# The Kinetics of NO<sub>x</sub> Decomposition and NO Reduction by $CH_4$ over $La_2O_3$ and $Sr/La_2O_3$

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The kinetics of four different reactions over two rare earth oxide catalysts have been determined at 923 K-N<sub>2</sub>O decomposition, NO decomposition, NO reduction by CH<sub>4</sub> in the absence of O<sub>2</sub>, and NO reduction by CH<sub>4</sub> with excess O<sub>2</sub> present. After examination of many different reaction mechanisms and the rate expressions derived from each of them, the sequence of elementary steps and the resulting rate equation which best describe the experimental results for each are reported here. The Langmuir-Hinshelwood-type expressions indicate that N2O proceeds via unimolecular decomposition, whereas the rate determining step for NO decomposition involves a surface reaction between two adsorbed NO molecules. The reduction of NO by CH<sub>4</sub> in the absence of O<sub>2</sub> proceeds with methyl radical formation via hydride abstraction by NO implied as the slow step, and the rate determining step for NO reduction when both CH<sub>4</sub> and O<sub>2</sub> are present again appears to be methyl radical formation by reaction between adsorbed CH<sub>4</sub> and NO<sub>2</sub>. The rate enhancements for NO reduction to N2 and O2 when CH4, or CH4 plus O<sub>2</sub>, is utilized are attributed to the formation of methyl radicals and subsequent C-containing surface intermediates which rapidly interact with NO. The proposed chemistry is consistent with both that associated with methane oxidative coupling over rare earth oxides and that describing homogeneous free-radical reactions involving these intermediates. Consequently, a complete catalytic cycle of elementary steps is proposed for each reaction to demonstrate the possible presence of these various intermediates and to allow the testing of these models in the future. © 1996 Academic Press, Inc.

## INTRODUCTION

Lean NO<sub>x</sub> reduction has attracted great attention in both university and industry laboratories because of the need to find catalysts which can work effectively under lean-burn conditions to reduce NO<sub>x</sub> emissions. The most significant progress in this area recently has been the discovery of zeolite catalysts, such as Cu/ZSM-5 and Co/ZSM-5, which can effectively convert NO into N<sub>2</sub> under appropriate conditions as discussed in the review by Armor (1–3). Of particular interest has been the use of CH<sub>4</sub> to reduce NO<sub>x</sub> because of the availability of natural gas and its potential to replace the SCR process utilizing ammonia. Correspondingly, numerous studies of the roles of metals and oxygen have been conducted; however, only a few measurements of kinetic parameters have been reported (2-4) and only one detailed sequence of reaction steps involving CH<sub>4</sub> based on kinetic behavior has been proposed (5). A family of rare earth oxide (REO) catalysts has been prepared, characterized, and tested (6-9), and the results have shown that good methane oxidative coupling catalysts can also be good NO reduction catalysts, even in the presence of excess O<sub>2</sub>. Among the rare earth oxides tested, La2O3 and Sm2O3 with and without Sr doping were the most active catalysts, although their rates per gram were still 1-2 orders of magnitude lower than that for Co/ZSM-5; however, when normalized to unit surface area or represented as a turnover frequency based on NO adsorption sites, the specific activities of these REO catalysts were comparable to those reported for the zeolite catalysts (7). Furthermore, unlike the zeolite catalysts, the activities of these catalysts continuously increased with reaction temperature with no bend-over, and high selectivities of methane utilization could be achieved over the best catalysts.

This paper examines, in both the absence and presence of  $O_2$ , the kinetic behavior of NO reduction by  $CH_4$  as well as NO decomposition over  $La_2O_3$  and 4%  $Sr/La_2O_3$ , and it also addresses  $N_2O$  decomposition over these two catalysts. Possible reaction mechanisms are discussed and for each reaction the derived rate expression which best fits the data is presented. The proposed sequences of elementary steps strive for consistency with the chemistry associated with methane oxidative coupling as well as that describing homogeneous, free-radical reactions among the possible reaction intermediates.

#### **EXPERIMENTAL**

Kinetic studies of NO decomposition and NO reduction by  $CH_4$  in both the absence and presence of  $O_2$  over  $La_2O_3$ and  $Sr/La_2O_3$  have been described in detail in two previous papers, and some of the kinetic data presented in this paper were contained in those studies (6, 9). Briefly, 4%

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## TABLE 1

Pessure (Torr)		App $F_{aa}^{a}$	Reaction		
N <sub>2</sub> O	O <sub>2</sub>	(kcal/mole)	order <sup>a</sup>		
0.38-3.40	0	24	1.02		
0.38-3.40	7.5	_	0.97		
$r (\mu \text{mole N}_2/\text{sec} \cdot \text{m}^2) = 0.081 P_{\text{N}_2\text{O}} / (1 + 0.027 P_{\text{N}_2\text{O}})$					

Kinetic Behavior of  $N_2O$  Decomposition over 4% Sr/La\_2O\_3 at 923 K

<sup>*a*</sup> From Ref. (9).

<sup>b</sup> Pressure units are Torr.

