JOURNAL OF CATALYSIS 86, 137–146 (1984)

Nitric Oxide Reduction by Methane over Rh/Al_2O_3 Catalysts

JOHN R. HARDEE[1] AND JOE W. HIGHTOWER[2]

Department of Chemical Engineering, Rice University, Houston, Texas 77251

Received February 1, 1983; revised October 14, 1983

The mechanism of nitric oxide reduction with methane has been investigated over an alumina-supported rhodium catalyst. A series of kinetic studies were performed using initial rate data obtained in a recirculation reactor. Between 300 and 400°C NO elimination is initially fast over a reduced catalyst, but the reaction rate rapidly decreases due to oxidation of the catalyst surface. The decomposition is apparently a noncatalytic stoichiometric reaction between nitric oxide and surface rhodium atoms. The initial rate of disappearance of NO is adequately described by a dual-site Langmuir–Hinshelwood expression. In presence of reducing agents such as CO or CH_4, oxygen is effectively removed as CO_2 (plus H_2O). In the reduction of NO with CH_4, the initial rate of NO disappearance fits the following empirical rate expression

$$\text{Rate} = Ae^{-E/RT}(P_{\text{NO}})^{-0.63}(P_{\text{CH}_4})$$

where $A = 3.57 \times 10^3$ NO/$\text{Rh}_\text{s} \cdot \text{sec} \cdot (\text{N/m}^2)^{0.37}$ and $E = 77$ kJ/mole. A deuterium isotope effect of 1.9 is observed in the reduction of NO with mixtures of CH_4 and CD_4. This, along with the linear rate dependence on CH_4 partial pressure, indicates that the dissociative adsorption of CH_4 is the rate limiting step of the reaction. An experiment run with a ^{15}NO, N_2O, and CH_4 mixture indicated that N_2O is not an exclusive *gas phase* intermediate in the pathway to N_2 formation from NO. However, all these results are consistent with N_2O being a true *surface* intermediate. A reaction mechanism is proposed for NO reduction by methane. It is based on the assumption that two adsorbed NO molecules disproportionate to $(N_2O)_a + (O)_a$. Adsorbed $(N_2O)_a$ either desorbs as N_2O or decomposes to N_2 and $(O)_a$. The role of the reductant is to remove the strongly adsorbed $(O)_a$ and to keep the catalyst in an active reduced state for NO reaction.

INTRODUCTION

NO_x in exhaust streams can be reduced to innocuous products by CO, H_2, NH_3, hydrocarbons, etc. in the presence of appropriate catalysts. A fundamental understanding of the behavior of NO in the presence of these reductants would be most helpful in developing a catalyst that will more effectively decrease NO_x emissions. Many kinetic and mechanistic studies have appeared on the reduction of NO with CO (*1–8*), but little work has been done on the reduction with hydrocarbons. Peters and co-workers (*9–11*) studied the reduction of NO by CH_4 over a zinc-promoted copper chromite catalyst. Their rate data were explained with a dual-site Langmuir–Hinshelwood expression from which they deduced that the rate limiting step involved the reaction between adjacent NO and CH_4 molecules. Sotoodehnia-Korrani and Nobe (*12*) found a similar kinetic expression for the reduction of NO with ethylene over Cu on silica. Ault and Ayen (*13*) used hydrocarbons varying in length from 1 to 8 carbon atoms to reduce NO over a barium promoted copper chromite catalyst. They reported an empirical rate expression but did not speculate on the reaction mechanism. Hu and Hightower (*14*) found that a triple-site Langmuir–Hinshelwood rate expression accounted for the disappearance of NO when reduced by methane over Pt/Al_2O_3. Using isotopic tracers they deduced that the mechanism of NO reduction involves a disproportionation of NO into adsorbed $(N_2O)_a$ and adsorbed oxygen atoms.

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[1] Present address: Department of Sciences, Louisiana State University–Eunice, P.O. Box 1129, Eunice, La. 70535.

[2] To whom correspondence should be sent.

