JOURNAL OF CATALYSIS **92**, 247–259 (1985)

Reduction of NO by H_2 over Silica-Supported Rhodium: Infrared and Kinetic Studies

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Received August 23, 1984; revised November 6, 1984

The kinetics of NO reduction by H_2 have been investigated over a Rh/SiO_2 catalyst. The specific activity and product selectivity are both sensitive functions of the catalyst pretreatment. Preoxidation in NO increases the NO reduction activity by 30 to 50% over that observed when the catalyst is prereduced. It is also noted that the preoxidized catalyst generally favors the formation of N_2. *In situ* infrared spectra of the catalyst show that at NO conversion levels below 60%, the catalyst surface is virtually saturated by adsorbed NO. The power law rate expressions obtained from the experimental data can be interpreted in the light of a mechanism for NO reduction.

INTRODUCTION

There is considerable interest in the catalytic reduction of NO over Rh since this metal is now being used in catalytic converters to control NO_x emissions from automobiles (*1*). Previous studies (*1–6*) have demonstrated that both CO and H_2 participate in the reduction process, and that the degree to which one or the other reducing agent is active is a strong function of reaction conditions. In view of this, it is desirable to develop an understanding of the interactions between NO and each of the reducing agents separately before addressing questions related to the interactions of all three components. A discussion of NO reduction by CO over a Rh/SiO_2 catalyst has been presented recently by Hecker and Bell (*7*). The present paper describes the results of a complementary investigation concerning the reduction of NO by H_2 over the same catalyst. Insights into the reduction mechanism were obtained from measurements of the reaction kinetics and from infrared spectra taken under reaction conditions.

Several investigations of NO reduction by H_2 have been reported in the literature. Kobylinski and Taylor (*2*), as part of a study comparing the performance of Group VIII metals, observed that the extent of NO reduction over a Rh/Al_2O_3 catalyst is a strong function of temperature. The product distribution at conversions below 100% was not reported, but it was shown that at the onset of complete conversion, 60% of the product is NH_3, the balance presumably being N_2. At yet higher temperatures, the selectivity to NH_3 is reduced due to NH_3 decomposition. Yao *et al.* (*8*) reported that the level of Rh dispersion on Al_2O_3 has a strong influence on catalyst activity and selectivity. At low metal loadings (<5%), where the metal was fully dispersed, the turnover frequency for NO reduction was fivefold lower than that for high metal loadings (>5%) where the metal forms three-dimensional crystallites. It was also noted that at 473 K on the high dispersion catalysts the product selectivities were: N_2O—81%; N_2—9%; and NH_3—10%; whereas, on the lower dispersion catalyst the product selectivities were: N_2O—41%; N_2—34%; and NH_3—25%. The authors proposed that the observed changes with Rh dispersion might be due to a change in the mechanism of NO reduction. More recently, Savatsky

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0021-9517/85 $3.00

and Bell (*9*) investigated the reduction of NO by H_2 over a Rh/SiO_2 catalyst. They observed that under steady-state conditions, the catalyst is nearly saturated by adsorbed NO. *In situ* infrared spectra showed the presence of two principal species: $Rh-NO^{\delta-}$, characterized by $\nu_{NO} = 1680\ cm^{-1}$, and Rh–NO, characterized by $\nu_{NO} = 1850\ cm^{-1}$. Very rapid exchange between gas-phase and adsorbed NO was revealed by isotopic tracer experiments. Based on transient response experiments it was proposed that the reduction of NO is initiated by the dissociation of NO. N_2O and N_2 were assumed to be formed via reactions involving adsorbed N atoms. The formation of NH_3 and H_2O was assumed to occur via the stepwise hydrogenation of N and O atoms, respectively. The results obtained in this study suggest that the mechanism proposed by Savatsky and Bell (*9*) must be modified somewhat in order to rationalize the kinetics of NO reduction by H_2 under steady-state conditions.

EXPERIMENTAL METHODS

Apparatus. The apparatus used for this study is identical to that described in Ref. (*7*). The catalyst, in the form of a thin disk, is contained in a small reactor equipped with infrared-transparent windows so that *in situ* infrared spectra can be taken of species adsorbed on the catalyst surface. The design of this reactor is similar to that given in Ref. (*10*). Reactants are delivered to the reactor from a flow manifold, and the products are analyzed by gas chromatography using a specially designed system (*11*). A metal bellows pump is connected between the reactor inlet and outlet, to recycle the reactor effluent. With a nominal flow rate of 200 cm^3/min to the loop, a recycle ratio of 200 : 1 can be achieved, allowing the reactor to be characterized as a CSTR.