Sr/La<sub>2</sub>O<sub>3</sub>, prepared by following the method employed for Li-promoted MgO (10), and La2O3 were pretreated in situ at 973 K under 9.8%  $O_2$  in He at a flow rate of 20 cm<sup>3</sup>/min until no CO2 could be detected. All kinetic studies were made at 923 K and atmospheric pressure under steady-state reaction conditions in a quartz microreactor system containing ca. 100 mg of catalyst, as described previously (6, 10). The ranges of partial pressure are summarized in Tables 1-4. NO conversions were typically below 5% during NO decomposition and reduction by CH<sub>4</sub> and were usually less than 10% during NO reduction by CH<sub>4</sub> in excess O<sub>2</sub>. The reactor effluent was analyzed with a Perkin-Elmer Sigma 2B gas chromatograph equipped with either a Carboxen<sup>1000</sup> column (Supelco) or a 5A molecular sieve column and a P-E Nelson 1020S integrator. All gases used were UHP Grade (MG Ind.) except for the NO mixed in He, which was 99.0<sup>+</sup>%, with major mixture impurities of N<sub>2</sub> ( $\sim$ 600 ppm), N<sub>2</sub>O ( $\sim$ 100 ppm), and CO<sub>2</sub> (ca. 100 ppm). All rates were based upon the formation of N2. Data-fitting was conducted using a nonlinear regression technique contained in a SAS computer package employing the Marquardt method with a convergence criterion requiring a change in the residual to decrease below  $10^{-12}$ . Three adjustable parameters were used for all equations except that for NO reduction by CH<sub>4</sub> with O<sub>2</sub> present, which contained four parameters.

#### **RESULTS AND DISCUSSION**

Tables 1–4 summarize the results of the kinetic studies over La<sub>2</sub>O<sub>3</sub> and Sr/La<sub>2</sub>O<sub>3</sub>. The reaction orders listed here were determined by the best fit of the data to a power rate law. All pressure units in the rate expressions are in Torr. During the runs in Table 3, the CH<sub>4</sub> pressure was held at 3.4 Torr while the NO pressure was varied, and the NO pressure was held at 13.6 Torr while the CH<sub>4</sub> pressure was varied. In Table 4, the respective O<sub>2</sub> and NO pressures were 7.56 and 13.7 Torr while the CH<sub>4</sub> pressure was varied, the respective O<sub>2</sub> and CH<sub>4</sub> pressures were 7.56 and 3.42 Torr while the NO pressure was varied, and the respective CH<sub>4</sub> and NO pressures were 3.40 for Sr/La<sub>2</sub>O<sub>3</sub> (25.6 for La<sub>2</sub>O<sub>3</sub>) and 13.6 Torr while the O<sub>2</sub> pressure was varied.

#### $N_2O$ Decomposition

This reaction is of interest not only because  $N_2O$  is considered an environmental pollutant arising as a coproduct from certain processes (11), but also because  $N_2O$  has been detected in the product stream during NO reduction by CH<sub>4</sub> over certain REO catalysts (6–9). Thus the possibility exists that it may be a reaction intermediate during this sequence; alternatively, it may be formed as a product in a parallel reaction during NO reduction. The analysis of the effluent stream from this reaction was very easy and the ratio of the N<sub>2</sub> and O<sub>2</sub> products was routinely near 2.

One of the simplest reaction sequences that can be proposed is a Langmuir–Hinshelwood (L–H) model involving unimolecular decomposition of adsorbed  $N_2O$  as the rate determining step (rds), i.e.,

$$2[N_2O + * \stackrel{K_{N_2O}}{\Rightarrow} N_2O*]$$
[1]

$$2[N_2O* \xrightarrow{k} N_2 + O*] \quad (rds) \qquad [2]$$

$$2O* \stackrel{1/K_{O_2}}{\clubsuit} O_2 + 2*$$
 [3]

$$2N_2O \rightarrow 2N_2 + O_2.$$
 [4]

TABLE 2	

Kinetic Behavior of NO Decomposition at 923 K

	$F_{a}$	Partial pressure (Torr)		Reaction order	
Catalyst	(kcal/mole)	NO	O <sub>2</sub>	in NO	
La <sub>2</sub> O <sub>3</sub>	$23^a$	2.70-13.5	0	1.22	
	_	2.73-13.7	7.53	1.46	
	r (µmole N <sub>2</sub> /	$(\sec \cdot m^2) = 8.3$	$\times 10^{-5} P_{\rm NO}^2 / ($	$(1+0.10 P_{\rm NO}+0.26 P_{\rm O_2}^{1/2})^{2c}$	
Sr/La <sub>2</sub> O <sub>3</sub>	$28^b$	2.67-13.4	0	$1.08^{b}$	
	_	2.71-13.5	7.48	$1.11^{b}$	
	r (µmole N <sub>2</sub> /s	$\sec \cdot m^2$ = 2.4	$\times 10^{-4} P_{\rm NO}^2 / (2$	$1 + 0.077 P_{\rm NO} + 0.52 P_{\rm O2}^{1/2})^{2c}$	

<sup>*a*</sup> From Ref. (6).

<sup>b</sup> From Ref. (9).