0021-9517/84 $3.00

The role of methane is to maintain the catalyst in an active state for NO decomposition by removing adsorbed oxygen from the catalyst

This work involves the reduction of NO with methane over Rh/Al_2O_3 This is an interesting catalyst because it will apparently catalyze NO reduction in the presence of small amounts of oxygen (*15, 16*), a feat not performed easily by other noble or base metal catalysts, except Ir Also, it is a highly active catalyst for the reduction of NO to N_2 by carbon monoxide (*17*) and is currently being used in automobile emission control devices Dubois *et al* (*8*) studied the mechanism of NO reduction with CO and found that NO dissociates on rhodium CO reacts with an adsorbed oxygen intermediate to form CO_2 Iizuka and Lunsford (*7*) studied NO reduction with CO over Rh–Y zeolites Finding the reaction to be zero order with respect to CO and 0 4 order with respect to NO, they proposed that the complex $(Rh^I(CO_2)NO)^+$ served as a reaction intermediate

It is our objective in this work to study the kinetics and the mechanism of NO reduction with methane over Rh/Al_2O_3 The following reactions are also studied since they are important in the overall mechanism of NO reduction NO decomposition, N_2O decomposition, and the reduction of NO with CO

EXPERIMENTAL PROCEDURES

The supported rhodium catalyst used throughout this work was a commercial preparation from Engelhard Industries It was donated by the Shell Research and Development Co , Houston, Texas The catalyst contained 0 5 wt % rhodium on gamma alumina, had a BET surface area of 84 m^2/g, and had a rhodium dispersion of 0 64 when measured by hydrogen chemisorption (H_{ads}/Rh_{total}) on a reduced catalyst

Nitric oxide (Matheson Gas Products) was purified by freezing it in a trap at liquid nitrogen temperature and retaining only the center portion of a distillation cut This center cut of NO was again frozen at −195°C and degassed for 1 min The solid NO was warmed slowly until the liquid phase formed, at which time the pumping was terminated The liquid nitrogen bath was replaced with a dry ice–acetone bath, and the NO was distilled into another trap at −195°C The contents remaining in the dry ice–acetone trap were discarded This procedure was repeated four times before the NO was ready for use

^{15}NO (Prochem B O C Ltd) had a listed purity of 97 2 atom% nitrogen-15 Mass spectral analysis confirmed this purity CH_4 (Phillips Research Grade, listed purity 99 9+%) was passed through a dry ice–acetone trap before being used CD_4 (Merck, Sharp, and Dohme of Canada, Ltd) had a purity of 99 atom% deuterium and was used without further purification Nitrous oxide (Liquid Carbonic) was first frozen at −195°C and degassed for 1 min It was subjected to four freeze-pump-thaw cycles before it was used H_2, O_2, and CO (Matheson Gas Products) were passed through traps at liquid nitrogen temperature before being used

All reactions were carried out in an all-Pyrex recirculation system that has been described elsewhere (*18*) A key feature of the system was a 2 23 cm^3 doser through which known amounts of gases could be added at any time to the circulating reactants Analysis of reactants and products was achieved with either a GLC (Poropak Q column thermostated at 0°C) or a mass spectrometer (CEC 21-104)

The standard catalyst pretreatment involved a slow heating of the catalyst to 350°C and evacuation to $1\ 3 \times 10^{-4}$ N/m^2 Oxygen ($2\ 0 \times 10^4$ N/m^2) was circulated over the catalyst for 30 min at this temperature After evacuation, the catalyst was heated to 450°C and evacuated again to $1\ 3 \times 10^{-4}$ N/m^2 To reduce the catalyst, hydrogen ($2\ 0 \times 10^4$ N/m^2) was circulated over the catalyst for 2 hr at 450°C The system was evacuated to $1\ 3 \times 10^{-4}$ N/m^2 and the catalyst was cooled to the reaction temperature In all cases the reactant gases were well mixed in the recirculation system for 30 min before contacting the catalyst

For isotopic analysis of the CH_4–CD_4 and the $^{14}N_2O$–^{15}NO–CH_4 reaction mixtures, a capillary bleed fed small amounts of the reacting gases continuously into the mass spectrometer The sensitivity of the mass spectrometer to each gas was calibrated using an MKS Baratron Pressure Meter type 220-2Al-1 The fragmentation patterns suggested by Schissler *et al* (*19*) were used to correct the fragmentation data obtained from CH_3D, CH_2D_2, and CHD_3 The method is based on probability of hydrogen/deuterium loss and was claimed to fit their data well

RESULTS

NO Decomposition

Nitric oxide decomposition was studied between 300 and 400°C over 85 mg of Rh/Al_2O_3 The reaction is initially fast over a reduced surface, but it rapidly slows down and almost completely stops after a short time This behavior is shown in Fig 1 The reaction products observed are N_2 and N_2O with only N_2O being formed initially Gas phase O_2 and NO_2 were never observed as products of this reaction