Materials. A 4.6% Rh/SiO_2 catalyst was prepared by incipient wetness impregnation of Cab-O-Sil HS-5 with an aqueous solution of $RhCl_3 \cdot 3H_2O$. The resulting mixture was dried in a vacuum oven and then calcined in air for 1 hr at 773 K. The catalyst was then reduced in flowing H_2 at 673 K for ~2 hr and at 573 K for an additional 16 hr. The dispersion of the reduced catalyst was determined to be 38%, by means of H_2 chemisorption. A 29-mm-diameter disk of the catalyst, weighing 0.123 g, was prepared by pressing a 120-mesh cut of the catalyst in a special die made of tool steel.

All gases were purified prior to use. Helium (99.998%) was passed through an Oxyclear unit (Labclear) followed by a bed of molecular sieve. Hydrogen (99.999%) was purified by passage through a Deoxo unit (Engelhard) followed by a bed of molecular sieve. These procedures served to remove oxygen and water from each gas. The nitric oxide used for these studies was in the form of either 6.15 or 11.5% NO mixtures in helium. These mixtures were found to contain several hundred ppm of N_2O and N_2 as impurities. The N_2O was removed by passage of the gas through a molecular sieve trap. The N_2 impurity could not be removed, but was accounted for in determining the rate of N_2 produced during NO reduction.

RESULTS

Rate Measurements

Initial experiments indicated that the activity and selectivity of the catalyst changed depending upon whether the catalyst was reduced or oxidized prior to use. To explore this phenomenon, two sets of experiments were performed, differing only in the manner of catalyst pretreatment. For the first set, the catalyst was reduced in flowing H_2 for at least 24 hr at 523 K. For the second set, the catalyst was oxidized in a 2% NO/He stream for 1 to 2 hr at 423 K. Following pretreatment, the catalyst was conditioned at 445 K for 20 to 25 hr, using a feed mixture containing 1.0% NO and 2.2% H_2 flowing at 200 (STP) cm^3/min. The catalyst activity and selectivity at the end of the break-in period was stable, and for a given pretreatment could readily be reproduced. Measurements of the Rh dispersion made after the reaction had proceeded for 10 hr or more showed that the dispersion was the same as that measured prior to reaction, independent of the manner of catalyst pretreatment. There was also no change in dispersion with continued catalyst use. Because of this, turnover frequencies were based on the dispersion of the freshly prepared catalyst.

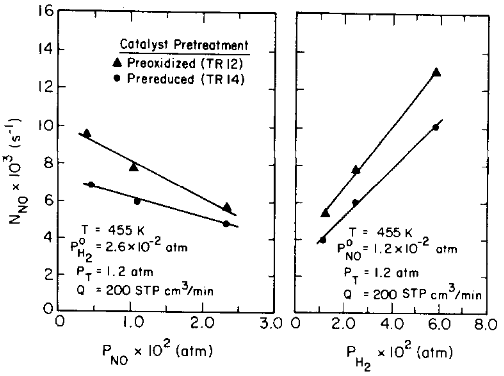

FIG. 1. Effects of pretreatment on the turnover frequency for NO reduction.

Table 1 and Fig. 1 illustrate the effects of pretreatment on the activity of the catalyst. Figure 1 shows that at 445 K, the turnover frequency for NO reduction, N_{NO}, is 30% higher for the preoxidized catalyst compared to the prereduced catalyst. The small change in the slopes of the lines shows that pretreatment also has an effect on the dependence of N_{NO} on the partial pressures of NO and H_2. The influence of pretreatment on the rates of formation of N_2O, N_2, and NH_3 are presented in Table 1. Pretreatment has little effect on the rate of NH_3 formation at 445 K, and thus, the higher rates of NO reduction observed over the preoxidized catalyst are due to increase in the rates of N_2 and N_2O formation. Since the rate of N_2 formation is influenced much more strongly than the rate of N_2O formation, the N_2 selectivity for the preoxidized catalyst is 60% higher than that for the prereduced catalyst.