<sup>c</sup> Pressure units are Torr.

TABLE :	3
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	East	Partial pressure (Torr)		Reaction order	
Catalyst	(kcal/mole)	CH <sub>4</sub>	NO	$CH_4$	NO
La <sub>2</sub> O <sub>3</sub>	$24^a$ r (µmole N <sub>2</sub> /s	0.68-3.40 sec $\cdot$ m <sup>2</sup> ) = 1.6	2.72-13.6 $5 \times 10^{-3} P_{\rm NO} F$	$0.26^{a}$ $P_{CH4}/(1+0.00)$	$0.98^{a}$ 041 $P_{\rm NO} + 0.30 P_{\rm CH4})^{2c}$
Sr/La <sub>2</sub> O <sub>3</sub>	26 <sup>b</sup> r (μmole N <sub>2</sub> /	0.68-3.40 (sec $\cdot$ m <sup>2</sup> ) = 1.	2.72-13.6 $7 \times 10^{-3} P_{\rm NO}$	$0.19^b$ $P_{CH4}/(1+0.0)$	$0.73^b 36 P_{\rm NO} + 0.49 P_{\rm CH4})^{2c}$

Kinetic Behavior of NO Reduction by CH<sub>4</sub> at 923 K

<sup>*a*</sup> From Ref. (6).

<sup>*b*</sup> From Ref. (9). <sup>*c*</sup> Pressure units are Torr.

Here \* represents an empty active site while  $K_{N_{2O}}$  and  $K_{O_2}$  represent equilibrium adsorption constants. A site balance for the concentration of active sites, *L*, combined with quasi-equilibrated steps [1] and [3], gives the rate expression.

$$r = Lk\theta_{N_2O} = k'K_{N_2O}P_{N_2O}/(1 + K_{N_2O}P_{N_2O} + K_{O_2}^{1/2}P_{O_2}^{1/2}).$$
[5]

Fitting this equation to the experimental data produced the following equation with pressures in units of Torr.

$$r = 0.081 P_{\rm N_2O} / (1 + 0.027 P_{\rm N_2O}),$$
 [6]

whose correlation with the rate data is shown in Fig. 1. The decomposition reaction was conducted in the presence and absence of  $O_2$  in the feed and the lack of dependence on the  $O_2$  pressure is clearly evident. This implies the surface concentration of chemisorbed O atoms is very low under these conditions. The apparent activation energy of Eq. [5] between 773 and 973 K was 24 kcal/mole (9). It should be mentioned that other sequences can also provide satisfactory rate expressions. For example, Eq. [5] is also obtained if no rds is assumed, both steps [2] and [3] are irreversible, and the surface coverage of O atoms is assumed to be small compared to that of adsorbed N<sub>2</sub>O; however, rapid isotopic

 $O_2$  exchange occurs on  $La_2O_3$  at these temperatures (12), thus the model above is preferred.

The general L-H model for Eq. [4] has been proposed by others for  $N_2O$  decomposition over  $Mn_2O_3$  (13, 14) and REOs including  $La_2O_3$  (15, 16), whereas a redox sequence involving lattice oxygen has been proposed for Feexchanged zeolites (17). At lower temperatures, Winter found the best rate expression was  $r = k P_{N_2O} / P_{O_2}^{1/2}$ , which implies that reversible oxygen chemisorption now becomes significant and covers most of the sites, and his apparent  $E_{act}$ value for La<sub>2</sub>O<sub>3</sub> was 20 kcal/mole (15). For many different oxides over a range of temperatures, a rate expression of the form  $r = k P_{N_2O} / (1 + K P_{O_2}^{1/2})$  has been reported (18), again consistent with the above mechanism. In the present study,  $O_2$  does not inhibit the reaction, in contrast to these earlier results. This difference could be due simply to the fact that a higher temperature (923 K) was employed in this work, under which the rate of recombination and desorption of adsorbed atomic O would be enhanced. In fact, when CH<sub>4</sub> was co-fed along with N<sub>2</sub>O at 923 K, the decomposition of N<sub>2</sub>O over Sr/La<sub>2</sub>O<sub>3</sub> was not increased, but actually was slightly decreased. These results suggest that the removal of adsorbed O, which could be facilitated by CH<sub>4</sub> combustion, is not a slow step under our conditions.

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	F		Partial pressure (Torr)			Reaction order		
Catalyst	(kcal/mole)	$CH_4$	NO	O <sub>2</sub>	$\mathrm{CH}_4$	NO	O <sub>2</sub>	
$La_2O_3$	26 <sup>a</sup>	0.69–3.42	2.74–13.7	0.38-22.8	0.62 <sup>a</sup>	0.53 <sup>a</sup>	0.50 <sup>a</sup>	
	$r (\mu \text{mole N}_2/2)$	$\sec \cdot m^2$ = 6.1	$1 \times 10^{-3} P_{\rm NO}$	$P_{\rm CH4} P_{\rm O_2}^{1/2} / (1 +$	$-0.081 P_{\rm N}$	$_{\rm O} + 0.093 P_{\rm CH4}$	$+0.035 P_{O_2}^{1/2})^{2c}$	
Sr/La <sub>2</sub> O <sub>3</sub>	$26^{b}$	0.69-3.42	2.76-13.8	0.38-7.56	$0.87^{b}$	$0.55^{b}$	$0.26^{b}$	
	$r (\mu mole N_2)$	$sec \cdot m^2 = 1$	$.9 \times 10^{-2} P_{\rm NC}$	$P_{CH4}P_{O_{2}}^{1/2}/(1$	$+0.10 P_{\rm N}$	$0 + 0.068 P_{CH4}$	$+0.32 P_{0r}^{1/2})^{2c}$	

TABLE 4

Kinetic Behavior of NO Reduction by CH4 in the Presence of O2 at 923 K

<sup>*a*</sup> From Ref. (6).

