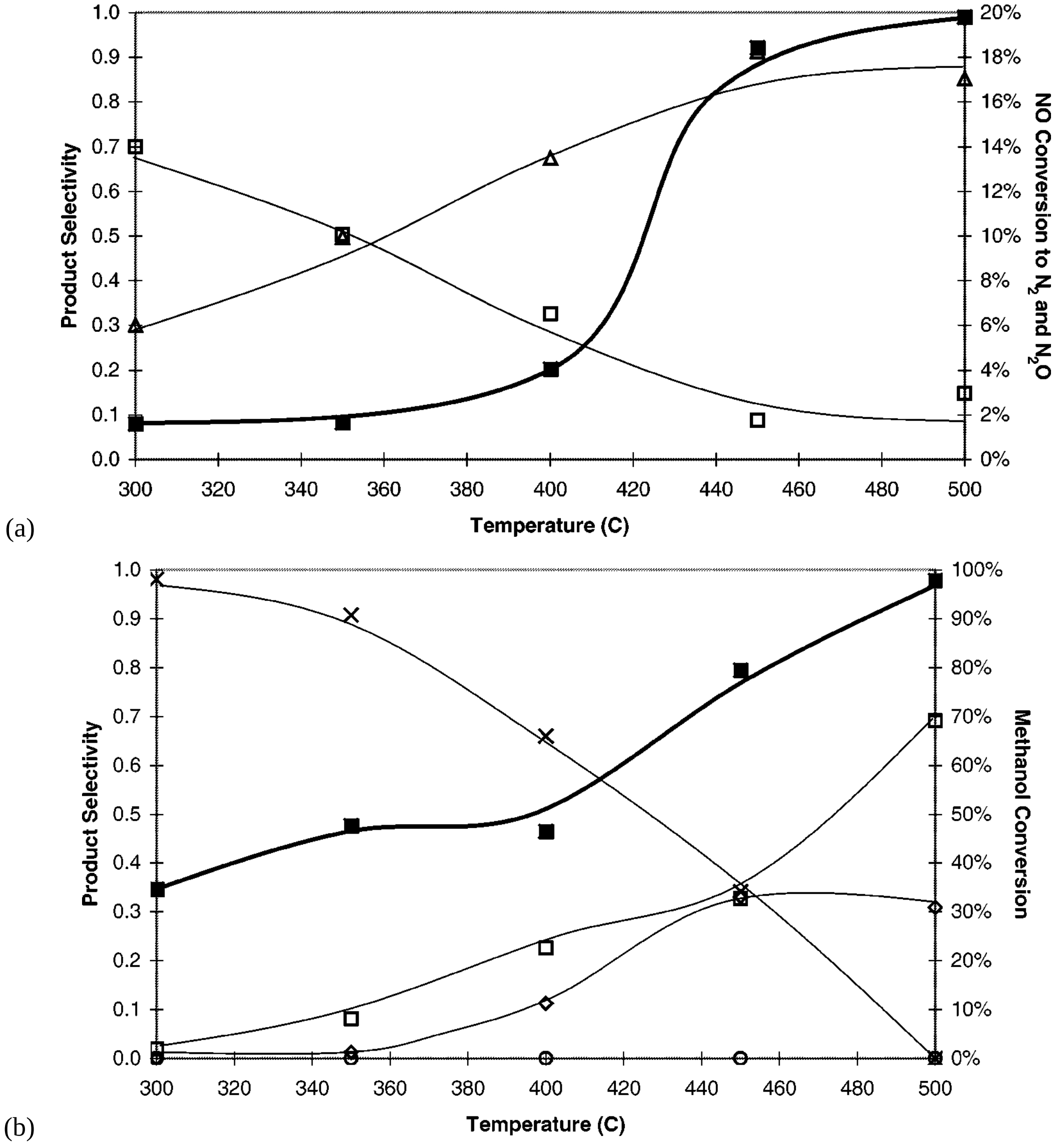


Figure 5. Reduction of NO by CH_3OH over La_2O_3 in the presence of O_2. (a) N-based products: (□) dinitrogen, (△) nitrous oxide, (■) nitric oxide conversion; and (b) C-based products: (◇) carbon monoxide, (□) carbon dioxide, (○) formaldehyde, (×) methyl nitrite, (■) methanol conversion. Reaction conditions: 1.8% NO, 0.6% CH_3OH, 1.2% O_2, in He, $P = 1$ atm.