The effects of pretreatment were also investigated at reaction temperatures above and below 445 K. For this part of the work, prereduction was carried out at 573 K, as

TABLE 1

Effects of H_2 and NO Partial Pressure on the Rate of NO Reduction over Prereduced and Preoxidized Rh[a]

Pretreatment	$P^0_i \times 10^2$ (atm)		$P_i \times 10^2$ (atm)		X_{NO} (%)	$N_i \times 10^3$ (s^{-1})[b]			
	H_2	NO	H_2	NO		NO	N_2O(×2)	N_2(×2)	NH_3
Red.	2.6	0.6	2.49	0.47	23	7.0	4.3	1.10	1.9
Oxid.			2.44	0.41	31	9.8	5.1	2.5	2.3
Red.	1.2	0.6	1.13	0.52	14	4.3	2.9	0.7	1.1
Oxid.			1.11	0.49	20	6.0	3.5	1.7	1.1
Red.	1.2	1.2	1.15	1.13	6.3	4.0	2.5	0.7	0.9
Oxid.			1.23	1.10	8.6	5.4	3.1	1.4	0.9
Red.	2.6	1.2	2.54	1.09	9.6	6.1	3.8	0.8	1.4
Oxid.			2.51	1.05	12	8.0	4.4	1.8	1.3
Red.	6.0	1.2	5.81	1.01	16	10.3	6.1	1.3	2.9
Oxid.			5.76	0.95	21	13.3	6.7	2.8	3.1
Red.	6.0	2.4	5.90	2.31	6.4	8.4	5.2	1.2	1.9
Oxid.			5.88	2.24	7.6	9.8	5.8	2.3	1.7
Red.	2.6	2.4	2.57	2.33	3.8	4.9	3.0	0.9	1.0
Oxid.			2.56	2.32	4.5	5.7	3.4	1.6	1.0
Red.	12.0	2.4	11.8	2.16	10	13.0	8.0	1.8	3.4
Oxid.			11.8	2.12	12	14.9	8.4	3.1	3.4

[a] T = 445 K; P_T = 1.2 atm; and Q = 200 (STP) cm^3/min.

[b] Based on D_{Rh} = 0.38.

well as at 523 K. As seen in Fig. 2, the activity of the preoxidized catalyst is consistently higher, by an average of about 50%, than the activity of the prereduced catalyst. The influence of pretreatment on the turnover frequencies for the formation of N_2O, N_2, and NH_3 are given in Table 2. For temperatures below 465 K, where very high NO conversions are achieved, the data in Table 2 show that the rates of formation of all three nitrogen-containing products are highest over the preoxidized catalyst and lowest over the catalyst prereduced at 573 K.

The dependence of product selectivity on reaction temperature is illustrated in Fig. 3 for the preoxidized catalyst, and in Fig. 4 for the catalyst prereduced at 573 K. Both figures show that the distribution of reaction products is a strong function of temperature, particularly for temperatures above which the conversion of NO exceeds 50%. Independent of pretreatment, the selectivity of N_2O increases with increasing temperature up to about 463 K and thereafter rapidly decreases to zero. The selectivity to NH_3 follows a pattern which is generally opposite to that of N_2O, decreasing with

TABLE 2

Effects of Temperature on the Rate of NO Reduction over Prereduced and Preoxidized Rh[a]

Pretreatment	T (K)	X_{NO} (%)	$N_i \times 10^3$ (s^{-1})[b]			
			NO	$N_2O(\times 2)$	$N_2(\times 2)$	NH_3
Oxid.	424	6.3	4.09	1.34	0.80	1.80
Red. (523 K)		3.5	2.25	1.09	0.42	1.00
Red. (573 K)		3.2	2.03	1.06	0.50	0.54
Oxid.	435	8.9	5.74	2.50	1.50	1.80
Red. (523 K)		7.2	4.63	2.30	0.86	1.40
Red. (573 K)		5.7	3.65	2.20	0.59	0.77
Oxid.	445	13.0	8.90	4.50	2.40	2.00
Red. (523 K)		12.0	8.00	4.40	1.60	2.10
Red. (573 K)		10.0	6.40	4.20	1.00	1.30
Oxid.	456	27.0	17.40	9.30	5.00	3.30
Red. (523 K)		23.0	14.30	8.20	2.80	2.30
Red. (573 K)		19.0	11.90	8.10	2.00	2.30
Oxid.	465	48.0	30.80	14.50	9.80	6.20
Red. (523 K)		40.0	25.50	13.40	5.50	6.30
Red. (573 K)		33.0	21.10	13.90	3.40	4.40
Oxid.	472	90.0	59.00	1.50	26.00	31.00
Red. (523 K)		65.0	41.00	17.00	11.00	13.00
Red. (573 K)		51.0	32.00	18.00	6.10	9.40
Oxid.	479	95.0	61.00	0.00	27.00	34.00
Red. (523 K)		91.0	58.00	0.90	23.00	33.00
Red. (573 K)		78.0	50.00	13.00	17.00	20.00
Oxid.	484	97.0	62.00	0.00	25.00	38.00
Red. (573 K)		89.0	57.00	1.30	23.00	32.00