<sup>b</sup> From Ref. (9).

<sup>*c*</sup> Pressure units are Torr.



FIG. 1. Rate dependence on N<sub>2</sub>O pressure for N<sub>2</sub>O decomposition over Sr/La<sub>2</sub>O<sub>3</sub>: (•) without O<sub>2</sub> in the feed; ( $\blacksquare$ ) with 1% O<sub>2</sub> in the feed; ( $\frown$ ) fitting obtained with Eq. [6].

Further support of this conclusion comes from the fact that almost all the surface oxygen produced from NO adsorption and decomposition desorbed below 923 K, as revealed by our recent TPD studies with Sr/La<sub>2</sub>O<sub>3</sub> (19).

#### NO Decomposition

Analyses of these effluent streams were more difficult because the O<sub>2</sub> formed reacted with NO to form NO<sub>2</sub> between the reactor and the GC columns; consequently, little or no molecular O<sub>2</sub> was detected by gas chromatography. Under differential reaction conditions with no O<sub>2</sub> in the feed, O<sub>2</sub> partial pressures were negligible and could be ignored in the curve-fitting procedures; when 1% O<sub>2</sub> was added to the feed, the O<sub>2</sub> partial pressure utilized was that represented by the 2NO + O<sub>2</sub>  $\Rightarrow$  2NO<sub>2</sub> equilibrium at 923 K. However, this did not alter the inlet pressure significantly.

The reaction orders on NO were consistently higher than first-order, whether O<sub>2</sub> was co-fed or not, as listed in Table 2. This strongly suggests a bimolecular surface reaction was occurring. Because of the NO chemisorption we have measured on these catalysts combined with the finding that it decreases as temperature increases from 300 to 573 K (7, 9)and that some NO desorbs molecularly above 400 K (19), a quasi-equilibrated NO adsorption step was assumed and different bimolecular surface reactions were proposed as the rate determining step. These included adsorbed NO reacting with another NO molecule, or an adsorbed N atom or an adsorbed O atom, as well as the recombination and desorption of 2N atoms or 2O atoms. Some of the derived rate expressions could be rejected because they did not predict the observed inhibitive effect of O2 when it was co-fed, as evidenced in Fig. 2. One model gave a clearly superior fit-again it was a simple L-H sequence with the reaction



**FIG.2.** Rate dependence on NO pressure for NO decomposition over (a) La<sub>2</sub>O<sub>3</sub> (open symbols) and (b) Sr/La<sub>2</sub>O<sub>3</sub> (filled symbols):  $(\circ)$ ,  $(\bullet)$ , without O<sub>2</sub> in the feed;  $(\Box)$ ,  $(\blacksquare)$ , with 1% O<sub>2</sub> in the feed; (----) fittings obtained with Eq. [12] as represented in Table 2.

of two adsorbed NO species as the rds, as shown below:

$$2[NO + * \stackrel{K_{NO}}{\clubsuit} NO*]$$
[7]

$$2NO* \xrightarrow{k} N_2O* + O* \quad (rds) \qquad [8]$$

$$N_2 O \ast \stackrel{K}{\Rightarrow} N_2 + O \ast$$

$$2O* \stackrel{1/K_{O_2}}{\clubsuit} O_2 + 2*$$
 [10]

$$2NO \rightarrow N_2 + O_2.$$
[11]

If the surface coverage of  $N_2O$  is assumed small due to its much weaker adsorption and high reactivity, then the following rate expression can be easily derived,

$$r = Lk\theta_{\rm NO}^2 = LkK_{\rm NO}^2 P_{\rm NO}^2 / (1 + K_{\rm NO}P_{\rm NO} + K_{\rm O_2}^{1/2}P_{\rm O_2}^{1/2})^2,$$
[12]

where  $K_{\rm NO}$  and  $K_{\rm O2}$  again represent equilibrium adsorption constants. After data fitting, the two quantitative rate equations obtained are given in Table 2, and the correlations with the data are shown in Fig. 2.