specific activity, as well as the lower activation energy, strongly suggests that the principal NO reaction sequence with methanol does not proceed via CH_3OH decomposition to H_2 and CO, with these two compounds then reacting directly with NO to reduce it. As has been shown, CH_3OH decomposition does occur and H_2 and CO can be detected, but the latter two compounds do not appear to be active reductants at these temperatures based on an earlier study [19].

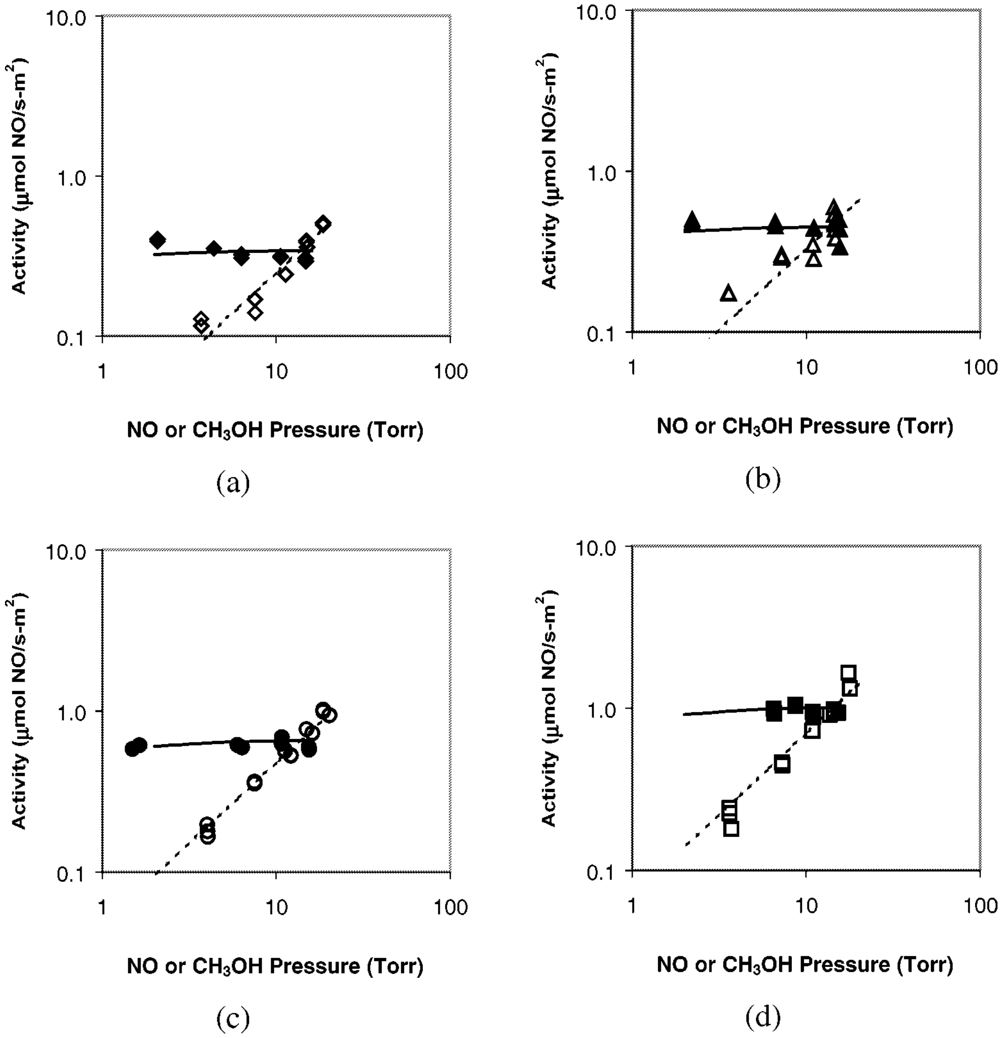
Upon the addition of dioxygen to the feed stream, a significant homogeneous reaction was observed. The recent catalytic studies of NO reduction by methanol do not report this reaction which leads to methyl nitrite [12–15], but this reaction has been reported and examined in publications outside of the heterogeneous catalysis field [27–31], with most studies involving methanol-fueled vehicles. Pyrex and stainless steel have been reported to catalyze this reaction [26]. Koda et al. [27] and Niki et al. [30] have proposed that N_2O_4 is involved in the reaction and reacts with CH_3OH to form methyl nitrite:

$$2NO + O_2 \rightarrow 2NO_2 \tag{3}$$

$$2NO_2 \rightarrow N_2O_4 \tag{4}$$

$$N_2O_4 + CH_3OH \rightarrow CH_3ONO + HNO_3 \tag{5}$$

No GC peak for nitric acid was detected in our study, but this is possibly due to a separation problem with the water peak. The formation of methyl nitrite was confirmed by a GC-MS analysis at the Penn State Mass Spectrometry Center, which reported large quantities of methyl nitrite with no significant dimethyl ether present. There are several possible reasons why previous studies of NO reduction by methanol did not report this homogeneous reaction. Both Hamada et al. and Tabata et al. were working above 523 K,



(a) (b) (c) (d)

Figure 6. Fit of experimental data using equation (11): (a) 723, (b) 748, (c) 773, and (d) 798 K. Solid lines and points represent methanol and dashed lines and open symbols represent NO.

Table 2
Summary of reaction orders for NO reduction in the absence of oxygen.

	Temperature (K)	Reaction order	
		CH_3OH	NO
NO disappearance	723	−0.1	0.9
	748	−0.1	0.7
	773	−0.1	1.0
	798	−0.1	1.1

where methyl nitrite formation is less favored [12,15]. They also report high $O_2 : NO : CH_3OH$ ratios around 100 : 1 : 1 (compared to our ratio of 2 : 3 : 1), which may lead to different chemistry. It may also be that the reaction was just overlooked because most studies reported NO reduction based on N_2 and N_2O formation and methanol conversion based on CO_x formation [12,14–16]. Masters and Chadwick used a mass spectrometer but did not monitor the atomic mass of methyl nitrite (61 amu); however, they did report the presence of dimethyl ether [15], which has an elution time similar to that for methyl nitrite with a Chromosorb 102 GC column, which they (and we) also used. This homogeneous reaction significantly complicates any heterogeneous catalytic study of NO reduction in the presence of oxygen, at least in this temperature range, even though Jonsson reported no methyl nitrite formation above 573 K in a diesel engine using a methanol/diesel blend [25], and Morikawa and Ito reported no methyl nitrite present in the exhaust of a methanol vehicle [31].

It is difficult to quantitatively compare the reduction of NO by CH_3OH over La_2O_3 in the presence of O_2 with other catalysts because the conditions used in other studies were substantially different from those used here and no studies of this reaction in the absence of O_2 have been reported. Regardless, a general comparison can still be made and a summary of rates and conversions for various catalysts is given in table 4. Comparing either rates (mol/s g) or specific activities for NO conversion (mol/s m^2) to $N_2 + N_2O$, La_2O_3 is substantially more active; however, reactant concentrations are much higher in our study, which also accounts for the lower NO conversions. For a more accurate comparison, rates and specific activities over La_2O_3 have been estimated at the feed conditions of previous studies

Table 3
Comparison of NO reduction over La_2O_3 (no O_2).

Reductant	E_a (kcal/mol)			Activity at 773 K (μmol/s m^2 $\times 10^3$)		
	NO	N_2	N_2O	NO	N_2	N_2O
CH_4[a]	19	19	–	3.5	1.7	–
H_2[a]	–	31	29	35.0	3.5	13.6
CO[a]	–	35	19	15	0.9	6.6
CH_3OH[b]	14	10	21	638	128	191

[a] Taken from [19]. Reaction conditions: 1.7% NO and 0.45% CH_4 or 1.7% H_2 or 1.7% CO in He.
[b] Reaction conditions: 1.8% NO and 0.6% CH_3OH in He, average values.