[a] $P^0_{H2} = 2.6 \times 10^{-2}$ atm; $P^0_{NO} = 1.2 \times 10^{-2}$ atm; $P_T = 1.2$ atm, and $Q = 200$ (STP) cm^3/min.

[b] Based on $D_{Rh} = 0.38$.

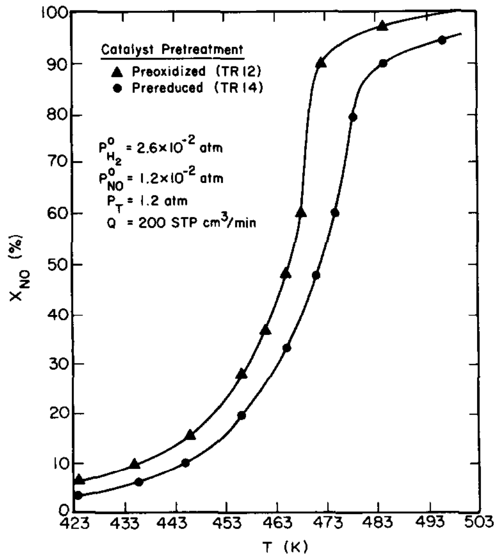

FIG. 2. Effect of pretreatment on NO conversion as a function of temperature.

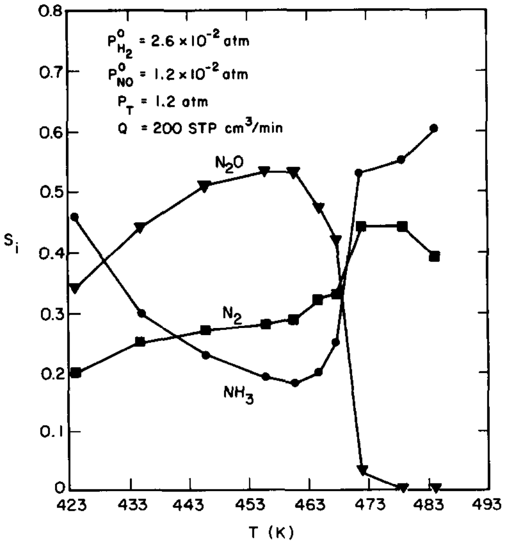

FIG. 3. Effect of temperature on the selectivities to N_2O, N_2, and NH_3 observed over a preoxidized catalyst.

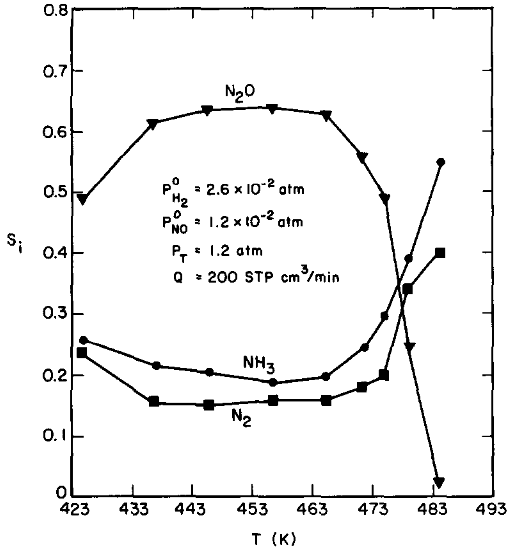

FIG. 4. Effects of temperature on the selectivities to N_2O, N_2, and NH_3 observed over a prereduced catalyst.

increasing temperature and then rapidly increasing for temperatures above 463 K. The response of the N_2 selectivity to increasing temperature is seen to depend on the nature of the pretreatment. For the preoxidized catalyst, the N_2 selectivity increases gradually with increasing temperature up to 463 K. Above this temperature the N_2 selectivity increases more rapidly and passes through a maximum. When the catalyst is prereduced, the N_2 selectivity decreases and passes through a very broad minimum for temperatures between 423 and 473 K. Above 473 K, the N_2 selectivity increases rapidly. Comparison of Figs. 3 and 4 shows that at a given temperature, pretreatment can strongly influence the distribution of nitrogen products. It is also evident that by contrast to prereduction, preoxidation causes an increase in the N_2 selectivity for temperatures below 483 K and an increase in the NH_3 selectivity for temperatures below 443 K. The selectivity data obtained when the catalyst was prereduced at 523 K are intermediate between those shown in Figs. 3 and 4. These results indicate that the selectivity of Rh changes in a systematic fashion as the catalyst is reduced to a greater degree.