Experimentally measured reaction orders in NO for its decomposition over oxides have fallen between 0 and 2, as reviewed by Amirnazmi *et al.* (20), and two of these studies by Winter and Amirnazmi *et al.*, in which a first-order dependence was observed, proposed NO adsorption as the rds with  $O_2$  desorption being quasi-equilibrated (20, 21). A similar reaction sequence has been proposed recently by Li and Hall for Cu-exchanged zeolites (22). Although the adsorption sites on these REO surfaces have not been unambiguously identified, it is reasonable to associate them with anion vacancies, which can be F-centers if they contain

a trapped electron, as originally proposed by Winter (15, 21), and more recently associated with the  $La_2O_3$  surface (12). Winter reported an activation energy of 16 kcal/mole for NO decomposition over  $La_2O_3$  (21), which is noticeably lower than the value of 23 kcal/mole obtained in this study.

#### NO Reduction by $CH_4$ (Absence of $O_2$ )

Analyses of the effluent stream for this reaction were not complicated as no  $O_2$  or  $NO_2$  was detected; however,  $H_2O$ peaks could not be quantified and sometimes with the 5A column neither could the  $CO_2$  peaks. The reaction orders in  $CH_4$  were relatively low and positive, while those in NO were near but less than one, as given in Table 3.

The use of CH<sub>4</sub> as a reductant significantly enhances the rate of N<sub>2</sub> formation over REO catalysts (6–9), and this can be seen by a comparison of Figs. 2 and 3. Seven different reaction sequences were considered—these included quasi-equilibrated dissociative and nondissociative NO adsorption along with a rds invoking either CH<sub>3</sub> formation via hydride abstraction, a surface reaction between adsorbed CH<sub>3</sub> and adsorbed NO, or a surface reaction between adsorbed CH<sub>2</sub> and NO. These either gave derived rate expressions with inappropriate reaction orders or they did not fit the data well. Only one kinetic sequence provided a good fit of the data—a L–H model assuming a surface reaction between adsorbed NO and adsorbed CH<sub>4</sub> to form a methyl radical, with NO and CH<sub>4</sub> adsorption in quasi-equilibrium, as shown below:

KCu

$$4[\text{NO} + * \stackrel{K_{\text{NO}}}{\clubsuit} \text{NO*}]$$
[13]

$$CH_4 + * \bigoplus^{n \in n_4} CH_4 *$$
 [14]

$$NO* + CH_4* \xrightarrow{\kappa} HNO* + CH_3* \quad (rds) \qquad [15]$$

$$NO* + HNO* \Rightarrow N_2O* + OH*$$
[16]

$$NO* + CH_3 * \Rightarrow HCN* + H_2O + *$$
[17]

$$NO* + HCN* \Rightarrow HCO* + N_2 + *$$
[18]

$$HCO* + O* \Rightarrow CO* + OH*$$
 [19]

$$CO_* + O_* \Rightarrow CO_2 + 2_*$$
 [20]

$$N_2O* \Rightarrow N_2 + O*$$
 [21]

$$2OH * \Rightarrow H_2O + O * + *$$
 [22]

$$4NO + CH_4 \rightarrow 2N_2 + CO_2 + 2H_2O.$$
 [23]

If NO\* and CH<sub>4</sub>\* are assumed to be the most abundant surface intermediates, then a site balance gives  $L = [NO*] + [CH_{4}*] + [*]$  and the following rate expression can be derived:

$$r = Lk\theta_{\rm NO}\theta_{\rm CH_4} = LkK_{\rm NO}K_{\rm CH_4}P_{\rm NO}P_{\rm CH_4}/(1+K_{\rm NO}P_{\rm NO}+K_{\rm CH_4}P_{\rm CH_4})^2.$$
[24]

**FIG. 3.** Rate dependence on reactant pressure for NO reduction by CH<sub>4</sub> over (a) La<sub>2</sub>O<sub>3</sub> (open symbols) and (b) Sr/La<sub>2</sub>O<sub>3</sub> (filled symbols): ( $\circ$ ), ( $\bullet$ ), CH<sub>4</sub> with NO constant; ( $\Box$ ), ( $\blacksquare$ ), NO with CH<sub>4</sub> constant; ( $\longrightarrow$ ) fittings obtained with Eq. [24] as represented in Table 3. Experimental points from references (6) and (9).

The curve-fitting procedure gave the two quantitative rate equations for  $La_2O_3$  and  $Sr/La_2O_3$  listed in Table 2.

We have found no other kinetic model in the literature describing NO reduction by CH<sub>4</sub> in the absence of molecular oxygen. Essentially, this sequence suggests that, in the absence of O<sub>2</sub>, adsorbed NO acts as a hydride abstractor to form methyl radicals, thus replacing chemisorbed oxygen as proposed by Lunsford and co-workers for the methane oxidative coupling reaction over  $La_2O_3$  and  $Sr/La_2O_3$  (23, 24). This same role for NO has been stated previously for the gas-phase reaction to form  $CH_3 \cdot radicals$  (25). We have admittedly speculated here on the surface chemistry following the rds that could constitute a complete catalytic cycle; however, all the proposed elementary steps are based on known homogeneous gas-phase reactions between free radicals (26), and the homogeneous reaction between NO and HCN is known (27). This sequence contains adsorbed N<sub>2</sub>O as an intermediate, and its desorption, rather than decomposition, could account for the small amounts of N<sub>2</sub>O that are observed, sometimes up to 5-20% of the nitrogen products (6-9). Clearly additional work is needed to verify this complicated sequence because other intermediates and other steps can also be suggested, but this series of elementary steps is proposed in a heuristic spirit to close the catalytic cycle and to allow its testing; however, another equilibrated sequence does not alter the kinetic rate equation.