Table 4
NO reduction by CH_3OH over various catalysts, $P_{\text{Total}} = 1$ atm.

Catalyst	Concentration (ppm)		NO conv. at 673 K[a] (%)	Rate of NO disappearance at 673 K to form $N_2 + N_2O$		P_{O_2} (atm)	P_{H_2O} (atm)	Reference
	NO	CH_3OH		(μmol NO/s g_{cat} $\times 10^3$)	(μmol NO/s m^2 $\times 10^3$)			
La_2O_3[b]	18000	6000	4.0	996	293	0.012	0	This study
La_2O_3	926	1511	–	50[c]	15[c]	0.012	0	This study
La_2O_3	1000	1000	–	53[c]	16[c]	0.012	0	This study
La_2O_3	1500	2000	–	160[c]	48[c]	0.012	0	This study
(1) Al_2O_3	926	1511	33	13.6	0.07	0.09	0.085	12
2% Co/Al_2O_3	926	1511	25	10.3	0.06	0.09	0.085	12
H/ZSM-5	926	1511	57	11.8	n/a	0.093	0.085	14
Cu/ZSM-5	926	1511	1	0.0	n/a	0.093	0.085	14
(2) Al_2O_3	1000	1000	36	80.3	0.42	0.10	0.08	16
1% Mo/Al_2O_3	1000	1000	29	64.7	0.34	0.10	0.08	16
1% W/Al_2O_3	1000	1000	27	30.0	0.16	0.10	0.08	16
1% Ga/Al_2O_3	1000	1000	39	87.0	0.46	0.10	0.08	16
1% Bi/Al_2O_3	1000	1000	13	29.0	0.15	0.10	0.08	16
1% Sb/Al_2O_3	1000	1000	23	51.1	0.27	0.10	0.08	16
1% Sn/Al_2O_3	1000	1000	33	73.5	0.39	0.10	0.08	16
Al_2O_3	1500	3000	10	14	0.06	0.025	0	15
6% V_2O_5/Al_2O_3	1500	3000	33	48	0.23	0.025	0	15
3% MoO_3/Al_2O_3	1500	3000	35	37	0.16	0.025	0	15
50% (6% V_2O_5/Al_2O_3) + 50% (3% MoO_3/Al_2O_3)	1500	3000	38	46	0.21	0.025	0	15

[a] Reported selectivity to N_2 was 100%.
[b] Reported selectivity to N_2 was 33%.
[c] Predicted by equation (11).

by using equation (11), and these values are also listed in table 4. The rates with La_2O_3 are still routinely 2–5 times higher than those for the other catalysts, while the specific activities remain markedly higher as they are consistently two orders of magnitude greater per square meter. The temperature range examined in table 4 does not include the more active region for La_2O_3, which lies above 773 K at our reaction conditions. Few of the catalysts reported show activity above 773 K, so La_2O_3 could possibly expand the operating window when combined with one of the other catalyst systems.

A straightforward reaction model, i.e., a Langmuir–Hinshelwood type model with a bimolecular, surface reaction rate-controlling step involving adsorbed NO and adsorbed CH_3OH, is able to provide a reasonable fit to the kinetic data obtained at four different temperatures. If only one type of adsorption site is assumed, with adsorbed methanol being the most abundant surface intermediate (masi), then the following familiar rate expression is obtained [32]:

$$r_{NO} = \frac{kP_{NO}P_{CH_3OH}}{(1 + K_{CH_3OH}P_{CH_3OH})^2}. \tag{6}$$

If, however, two different types of adsorption sites are assumed to exist on the La_2O_3 surface, which is very justifiable [33], the reaction sequence for the above model can be represented as

$$6\left[NO + S \overset{K_{NO}}{\rightleftharpoons} NO\text{–}S\right] \tag{7}$$

$$2\left[CH_3OH + * \overset{K_{CH_3OH}}{\rightleftharpoons} CH_3OH\text{–}*\right] \tag{8}$$

$$2\left[NO\text{–}S + CH_3OH\text{–}* \xrightarrow{k} HNO\text{–}S + CH_3O\text{–}*\right] \quad \text{(rds)} \tag{9}$$

$$4NO\text{–}S + 2HNO\text{–}S + 2CH_3O\text{–}* \rightleftharpoons 3N_2 + 4H_2O + 2CO_2 + 6S + 2* \tag{10}$$

$$\overline{}$$

$$6NO + 2CH_3OH \rightarrow 3N_2 + 4H_2O + 2CO_2$$

Table 5
Rate parameters from optimized equation (11) for methanol reduction of NO.