The dependence of the rate of NO reduction, and the rates of N_2O, N_2, and NH_3 formation, on the partial pressures of NO and H_2 were determined from rate data obtained at 445 K. The turnover frequency for each species, N_i, were fit to a power law expression of the form

$$N_i = k_i P_{H_2}^{m_i} P_{NO}^{n_i},$$

where $i = 1, 2, 3$, and 4 correspond to NO, N_2O, N_2, and NH_3, respectively; k_i is the rate coefficient for species i; and m_i and n_i are the exponents on the partial pressures of H_2 and NO, respectively. A nonlinear regression technique was used to determine the parameter values which are listed in Table 3. The quality of the agreement between the predicted and observed rates for NO reduction and for N_2O and N_2 formation is quite good, with deviations ranging between 2 and 5%. The agreement between

TABLE 3

Power Law Parameters for NO Reduction by H_2

$N_i = k_i P_{H_2}^{m_i} P_{NO}^{n_i}$

	NO			N_2O			N_2			NH_3		
Pretreatment	$k_1 \times 10^3$	m_1	n_1	$k_2 \times 10^3$	m_2	n_2	$k_3 \times 10^3$	m_3	n_3	$k_4 \times 10^3$	m_4	n_4
Red.	20.1	0.59	−0.22	6.9	0.59	−0.19	1.1	0.40	−0.14	3.8	0.71	−0.37
Oxid.	22.0	0.58	−0.24	7.7	0.54	−0.16	2.0	0.46	−0.21	3.1	0.82	−0.50

Note. $[k_i] = \text{atm}^{-(m_i+n_i)}\ s^{-1}$.

the predicted and observed rates of NH_3 formation are somewhat poorer, ranging between 5 and 9%. All species exhibit a positive-order dependence on H_2 and an inverse-order dependence on NO. While some differences in the values of m_i and n_i for the preoxidized and prereduced catalyst can be seen, these variations are not very large, suggesting that the kinetics are essentially independent of the mode of pretreatment. It is also noted that the absolute values of m_4 and n_4, associated with the formation of NH_3, are significantly higher than the absolute values of m_i and n_i for all the other species, and exhibit a somewhat stronger dependence on the manner of catalyst pretreatment.

Apparent activation energies for NO reduction, obtained from plots of ln k_1 versus T^{-1}, are given in Table 4. Two values were obtained for each mode of pretreatment. For temperatures below 435 K, E_a is between 13 and 19 kcal/mol, and above 435 K, E_a is between 22 and 23 kcal/mol. No clear interpretation can be given for the change in the value of the activation energy with temperature. It is interesting to note, though, that a similar pattern was observed during studies of NO reduction by CO over the same catalyst (*7*).

To determine whether N_2O and NH_3, once formed, undergo further reaction, an experiment was performed in which the space velocity of the reactants was varied while maintaining the feed composition constant. A temperature of 435 K was used for this experiment in order to limit the NO conversion to 10% or less. The results, presented in Fig. 5, show that the product selectivities change very little with space time, indicating that at low to moderate temperatures (<463 K), N_2O and NH_3 do not participate in secondary reactions.

TABLE 4

Apparent Activation Energies for NO Reduction

Pretreatment	Temp. range (K)	E_a (kcal/mol)
Oxid.	414–435	13.0
Oxid.	435–472	23.3
Red.	414–436	19.0
Red.	436–479	21.7

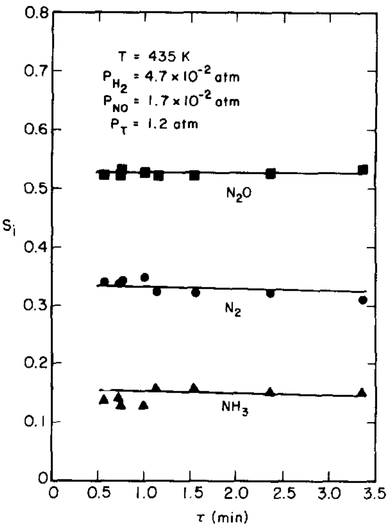

FIG. 5. Effect of space time on the turnover frequencies for NO reduction and for N_2O, N_2, and NH_3 formation.