# NO Reduction by $CH_4$ (Presence of $O_2$ )

Analyses of this product mixture were the most difficult due to the reactivity of excess  $O_2$  and NO to form  $NO_2$  between the reactor exit and the GC column. Although rates





FIG. 4. Rate dependence on reactant pressure for NO reduction by CH<sub>4</sub> in the presence of O<sub>2</sub> over (a) La<sub>2</sub>O<sub>3</sub> (open symbols) and (b) Sr/La<sub>2</sub>O<sub>3</sub> (filled symbols): ( $\circ$ ), ( $\bullet$ ), (

of  $N_2$  formation could still be monitored,  $N_2$  balances could not be obtained because NO<sub>2</sub> was not eluted quantitatively from the gas chromatograph. NO conversions were typically below 10%; however, due to the CH<sub>4</sub> combustion reaction which can occur in parallel with NO reduction, CH<sub>4</sub> conversions could be high and they varied from 1 to 45%. Consequently, the partial pressures could change significantly in some cases and, when necessary, average partial pressures in the reactor were calculated in the following manner:

$$P_{\rm NO} = \left(1 - \frac{X_{\rm NO}}{2}\right) P_{\rm NO}^{\circ}, \qquad [25]$$

$$P_{\rm CH_4} = \left(1 - \frac{X_{\rm CH_4}}{2}\right) P_{\rm CH_4}^{\circ},$$
 [26]

$$P_{\rm H_2O} = X_{\rm CH_4} P_{\rm CH_4}^{\circ} + P_{\rm H_2O}^{\circ}, \qquad [27]$$

and

$$P_{\rm O_2} = P_{\rm O_2}^{\circ} - \left[ X_{\rm CH_4} P_{\rm CH_4}^{\circ} - \frac{1}{4} X_{\rm NO} P_{\rm NO}^{\circ} \right] - \frac{1}{2} P_{\rm NO_2}.$$
 [28]

 $X_i$  is the fractional conversion of *i*,  $P_i^{\circ}$  is the inlet partial pressure of *i*,  $P_i$  is the average partial pressure across the catalyst bed, and  $P_{NO2}$  is the partial pressure of NO<sub>2</sub> at 923 K as determined by the equilibrium of 2NO+O<sub>2</sub>  $\Rightarrow$  2NO<sub>2</sub>. The last correction was small.

With these REO oxide catalysts, the addition of  $O_2$  to the feed significantly increased activity compared to CH<sub>4</sub> only (6–9), as can be seen by a comparison of Figs. 3 and 4. Consequently, a reaction mechanism was sought that (i) could explain the rate-enhancing role of excess  $O_2$  but still retain chemical consistency with the three reaction sequences proposed earlier, (ii) was consistent with the surface chemistry

associated with CH<sub>4</sub> activation during oxidative coupling over REOs, and (iii) was also consistent with known gasphase, free-radical species and reactions. At the temperatures used, we have assumed that heterogeneous reactions predominate over any homogeneous reactions. More than a dozen sequences were examined involving, among others, dissociative and nondissociative NO adsorption as well as the presence and absence of  $NO_2$  species along with the following different rate determining steps: CH<sub>3</sub> radical formation by an adsorbed O atom or an NO<sub>2</sub> species, reaction between adsorbed CH<sub>3</sub> and an NO or NO<sub>2</sub> species, and reaction between adsorbed CH<sub>2</sub> and NO species. We have found only one kinetic model which can satisfy these constraints and still describe the reaction well over both REO catalysts. It invokes a surface reaction between adsorbed CH<sub>4</sub> and adsorbed NO<sub>2</sub> to generate a methyl species, and one possible complete catalytic cycle, again based on known gas-phase species (26), is

$$4[NO + * \stackrel{K_{NO}}{\clubsuit} NO*]$$
 [29]

$$2[O_2 + 2* \stackrel{\kappa_{O_2}}{\textcircled{2}} 2O*]$$
[30]

$$2[CH_4 + * \stackrel{\Lambda_{CH_4}}{\textcircled{3}} CH_4 *]$$
[31]

$$3[NO * +O* \stackrel{\Lambda_{NO_2}}{\Rightarrow} NO_2 * +*]$$
 [32]

$$2[CH_4* + NO_2* \xrightarrow{k} CH_3* + HNO_2*] \quad (rds) \quad [33]$$

$$2HNO_2 * \Rightarrow NO * + NO_2 * + H_2O \qquad [34]$$

$$2[CH_3* + NO* \textcircled{HCN} + H_2O + *]$$
[35]

$$2[HCN* + O* \oplus CN* + OH*]$$
[36]

$$2[CN* + NO_2* \Rightarrow NCO* + NO*]$$
[37]

$$2[NCO* + NO* \Rightarrow N_2O* + CO*]$$
[38]

$$2[CO* + O* \Rightarrow CO_2 + 2*]$$
[39]

$$2[N_2O* \Rightarrow N_2 + O*]$$
[40]

$$2OH * \Rightarrow O * + H_2O + *$$
[41]

$$4NO + 2CH_4 + 2O_2 \rightarrow 2N_2 + 4H_2O + 2CO_2.$$
 [42]