Temperature (K)	k (μmol/s m^2 atm^2) $\times 10^{-5}$	K_{CH_3OH} (atm^{-1}) $\times 10^{-3}$
723	1.4	7.6
728	1.2	4.8
773	1.2	3.0
798	1.1	2.1

where S and $*$ represent the two types of sites. The surface intermediates have counterparts in homogeneous gas-phase reactions, and their viability has been discussed before [19,34]. If the coverage of NO is low on the former sites and adsorbed CH_3OH is the masi on the latter sites, the rate equation obtained for NO disappearance is

$$r_{NO} = \frac{k' P_{NO} P_{CH_3OH}}{1 + K_{CH_3OH} P_{CH_3OH}}, \tag{11}$$

where $k' = k K_{NO} K_{CH_3OH}$ and incorporates the total number of sites. The assumption of reversibility in the last step (equation (10)) is unimportant kinetically because it follows a slow step containing the masi [35]. This latter rate expression is preferred at this time because it provides a better fit of the data, which is shown in figure 6, using the parameters given in table 5. A thermodynamic analysis of the equilibrium adsorption constant for methanol, K_{CH_3OH}, gives values of -20 kcal/mol and -10 cal/mol K for the enthalpy and entropy of adsorption, respectively, which are thermodynamically consistent and physically meaningful [35,36]. Because the $K_{CH_3OH} P_{CH_3OH}$ term in the denominator is large compared to unity, the apparent activation energy will be close to that of the term $k'/K_{CH_3OH} = k K_{NO}$, and this value of 16 kcal/mol compares favorably with the experimentally determined value of 14 kcal/mol. Consequently, the sequence represented by equations (7)–(10) represents a possible model for this reaction on La_2O_3 in the absence of O_2.

5. Summary

Reduction of NO by methanol over La_2O_3 occurred in either the presence or absence of O_2. In the absence of O_2, the specific activity for N_2 formation was an order of magnitude or more higher than that of other reductants such as CH_4, H_2 and CO. Methanol gave a lower selectivity to N_2 versus N_2O compared to methane, but it was comparable to that with H_2 and CO. The activation energy of this reaction with CH_3OH was 14 kcal/mol, and partial pressure dependencies in a power rate law were -0.1 and 1 on CH_3OH and NO, respectively. These data were used to develop a reaction model for NO reduction by methanol in the absence of O_2. After considering Langmuir–Hinshelwood models incorporating either one type or two types of adsorption sites for CH_3OH and NO, the latter was preferred and it yielded the following rate law:

$$r_{NO} = \frac{k' P_{NO} P_{CH_3OH}}{1 + K_{CH_3OH} P_{CH_3OH}}.$$

This expression satisfactorily fitted the data for all experiments, and the resulting rate constants were shown to be thermodynamically consistent.

NO reduction in the presence of O_2 was complicated by a gas-phase reaction that converted over 30% of the methanol to methyl nitrite at 300 K. This reaction was observed below 623 K, while typical oxidation products, i.e., CO_2 and H_2O, were observed at higher temperatures. Between 623 and 823 K, the conversion of NO to N_2 and N_2O was considerably higher than in the experiments without O_2, but further study was not performed since differential reactor conditions could not be achieved. Comparison to other catalysts used for NO reduction by methanol suggests that La_2O_3 has a wider operational temperature range and better NO reduction capabilities.