It appears that nitric oxide decomposition involves a stoichiometric reaction between NO and the catalyst which becomes poisoned in some manner after the reaction has proceeded for a short time The number of NO molecules that react range from 5 6 × 10^{19} to 14 0 × 10^{19}/g of catalyst These numbers are 2 to 7 times greater than the number of exposed rhodium atoms as measured by hydrogen chemisorption—1 9 × 10^{19}/g, assuming H_{ads}/Rh_s = 1 0

The reaction was carried out over both oxidized and reduced surfaces at 320°C, and the initial rate was about an order of magnitude faster on the reduced surface The initial rates were determined at conversions below 5% There is a strong initial rate dependence on NO pressure below 1 3 × 10^3 N/m^2, but the rate is essentially independent of NO pressure above 1 3 × 10^3 N/m^2

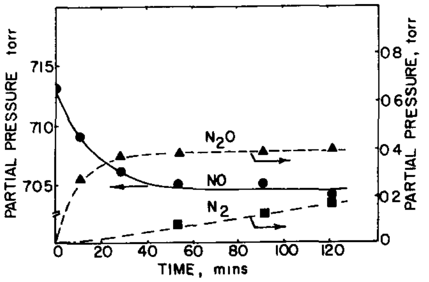

FIG 1 Decomposition of NO over 85 mg reduced Rh/Al_2O_3 in a 400 cm^3 batch recirculation reactor at 320°C (1 Torr = 133 3 N/m^2)

N_2O Decomposition

Nitrous oxide decomposition is extremely fast at 320°C over a reduced catalyst, at this temperature the reaction was probably limited by the recirculation rate in the system In contrast to NO decomposition, however, both O_2 and N_2 are observed as gas phase products At a lower temperature (150°C) the rates were sufficiently slow that they were not recirculation speed limited, the initial rate of N_2O decomposition versus N_2O pressure is shown in Fig 2 The rate appears to be near first order in N_2O at low N_2O pressure but approaches zero order at higher N_2O pressure

Addition of only a small amount of oxy-

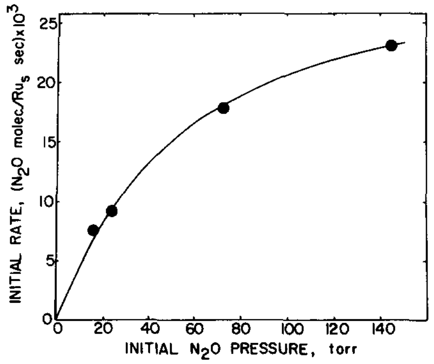

FIG 2 Effect of initial pressure on the initial rate of NO decomposition over 85 mg reduced Rh/Al_2O_3 in a batch recirculation reactor at 320°C

gen decreased the initial N_2O decomposition rate by about a factor of 3 However, the initial rate was not further decreased as the O_2 pressure was increased from 6 7 × 10^2 to 8 7 × 10^3 N/m^2

N_2O decomposition is fast at 320°C, yet N_2O is observed as a product in NO decomposition and reduction at 320°C In order to understand this, the effect of NO on N_2O decomposition was studied Figure 3 shows the effect of NO on the N_2O decomposition The circles represent an experiment where only N_2O was present in the system The reaction reached 50% conversion in about 50 min at 200°C The triangles represent an experiment in which 4 07 × 10^{-3} mole of NO were added to the system via the doser 10 min after the reaction began Obviously the NO poisoned the N_2O decomposition, which stopped at about 25% The temperature was too low for reduction of the NO to occur at a measurable rate

Reduction of NO with CO

Since CO is suspected of being a surface intermediate in the reaction of methane with NO (*14*), we looked at NO reduction with CO over Rh/Al_2O_3 This reaction is very fast at 320°C with the reaction products being N_2 and CO_2 The temperature was dropped to 135°C for kinetic studies, at this temperature N_2O is the major nitrogen-containing gas phase product, along with CO_2 and a small amount of N_2 The reaction is zero order with respect to CO and depends on NO to the 0 54 power

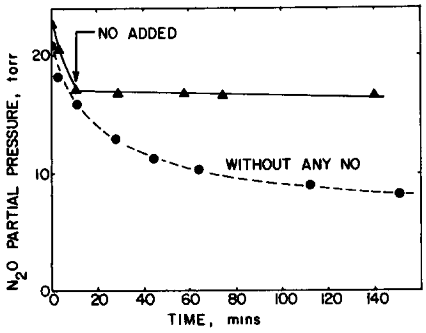

FIG 3 Effect of NO on N_2O decomposition over 85 mg reduced Rh/Al_2O_3 at 150°C

NO Reduction with CH_4

With NO as the only reactant, the rhodium catalyst quickly becomes poisoned for NO decomposition (see Fig 1), however, when CH_4 is present in the system the catalyst activity is maintained and NO reduction goes to completion Specifically, at 405°C NO decomposition reaches only about 25% conversion in 24 hr With methane present, NO conversion is complete in about 40 min at this temperature