The derivation of the rate expression is straightforward. If the concentrations of NO\*, CH<sub>4</sub>\*, and O\* are assumed to be predominant—NO<sub>2</sub>\* is assumed to be small compared to NO\*, in agreement with the gas-phase equilibrium concentrations at this temperature—a site balance gives  $L = [*] + [NO*] + [CH_{4}*] + [O*]$  and the rate expression becomes

$$r = Lk\theta_{\rm CH_4}\theta_{\rm NO_2}$$
  
=  $LkK_{\rm CH_4}K_{\rm NO_2}K_{\rm NO}K_{\rm O_2}^{1/2}P_{\rm CH_4}P_{\rm NO}P_{\rm O_2}^{1/2}/$   
 $(1 + K_{\rm NO}P_{\rm NO} + K_{\rm CH_4}P_{\rm CH_4} + K_{\rm O_2}^{1/2}P_{\rm O_2}^{1/2})^2.$  [43]

Fitting this to the data gave the two rate equations for  $La_2O_3$ and  $Sr/La_2O_3$  provided in Table 4, and the correlations are quite good, as shown in Fig. 4. The only dependence on  $H_2O$  and  $CO_2$  expected from this model would come if they were included in the site balance because of competitive adsorption; however, the data were successfully described without their inclusion.

Several comments are appropriate at this point. First, all the catalytic sequences examined which involved no NO<sub>2</sub> species gave a stoichiometry of  $6NO + 2CH_4 + O_2 \rightarrow$  $3N_2 + 2CO_2 + 4H_2O$  rather than that given by Eq. [42], i.e.,  $2NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2H_2O$ ; however, a catalytic cycle with the former stoichiometry can also be obtained with a surface NO<sub>2</sub> species by proposing different intermediates. The sequence above is suggested primarily for heuristic proposes and is preferred because steps 35-41 are known gas-phase free radical reactions (26, 27) and N<sub>2</sub>O is an intermediate, thus explaining its gas-phase presence and providing consistency with the previous sequences. This stoichiometry also suggests that definitions of selectivity (CH<sub>4</sub> combustion vs NO reduction) may have to be reexamined. Second, although this reaction clearly represents complex chemistry, step [34] is known chemistry (28) and step [33] has been proposed recently by Li et al. (5). Hall and co-workers have also proposed that NO2 is an intermediate whose role in this reaction over Co/zeolite catalysts is to generate CH<sub>3</sub> radicals (29), and Kikuchi and Yogo have proposed an initial reaction between NO2 and CH4 to form a reactive intermediate on Ga/ZSM-5 and In/ZSM-5 (30). We have already shown that  $NO_2$  is very active, but nonselective, for CH<sub>4</sub> combustion under oxidative coupling conditions over  $La_2O_3$  (6). Third, NO<sub>2</sub> reduction by CH<sub>4</sub> in

the absence of  $O_2$  gives specific activities and activation energies that are very similar to those for NO reduction by CH<sub>4</sub> in the presence of  $O_2$  (6), thus suggesting that the former reaction proceeds with surface chemistry similar to the latter. Fourth, as in the NO + CH<sub>4</sub> reaction, the generation of methyl radicals, which is known to occur in methane oxidative coupling (23, 24), is again the rds; hydride abstraction by an adsorbed O atom can also occur, but reaction orders in  $O_2$  as high as 0.5 could not be attained in the derived rate equations if this is the only CH<sub>4</sub> activation step. Finally, it should again be emphasized that different sequences and intermediates can be proposed following the rds to complete the cycle, but the derived reaction kinetics are independent of this chemistry as the last nine steps can be combined into a single, overall quasi-equilibrated step.

The only other in-depth kinetic study which has reported partial pressure dependencies and proposed a complete detailed catalytic cycle is that of Li *et al.* involving Co/ferrierites operating at lower temperatures (4, 5). The sequence represented by steps [29]-[41] is similar to that of Li et al. in that absorbed NO2 is proposed to generate methyl radicals in a rds, but it differs in that the model of Li et al. utilizes different chemical steps and does not explicitly propose the involvement of adsorbed oxygen or adsorbed CH<sub>4</sub>, thus it has an invariant half-order dependence on  $O_2$  and first-order dependence on CH<sub>4</sub>. Also, if the first two steps in their sequence are multiplied by a stoichiometric number of 2 to balance all species, the overall stoichiometry of their reaction is  $3NO + 1.5O_2 + CH_4 \rightarrow N_2 + CO_2 + 2H_2O + NO_2$ , thus NO<sub>2</sub> is generated as a product. The sequence represented by steps [29]-[41] is consistent with the study of Cant and co-workers which indicated that the rds over Co/ZSM-5 involves the breaking of a C-H bond (31).