Additional insight into the possible role of secondary reactions was gained by studying the reactions listed in Table 5. The results for reactions 1 and 2 indicate that N_2O and NH_3 decomposition does not occur, even at temperatures well in excess of those used in the studies of NO reduction by H_2. The reduction of N_2O by either H_2 or NH_3 can take place very readily in the absence of NO as demonstrated by the data presented for reactions 3 and 4. The fact that N_2O, formed during NO reduction, does not appear to participate in secondary reactions below 463 K suggests that when NO is present in the gas phase, the adsorption of NO occurs in preference to the adsorption of N_2O, and hence that N_2O reduction is suppressed. It is very likely, though, that above 463 K, where the conversion of NO rises very rapidly (see Figs. 2–4), the partial pressure of NO becomes small enough for N_2O to compete effectively for

TABLE 5

Summary of Observations Concerning Secondary Reactions[a]

Reaction	T (K)	$P_A^0 \times 10^2$ (atm)[b]	$P_B^0 \times 10^2$ (atm)[c]	X_A (%)
(1) $2N_2O \rightarrow 2N_2 + O_2$	523	0.62	—	<0.5
(2) $2NH_3 \rightarrow N_2 + 3H_2$	523	0.96	—	<0.1
(3) $N_2O + H_2 \rightarrow N_2 + H_2O$	473	0.54	16.80	95.0
(4) $3N_2O + 2NH_3 \rightarrow 4N_2 + 3H_2O$	473	0.50	0.48	80.0
(5a) $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$	523	0.84	2.00	94.0[d]
(5b) $8NO + 2NH_3 \rightarrow 5N_2O + 3H_2O$				

[a] $P_T = 1.2$ atm and $Q = 150$–200 (STP) cm^3/min.

[b] A is the first reaction partner.

[c] B is the second reaction partner.

[d] $S_{N_2O} = 0.60$ and $S_{N_2} = 0.40$.

adsorption sites. Under such circumstances, N_2O can undergo further reduction to N_2. This interpretation would explain the sudden decrease in N_2O selectivity, and rise in N_2 selectivity, seen in Figs. 3 and 4. The data in Table 5 also indicate that Rh is an effective catalyst for NO reduction by NH_3. The extent to which this reaction takes place during the reduction of NO by H_2 is unclear. The data in Fig. 5 suggest that below 463 K, NH_3 does not participate in NO reduction. The sudden rise in NH_3 selectivity at higher temperatures, observed in Figs. 3 and 4, would suggest that here too NH_3 does not react further, once formed.

Infrared Observations

The effects of pretreatment conditions on the infrared spectra observed during steady-state reduction of NO by H_2 are shown in Fig. 6. All of the bands seen in these spectra are due to vibrations of the N–O bond in adsorbed NO, and can be assigned to specific structures by analogy with the spectra of Rh-nitrosyl complexes (*12–16*). The bands in the region between 1630 and 1680 cm^{-1} are characteristic of Rh–NO$^{\delta-}$ species, and the bands in the region between 1750 and 1850 cm^{-1} are characteristic of Rh–NO species. These assignments are consistent with previous infrared studies of NO adsorption and reduction on supported Rh (*7, 9, 17, 18*). It is significant to note that no bands were observed in the vicinity of 1910 cm^{-1}, where features characteristic of Rh–NO$^{\delta+}$ have been reported (*9, 17, 18*).