The effect of changes in temperature, NO pressure, and CH_4 pressure on the rate of NO reduction was measured In all cases initial rates were determined from conversions below 15% N_2O and N_2 were the only observed nitrogen-containing products The ratio of N_2O to N_2 is fairly large initially but decreases as the reaction proceeds Other reaction products are CO_2 and H_2O, although H_2O did not appear in the chromatographic effluent because the column was kept at 0°C Mass spectral analysis of the reaction products confirmed the presence of H_2O

The reaction rate was about 6 times faster on a reduced surface than on an oxidized surface Also, the products CO_2 and H_2O were added to initial reaction mixtures to determine if there were any product poisoning CO_2 had no effect on the reaction rate, but H_2O caused a substantial decrease in catalyst activity For example, only a small amount of H_2O (~1 4 × 10^{17} mole-

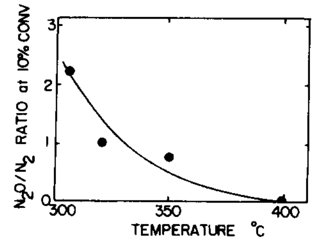

FIG 4 Effect of temperature on N_2O/N_2 ratio at 10% NO conversion during reduction with methane

cules) was needed to decrease the reaction rate by a factor of about 6

Figure 4 shows the ratio of N_2O to N_2 at 10% conversion at different temperatures The ratio decreases with increasing temperature and becomes zero at 400°C

The observed energy of activation for NO reduction was 79 kJ/mole

CH_4–CD_4 Scrambling

That the catalyst can activate C–H bonds in methane is reflected in its ability to promote hydrogen exchange between CH_4 and CD_4 This reaction was studied over 0 50 g of Rh/Al_2O_3 at 320°C, the results are shown in Fig 5 The equilibrium fractions were calculated from the equation

$$d_{4-i}(\text{Fraction of } CH_iD_{4-i}) = \frac{\left(\frac{i}{4}\right)\left(\frac{H}{D}\right)_f^i}{\sum_{i=0}^{4}\left(\frac{i}{4}\right)\left(\frac{H}{D}\right)_f^i}$$

where $(H/D)_f$ is the final (H/D) ratio in the system Initially the exchange is rapid with multiple exchange taking place All three products d_1, d_2, and d_3 are present from the initial stages of the reaction

Although the reaction is fast, the presence of NO and/or N_2O poisons the exchange Figure 6 shows the effect of adding NO during the exchange reaction At $t = 10$ min, 3 87 mmole of NO were introduced into the system via the doser The exchange between CH_4 and CD_4 completely stopped until all the NO was reduced At that time the exchange reaction began again but at a slower rate than was observed initially, probably due to adsorbed H_2O and oxygen atoms Addition of N_2O also impeded the exchange reaction, although the exchange was not totally halted as occurred with NO addition

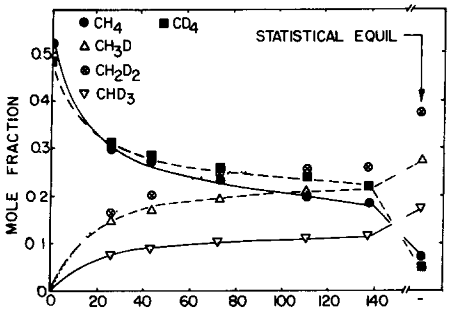

FIG 5 Intermolecular H/D scrambling between CH_4 and CD_4 during reaction over 0 5 g Rh/Al_2O_3 at 320°C in a batch recirculation reactor

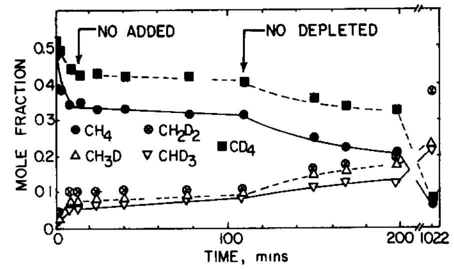

FIG 6 Effect of NO on CH_4/CD_4 scrambling over 0 5 g Rh/Al_2O_3 at 320°C

NO + CH_4 + CD_4

Since NO poisons the CH_4–CD_4 exchange reaction, it appears that cleavage of C–H bonds may be difficult in the presence of NO To test this possibility, CD_4, CH_4, and NO were circulated over the catalyst at 320°C The results are shown in Fig 7 The initial rate of disappearance of CH_4 is about 1 9 times faster than the rate of disappearance of CD_4 No intermolecular H/D exchange occurred