#### SUMMARY

In the kinetic analyses of these four reactions, we have examined many different reaction sequences: first, to find the ones mathematically capable of fitting the data; second, to select models consistent with both oxidative coupling chemistry and known homogeneous free-radical chemistry; and third, to retain consistency in the surface chemistry among the final four rate expressions best describing each of these reactions. The results of this effort are offered here not in a dogmatic manner, but in the spirit of providing guidance toward a better understanding of these complicated reaction systems. The rate expressions given here allow predictions to be made and tests to be conducted to verify their validity.

All the rate expressions derived here have been based on L–H models, i.e., a surface reaction represents the rate determining step. The chemistry for unimolecular  $N_2O$ decomposition is simple and in excellent agreement with past studies. For NO decomposition at these temperatures, our result support a bimolecular reaction between adsorbed NO as the rds, which is consistent with some older studies, but in others NO adsorption has also been proposed as the rds on certain oxides. The chemistry associated with NO reduction by CH<sub>4</sub> in the presence or absence of molecular  $O_2$  is very complex, but complete catalytic cycles can be obtained based on free-radical species and reactions, and we have taken the liberty to suggest one possible sequence for each situation. However, the kinetic behavior is of primary interest, and the results here indicate that in the absence of both CH<sub>4</sub> and O<sub>2</sub>, activation of NO is the slow step. The addition of only CH<sub>4</sub> enhances the rate by being more reactive with NO, forming a methyl radical intermediate, and allowing very rapid subsequent reduction reactions to occur between these C-containing intermediates and NO. The presence of  $O_2$  with  $CH_4$  further increases the rate because adsorbed NO2 is more reactive with CH4 than NO and forms a methyl radical species more rapidly. Thus a consistent trend in the rate-controlling surface chemistry appears to exist; i.e., the rate of reaction between two adsorbed NO molecules is slower than that between an absorbed NO molecule and an adsorbed CH4 molecule while the reaction between an adsorbed NO<sub>2</sub> species and an adsorbed CH<sub>4</sub> molecule is more rapid than either of the previous reactions.

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#### REFERENCES

- 1. Armor, J. N., Appl. Catal. B 1, 221 (1992).
- 2. Li, Y., and Armor, J. N., Appl. Catal. B 1, L31 (1992).

- 3. Li, Y., and Armor, J. N., Appl. Catal. B 2, 239 (1993).
- 4. Li, Y., and Armor, J. N., J Catal. 150, 376 (1994).
- 5. Li, Y., Slager, T. L., and Armor, J. N., J. Catal. 150, 388 (1994).
- Zhang, X., Walters, A. B., and Vannice, M. A., *Appl. Catal. B* 4, 237 (1994).
- Zhang, X., Walters, A. B., and Vannice, M. A., J. Catal. 155, 290 (1995).
- 8. Zhang, X., Walters, A. B., and Vannice, M. A., Catal. Today in press.
- 9. Zhang, X., Walters, A. B., and Vannice, M. A., Appl. Catal. B in press.
- Zhang, X., Walters, A. B., and Vannice, M. A., J. Catal. 146, 568 (1994).
- 11. Li, Y., and Armor, J. N., Appl. Catal. B 1, L21 (1992).
- 12. Lacombe, S., Geantet, C., and Mirodatos, C., J. Catal. 151, 439 (1994).
- 13. Rheaume, L., and Parravano, G., J. Phys. Chem. 63, 264 (1959).
- 14. Yamashita, T., and Vannice, M. A., submitted for publication.
- 15. Winter, E. R. S., J. Catal. 15, 144 (1969).
- 16. Read, J. F., J. Catal. 28, 428 (1973).
- 17. Fu, C. M., Korchak, V. N., and Hall, W. K., J. Catal. 68, 166 (1981).
- 18. Roussel, P., and Teichner, S. J., Catal. Rev. 6, 133 (1972).
- 19. Zhang, X., and Vannice, M. A., unpublished data.
- Amirnazmi, A., Benson, J. E., and Boudart, M., J. Catal. 30, 55 (1973).
- 21. Winter, E. R. S., J. Catal. 22, 158 (1971).
- 22. Li, Y., and Hall, W. K., J. Catal. 129, 202 (1991).
- Lin, C.-H., Campbell, K. D., Wang, J.-X., and Lunsford, J. H., J. Phys. Chem. 90, 534 (1986).
- 24. Xu, M., and Lunsford, J. H., Catal. Lett. 11, 295 (1991).
- Wojciechowski, B. W., and Laidler, K. J., Can. J. Chem. 38, 1027 (1968).
- Miller, J. A., and Bowman, C. T., Prog. Energy Combust. Sci. 15, 287 (1989).
- Ismagilov, Z. R., and Kerzhentsev, M. A., *Catal. Rev.-Sci. Eng.* 32, 51 (1990).
- Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry." p. 349. Interscience Publishers, New York, 1966.
- Lukyanov, D. B., Sill, G., D'Itri, J. L., and Hall, W. K., *J. Catal.* 153, 265 (1995).
- 30. Kikuchi, E., and Yogo, K., Catal. Today 22, 73 (1994).
- Cowan, A. D., Dümpelmann, R., and Cant, N. W., J. Catal. 151, 356 (1995).