The positions of the bands for Rh–NO$^{\delta-}$

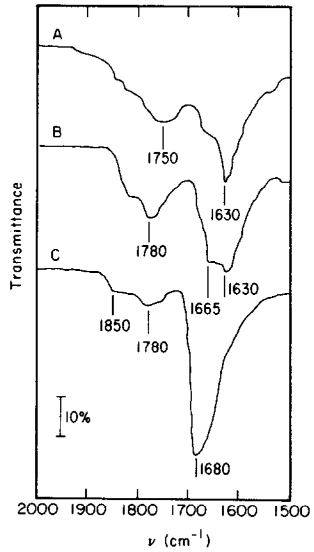

FIG. 6. Effects of pretreatment on the infrared spectrum observed under reaction conditions: (A) catalyst pretreatment—reduction at 603 K; reaction conditions—$T = 414$ K, $P_{H_2} = 5.8 \times 10^{-2}$ atm, $P_{NO} = 1.2 \times 10^{-2}$ atm; (B) catalyst pretreatment—reduction at 523 K; reaction conditions—$T = 443$ K, $P_{H_2} = 2.4 \times 10^{-2}$ atm; $P_{NO} = 1.1 \times 10^{-2}$ atm; (C) catalyst pretreatment oxidation at 423 K; reaction conditions—$T = 443$ K, $P_{H_2} = 2.4 \times 10^{-2}$ atm, $P_{NO} = 1.1 \times 10^{-2}$ atm.

and Rh–NO reflect the manner in which the catalyst is presented. When the catalyst is preoxidized, the band for Rh–NO$^{\delta-}$ is very intense and centered near 1680 cm^{-1}. Prereduction of the catalyst reduces the intensity of this band and shifts it to lower frequencies. For a reduction temperature of 603 K, two distinct bands characteristic of Rh–NO$^{\delta-}$ can be seen in Spectrum A of Fig. 6—a more intense band at 1630 cm^{-1} and a weaker one at about 1665 cm^{-1}. The latter feature is more pronounced when the reduction temperature is decreased to 523 K. In contrast to the behavior observed for the Rh–NO$^{\delta-}$ bands, the bands characteristic of Rh–NO are weak following preoxidation of the catalyst and are more intense when the catalyst is prereduced. Of the two bands seen in the region between 1750 to 1850 cm^{-1}, the one observed at 1740 to 1800 cm^{-1} appears to be more strongly affected by the mode of catalyst pretreatment.

Figure 7 illustrates the effects of reaction temperature on the intensities and positions of the bands for adsorbed NO. As the temperature increases from 424 to 468 K, little change is noted in any of the bands. Increasing the temperature to 472 K produces a noticeable reduction in the intensity of the Rh–NO$^{\delta-}$ band and shifts its position to 1660 cm^{-1}. At the same time, the bands for Rh–NO are almost totally eliminated. Further increases in the temperature result in additional loss of intensity from the Rh–NO$^{\delta-}$ band and shifts in its position to lower frequencies.

The influence of H_2 and NO partial pressures on the infrared spectrum of adsorbed NO was investigated at a reaction temperature of 445 K. For these experiments the catalyst was prereduced at 523 K. All of the spectra recorded for H_2 partial pressures between 1.1×10^{-2} and 1.2×10^{-1} atm, and NO partial pressures between 4.0×10^{-3} and 2.3×10^{-2} atm, were essentially identical to Spectrum B in Fig. 6, suggesting that over the specified range of conditions, the coverage by adsorbed NO remains very close to unity.

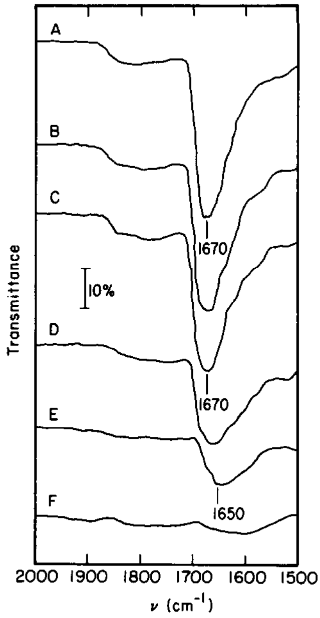

FIG. 7. Effect of temperature on the infrared spectra observed during NO reduction by H_2: $P^0_{H_2} = 2.6 \times 10^{-2}$ atm; (A) $T = 424$ K, $X_{NO} = 6\%$; (B) $T = 445$ K, $X_{NO} = 14\%$; (C) $T = 468$ K, $X_{NO} = 59\%$, (D) $T = 472$ K, $X_{NO} = 90\%$; (E) $T = 479$ K, $X_{NO} = 95\%$; (F) $T = 486$ K, $X_{NO} = 97\%$.