$^{14}N_2O$ + ^{15}NO + CH_4

In order to test whether N_2O is a true gas phase intermediate in the reduction of NO

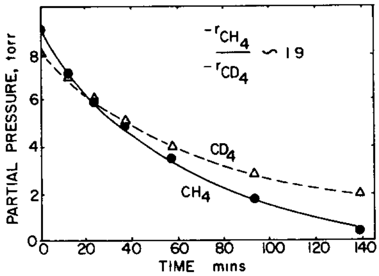

FIG 7 Comparison of reactivity of CH_4 and CD_4 during reduction of NO over Rh/Al_2O_3 at 320°C

with CH_4, an experiment was run with a mixture containing $^{14}N_2O$ ^{15}NO CH_4 = 15 20 20 Torr No mixed $^{14}N^{15}N$ dinitrogen molecules were observed among the products The $^{14}N_2/^{15}N_2$ ratio in the products is shown in Fig 8 as a function of time The ratio has a finite, nonzero intercept of about 1 5 and then goes through a maximum at about 3 5 before beginning to fall as the reaction proceeds Had the reaction been allowed to go to completion where all the nitrogen oxide molecules had disappeared, the ratio would have decreased to a limiting value of 1 5 which reflects the ratio of $^{14}N/^{15}N$ in the initial mixture

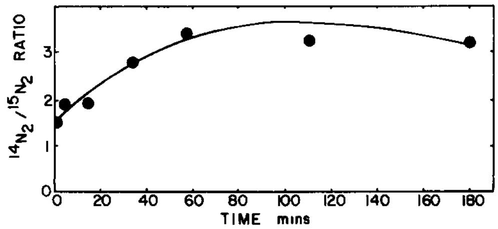

Fig 8 Ratio of $^{14}N_2/^{15}N_2$ products during reduction of $^{14}N_2O$–^{15}NO–CH_4 mixture over 0 5 g Rh/Al_2O_3 at 320°C

DISCUSSION

NO Decomposition

NO decomposition is initially fast but slows down as the catalyst becomes poisoned From the deficiency of oxygen atoms (relative to N atoms) among the gaseous products, the poisoning must be due to the build-up of oxygen atoms on the catalyst surface This is supported by the fact that the catalyst activity is much lower on an oxidized surface than on a reduced surface

The NO–Rh/Al_2O_3 system certainly deviates from ideal behavior The number of active sites changes as the reaction proceeds, the oxidation state of the catalyst is not constant, and there must certainly be a change in the heat of adsorption of NO with coverage Nevertheless, the initial rate data of NO decomposition can be described at least qualitatively by a simple dual-site Langmuir–Hinshelwood rate model of the form

$$\text{Initial Rate} = \frac{kK_{NO}{}^2P_{NO}{}^2}{(1 + K_{NO}P_{NO})^2} \qquad (1)$$

where k is the reaction rate constant, K_{NO} is the adsorption equilibrium constant for NO, and P_{NO} is the partial pressure of NO For strong NO adsorption, $K_{NO}P_{NO} \gg 1$ and Eq (1) reduces to

$$\text{Initial rate} = k \qquad (2)$$

Under these conditions, the reaction rate constant k (which is the same as the turnover frequency) was determined to be 4 9 × 10^{-3} (NO molecules)/(Rh_s sec) at 320°C

The discrepancy between the observed NO molecules that are decomposed (5 6 – 14 0 × 10^{19}/g) and the number of Rh atoms in the catalyst (2 9 × 10^{19}/g) can possibly be rationalized by the stoichiometric reaction

$$6NO + 2Rh \rightarrow Rh_2O_3 + 3N_2O \qquad (3)$$

If every Rh in the catalyst were converted to inactive Rh_2O_3, this would account for 8 8 × 10^{19}/g NO molecules reacted, which is in the middle range of the values observed in several experiments