References

[1] M. Shelef, Chem. Rev. 95 (1995) 209.
[2] K.C. Taylor and J.C. Schlatter, J. Catal. 63 (1980) 53.
[3] K.C. Taylor, Catal. Rev. Sci. Eng. 35 (1993) 457.
[4] K. Masuda, K. Tsujimura, K. Shinoda and T. Kato, Appl. Catal. B 8 (1996) 33.
[5] R.J. Farrauto, R.M. Heck and B.K. Speronello, C&EN (1992) 34.
[6] M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuyira and S. Kagawa, J. Chem. Soc. Chem. Commun. (1986) 1272.
[7] J.N. Armor, Appl. Catal. B 1 (1992) 221.
[8] F.J. Janssen, in: *Handbook of Heterogeneous Catalysis*, Vol. 4, eds. G. Ertl, H. Knözinger and J. Weitkamp (Wiley–VCH, Weinheim, 1997).
[9] X. Zhang, A.B. Walters and M.A. Vannice, Catal. Today 27 (1996) 41.
[10] C. Shi, A.B. Walters and M.A. Vannice, Appl. Catal. B 15 (1997) 175.
[11] K.C.C. Kharas, H.J. Robota and D.J. Liu, Appl. Catal. B 2 (1993) 225.
[12] H. Hamada, Y. Kintaichi, M. Sadaki, T. Ito and T. Yoshinari, Appl. Catal. A 88 (1992) L1.
[13] T. Yamamoto, A. Noda, T. Sakamoto and Y. Sato, Soc. Automot. Eng., Spec. Publ. 1140 (1996) 113.
[14] M. Tabata, H. Tsuchida, K. Miyamoto, T. Yoshinari, H. Yamazaki, H. Hamada, Y. Kintaichi, M. Sasaki and T. Ito, Appl. Catal. B 6 (1995) 169.
[15] S.G. Masters and D. Chadwick, Catal. Today 42 (1998) 137.
[16] M. Tabata, H. Hamada, F. Suganuma, Y. Yoshinari, H. Tsuchida, Y. Kintaichi, M. Sasaki and T. Ito, Catal. Lett. 25 (1994) 55.
[17] X. Zhang, A.B. Walters and M.A. Vannice, Appl. Catal. B 4 (1994) 237.
[18] X. Zhang, A.B. Walters and M.A. Vannice, Appl. Catal. B 7 (1996) 321.
[19] S.J. Huang, A.B. Walters and M.A. Vannice, J. Catal. 173 (1998) 229.
[20] D. Sodhi and M.A. Abraham, J. Air Waste Manage. Assoc. 40 (1990) 352.
[21] R.L. Williams, F. Lipari and R.A. Potter, J. Air Waste Manage. Assoc. 40 (1990) 747.
[22] C.-F. Mao and M.A. Vannice, J. Catal. 154 (1995) 230.
[23] R. Silverwood and J.H. Thomas, Trans. Faraday Soc. 63 (1967) 2476.

[24] A. Jonsson and S. Berg, Chemosphere 11/12 (1979) 835.
[25] A. Jonsson, Environ. Sci. Technol. 16 (1982) 106.
[26] H. Takagi, S. Hatakeyama and H. Akimoto, Environ. Sci. Technol. 20 (1986) 387.
[27] S. Koda, K. Yoshikawa, J. Okada and K. Akita, Environ. Sci. Technol. 19 (1985) 262.
[28] K. Ito, T. Yano and T. Ohkubo, Bull. JSME 27 (1984) 1168.
[29] A.M. Fairlie, Jr., J.J. Carberry and J.C. Treacy, J. Am. Chem. Soc. 75 (1953) 3786.
[30] H. Niki, P.D. Marker, C.M. Savage and L.P. Breitenbach, Int. J. Chem. Kinet. 14 (1982) 1199.
[31] T. Morikawa, T. Ito and K. Ito, Trans. Jpn. Soc. Mechan. Eng. (Nippon Kikai Gakkai Ronbonshu) B62 (1996) 380.
[32] T.J. Toops, Ph.D. thesis, The Pennsylvania State University, in progress.
[33] S.-J. Huang, A.B. Walters and M.A. Vannice, J. Catal., submitted.
[34] M.A. Vannice, A.B. Walters and X. Zhang, J. Catal. 159 (1996) 119.
[35] M. Boudart, AIChE J. 18 (1972) 465.
[36] M.A. Vannice, S.-H. Hyun, B. Kalpacki and W.C. Liauh, J. Catal. 56 (1979) 358.