N_2O Decomposition

In contrast to NO decomposition at 320°C, N_2O decomposition over Rh/Al_2O_3 is an extremely rapid, catalytic process The reaction temperature was lowered to 150°C in order to obtain reliable initial kinetic rate data The initial rate dependence on N_2O pressure can be described by a single-site Langmuir–Hinshelwood equation involving moderate adsorption of N_2O, viz

$$\text{Initial rate} = \frac{kK_{N_2O}P_{N_2O}}{1 + K_{N_2O}P_{N_2O}} \qquad (4)$$

where k is again the reaction rate constant, K_{N_2O} is the adsorption equilibrium constant for N_2O, and P_{N_2O} is the partial pressure of N_2O At 150°C this expression adequately fits the initial rate data when $k = 5.5 \times 10^{-4}$ (N_2O molecules)/(Rh_s sec). Since oxygen is a product of N_2O decomposition and inhibits N_2O decomposition, the more generally correct rate expression should contain a term in the denominator that indicates this poisoning. However, since such a small amount of O_2 (as little as 600 N/m^2) poisoned the reaction, no attempt was made to quantitatively describe this term.

A mechanism that is consistent with the observed rate expression is the same as that described by Winter (*20, 21*) where

$$N_2O \rightleftharpoons (N_2O)_a \tag{5}$$

$$(N_2O)_a \rightarrow N_2 + (O)_a \tag{6}$$

$$(O)_a + (O)_a \rightleftharpoons O_2 \tag{7}$$

It is assumed that step (6) is rate limiting.

Over an Fe–Y zeolite Fu *et al.* (*22*) used isotopic tracers to identify the reaction

$$N_2O + (O)_a \rightarrow N_2 + O_2 \tag{8}$$

as a major step for catalyst reduction. We do not believe this correctly describes our catalyst, since Eq. (8) implies that the presence of oxygen would have a beneficial effect on the reaction rate, contrary to the observations.

As shown in Fig. 3, NO poisons N_2O decomposition. Since N_2O decomposition is very fast at 320°C, this poisoning effect by NO explains why N_2O is observed as a product in NO reduction and decomposition reactions. This also explains the temperature dependence of the ratio of N_2O to N_2 at low conversions in the reduction of NO by CH_4. NO and N_2O apparently compete for the same active sites. The fact that NO is more strongly adsorbed at 200°C than is N_2O indicates that NO has a higher heat of adsorption than does N_2O. At 320°C, as soon as N_2O is formed it is rapidly displaced from the surface by NO before it has a chance to decompose. However, at higher temperatures, the selectivity for NO adsorption is thermally minimized so that above 400°C the N_2O that is formed immediately decomposes to N_2.

Reduction of NO by CO

The catalyst poisoning that was observed in NO decomposition at 320°C was not observed when CO was added to the system. Complete NO conversion was attained in roughly 20 min, and the reaction was probably limited by the stirring rate in the recirculation reactor. When the reaction is not transport limited (e.g., at 135°C), the initial rate data can be described very well by the equation

$$\text{Initial rate} = \frac{kK_{NO}{}^2P_{NO}{}^2}{(1 + K_{NO}P_{NO} + K_{CO}P_{CO})^2} \tag{9}$$

where k is the reaction rate constant, K_{NO} and K_{CO} are the adsorption equilibrium constants, and P_{NO} and P_{CO} are the partial pressures of NO and CO, respectively. For weak CO adsorption where $(1 + K_{NO}P_{NO}) \gg K_{CO}P_{CO}$, Eq. (9) reduces to

$$\text{Initial rate} = \frac{kK_{NO}{}^2P_{NO}{}^2}{(1 + K_{NO}P_{NO})^2} \tag{10}$$

where $k = 3.20 \times 10^{-2}$ (NO molecules)/(Rh_s sec) at 135°C. This is exactly the same as Eq. (1) except that the rate constant in the presence of CO is several orders of magnitude greater than the constant for the NO decomposition alone.

A possible mechanism which is consistent with this rate expression is

$$NO \rightleftharpoons (NO)_a \tag{11}$$

$$2(NO)_a \xrightarrow{\Lambda} (N_2O)_a + (O)_a \tag{12}$$

$$(N_2O)_a \rightleftharpoons N_2O \tag{13}$$

$$(N_2O)_a \rightarrow N_2 + (O)_a \tag{14}$$

$$CO \rightleftharpoons (CO)_a \tag{15}$$

$$(CO)_a + (O)_a \rightarrow CO_2 \tag{16}$$

Evidence for steps (12), (13), and (14) will be presented in the next section. The mechanism involves an oxidation of the catalyst by NO and N_2O (steps (12) and (14)) followed by reduction of the catalyst (step (16)). Step (13) becomes less important at higher temperatures.

Reduction of NO with CH_4

Although not so efficient as CO, CH_4 also removes adsorbed oxygen atoms and thus maintains the activity of Rh/Al_2O_3

A kinetic study of this reaction is difficult for a number of reasons First, the reaction products, particularly H_2O, compete for the active sites with the reactants This may disguise the true reaction kinetics and cause the conversion-versus-time plots to be nonlinear even at low conversions Another difficulty in determining the reaction kinetics stems from the reaction exothermicity, about 1170 kJ/mole This makes temperature control difficult Third, the oxidation state of the catalyst almost certainly changes during the reaction, which causes changes in the heats of adsorption with coverage and deviations from ideal adsorption Furthermore, the chemisorption studies done by Shelef and Otto (*23, 24*) show that NO adsorption fits Freundlich type equations rather than Langmuir isotherms Finally, the reduction of NO with CH_4 does not involve a single-step surface process but rather must involve a series of consecutive reactions All these reasons combine to discourage any attempts to describe the reaction kinetics in terms of ideal Langmuir–Hinshelwood or Eley–Rideal kinetics The initial rate of reduction of NO with CH_4 is less than zero order in NO and about first order in CH_4 The following empirical rate expression adequately fits the initial rate data for NO reduction at 320°C

$$\text{Initial rate} = A \exp(-E/RT)(P_{NO})^{-0\ 63}(P_{CH_4}) \quad (17)$$

where $A = 3\ 57 \times 10^3$ NO/(Rh_s sec $(N/m^2)^{0\ 37}$) and $E = 77$ kJ/mole

CH_4–CD_4 Scrambling

The isotopic hydrogen exchange between CH_4 and CD_4 is quite rapid over the Rh catalyst at 320°C However, when either NO or N_2O is present in the gas phase, the exchange ceases This implies that NO, N_2O, and CH_4 are competing for the same active sites Since CH_2D_2 appears as an initial product, the exchange reaction between CH_4 and CD_4 must involve a mechanism by which more than one hydrogen (deuterium) atom is introduced into methane on each interaction of methane with the catalyst For this multiple exchange to occur, the adsorption of methane probably involves several sites Adsorption of NO or N_2O on any of these sites would inhibit the dissociative adsorption of CH_4 This poisoning suggests that the cleavage of C–H and C–D bonds may be difficult in presence of N_2O and NO

Kinetic Isotope Effect

When CD_4 was substituted for CH_4, the rate of NO reduction was decreased by a factor of 1 9 The kinetic isotope effect, along with the first order rate dependence on CH_4, suggests that dissociative adsorption of CH_4 may be involved in the rate limiting step in the reduction of NO with CH_4 A similar kinetic isotope effect was found by Hu and Hightower (*14*) for NO reduction by methane over Pt/Al_2O_3

Role of N_2O

A fundamental question about NO decomposition and reduction is whether N_2 comes directly from NO or whether N_2O is an exclusive intermediate in the formation of N_2 As pointed out by Hu and Hightower (*14*), N_2O may be an exclusive *adsorbed* intermediate without being an intermediate in the gas phase Although the question about the gas phase intermediacy can be tested directly with isotopic tracers, the issue of adsorbed N_2O intermediacy can only be relegated to the realm of speculation based on indirect evidence If N_2O and N_2 are formed in parallel reactions, viz

$$2NO \begin{array}{l} \nearrow N_2O \\ \searrow N_2 \end{array} \qquad (18)$$

then if both N_2O and N_2 formation have similar kinetic expressions, the ratio of

N_2O/N_2 should be constant as the reaction proceeds On the other hand, if N_2O is an exclusive intermediate in the formation of N_2, viz

$$NO \rightarrow N_2O \rightarrow N_2 \qquad (19)$$

then the ratio of N_2O to N_2 should be large initially and decrease as the reaction proceeds This latter case was observed in the present study, although the initial ratio did not approach infinity

The experiment with $^{14}N_2O$, ^{15}NO, and CH_4 (Fig 8) was designed to examine the role of N_2O in the reduction of NO with CH_4 If N_2O were a true gas phase intermediate, then the ratio of $^{14}N_2/^{15}N_2$ should approach infinity at $t = 0$ If N_2O and N_2 are formed in parallel reactions with N_2O decomposition (reduction) providing only a minor pathway for N_2 formation, then the ratio $^{14}N_2/^{15}N_2$ should approach a value near zero at $t = 0$ The results in Fig 8 represent neither extreme case and indicate that both the parallel (Eq (18)) and series (Eq (19)) reaction schemes are followed simultaneously In other words, both N_2 and N_2O are primary products, and N_2O is not an exclusive gas phase intermediate in the overall reduction of NO by methane

We cannot, however, rule out the possibility that adsorbed N_2O is an exclusive *surface* intermediate in NO reduction If the NO first is adsorbed on a reduced site and then disproportionates into adsorbed $(N_2O)_a$ (Eqs (11) and (12)), this species can either be desorbed as gaseous N_2O (Eq (13)) or be reduced further to N_2 and $(O)_a$ (Eq (14)) At 320°C the $(N_2O)_a$ and gaseous N_2O are in pseudo equilibrium, thus accounting for the finite nonzero intercept in Fig 8 This scheme will also explain the results of the temperature dependence of the ratio N_2O/N_2

Mechanism of NO Reduction With CH_4

The kinetic expression for the reduction of NO by CH_4 is not inconsistent with an Eley–Rideal mechanism where the rate limiting step involves the reaction of a gas phase methane molecule with adsorbed oxygen atoms However, we do not think it is reasonable that one gas phase methane molecule would react with four adsorbed oxygen atoms at the same time to yield CO_2 and H_2O All the adsorption, decomposition, and disproportionation steps discussed to this point are probably involved in the reduction of NO by methane In addition, other reactions involving CH_4 dissociation and formation of CO species on the surface may also be involved in this highly complex reaction A summary of most of these reactions follows

$$NO \rightleftharpoons (NO)_a \qquad (11)$$

$$2(NO)_a \rightarrow (N_2O)_a + (O)_a \qquad (12)$$

$$(N_2O)_a \rightarrow N_2 + (O)_a \qquad (14)$$

$$(N_2O)_a \rightleftharpoons N_2O \qquad (13)$$

$$CH_4 \rightleftharpoons (CH_3)_a + (H)_a \qquad (20)$$

$$CH_4 \rightleftharpoons (CH_2)_a + 2(H)_a \qquad (21)$$

$$(CH_3)_a \rightleftharpoons (CH_2)_a + (H)_a \qquad (22)$$

$$(CH_2)_a \rightleftharpoons (CH)_a + (H)_a \qquad (23)$$

$$(CH)_a \rightleftharpoons (C)_a + (H)_a \qquad (24)$$

$$(C)_a + (O)_a \rightarrow (CO)_a \qquad (25)$$

$$(CO)_a + (O)_a \rightarrow CO_2 \qquad (16)$$

$$(H)_a + (O)_a \rightarrow (OH)_a \qquad (26)$$

$$(OH)_a + (H)_a \rightarrow H_2O \qquad (27)$$

$$(NO)_a + (O)_a \rightleftharpoons (NO_2)_a \qquad (28)$$

$$(NO_2)_a + (O)_a \rightleftharpoons (NO_3)_a \qquad (29)$$

$$(CH_2)_a + (O)_a \rightarrow (CH_2O)_a \qquad (30)$$

$$(CH_2O)_a + (O)_a \rightarrow (CO)_a + H_2O \qquad (31)$$

Normally, steps 20–24 are quite facile and rapidly approach equilibrium, as indicated by the rapid H–D scrambling of CH_4–CD_4 mixtures However, in the presence of NO or N_2O, these reactions are greatly impeded as the nitrogen oxides compete very successfully for the active Rh sites In fact, under these conditions it is one (or more) of the C–H bond breaking steps that is rate limiting

This is essentially the same mechanism reported by Hu and Hightower (*14*) for their Pt/Al_2O_3 The key assumptions of the scheme are that 2 NO molecules disproportionate on the catalyst to form $(N_2O)_a$ and $(O)_a$ The $(N_2O)_a$ either desorbs to form gaseous N_2O or decomposes (is reduced) to form N_2 and $(O)_a$ The role of the reductant CH_4 is to remove adsorbed oxygen which keeps the catalyst in an active reduced state Although this mechanism is similar to the one presented for reduction of NO by CO, there is at least one major difference The rate limiting step in CO reduction of NO probably involves the surface reaction of two NO molecules, while in this scheme the rate limiting step probably involves the breaking of carbon–hydrogen bonds in methane

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Robert A Welch Foundation, the National Science Foundation (Grant Number CHE 77-10541), and Haldor Topsøe A/S (Copenhagen, Denmark)

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