DISCUSSION

The results of the present study indicate that for NO conversions below about 50%, the reduction of NO by H_2 leads to the parallel formation of N_2O, N_2, and NH_3. Under these circumstances, the kinetics for NO reduction, and the kinetics for the formation of nitrogen-containing products, are positive order in H_2 partial pressure and negative order in NO partial pressure. The magnitude of the individual values of m_i and n_i reported in Table 3 can be rationalized in terms of a modified version of the reaction sequence proposed by Savatsky and Bell (*9*):

1. $NO + S \rightleftarrows NO_a$
2. $H_2 + 2S \rightleftarrows 2H_a$
3. $NO_a + H_a \rightarrow N_a + OH_a$
4. $NO_a + N_a \rightarrow N_2O + 2S$
5. $NO_a + N_a \rightarrow N_2 + O_a + S$
6. $O_a + H_a \rightarrow OH_a + S$
7. $OH_a + H_a \rightarrow H_2O + 2S$

8. $N_a + H_a \rightarrow NH_a + S$
9. $NH_a + H_a \rightarrow NH_{2_a} + S$
10. $NH_{2_a} + H_a \rightarrow NH_3 + 2S$

Reaction 1 represents the reversible adsorption of NO. The infrared spectra presented in Figs. 6 and 7, and those reported earlier by Savatsky and Bell (*9*), clearly demonstrate that at temperatures below 465 K the surface of silica-supported Rh is fully covered by associatively adsorbed NO. Isotopic tracer studies carried out by Savatsky and Bell (*9*) have demonstrated that the exchange between gas-phase and adsorbed NO is very rapid compared to the rate of NO reduction, and hence suggest that reaction 1 can be regarded as an equilibrium step. The equilibrium assumption is further supported by calculations of the rates of NO adsorption and desorption using the rate coefficients for these processes recently reported by Chin and Bell (*19*), for a Rh/SiO_2 catalyst. At 445 K, and for an NO partial pressure of 1.2×10^{-2} atom, the rates of adsorption and desorption are equal and exceed the measured rate of NO reduction by a factor of 10^4 to 10^6.

The reversible adsorption of H_2 is represented by reaction 2. A number of investigators have studied this process on both supported and unsupported Rh (*20–26*). Their work shows that at the temperatures used in this study, H_2 adsorption is dissociative and fully reversible. Calculations of the rates of H_2 adsorption and desorption performed using the rate coefficients for these processes determined by Chin and Bell (*26*) indicate that at 445 K, and in the presence of 2.6×10^{-2} atm of H_2, the rates of H_2 adsorption and desorption exceed the rate of H_2 consumption in the reduction of NO by a factor of 10^4 to 10^6. In view of this, it is assumed that reaction 2 is at equilibrium.

Temperature-programmed desorption and decomposition studies of NO on Rh (*19, 27–29*) have shown that adsorbed NO will dissociate at elevated temperatures. In the work of Hecker and Bell (*7*) on NO reduction by CO over silica-supported Rh, and in the work of Savatsky and Bell (*9*) on NO reduction by H_2 over the same catalyst, it was assumed that NO dissociation is the rate-limiting step. Moreover, in both cases, it was assumed that the reducing agent does not facilitate the dissociation process. In the present work we have postulated that NO dissociation proceeds with the assistance of an adsorbed H atom via reaction 3. This modification of the mechanism proposed by Savatsky and Bell (*9*) is required in order to obtain the observed partial pressure dependence on H_2.

The proposed mechanism indicates that N_2O and N_2 are both formed via the reaction of adsorbed NO with adsorbed N atoms. The occurrence of such Langmuir–Hinshelwood processes is supported by recent studies of the temperature-programmed decomposition of NO (*19, 27–29*). These investigations indicate that while N_2 can also form by the recombination of N atoms, the activation energy for this process is higher than that for reaction 5 (*19*). It therefore seems reasonable to assume that during NO reduction, N_2 will form via the lower energy pathway. The use of reaction 5 to describe the formation of N_2 differs from the mechanism proposed by Savatsky and Bell (*9*), in which it was assumed that N_2 is formed by recombination of N atoms.

H_2O and NH_3 are assumed to be formed by the stepwise hydrogenation of O and N atoms, respectively. The formation of H_2O by steps 6 and 7 is supported by the detailed studies reported by Thiele *et al.* (*25*), on unsupported Rh. While there is no direct evidence to indicate that steps 8 through 10 provide an accurate description of the kinetics of NH_3 formation, Savatsky and Bell (*9*) have demonstrated that this sequence of steps properly describes the formation of NH_3 during the reduction of NO by H_2 over a Rh/SiO_2 catalyst, under transient response conditions.

The turnover frequency for NO reduction, N_{NO}, can be expressed as

$$N_{NO} = \alpha k_3 \theta_{NO} \theta_H, \tag{1}$$

where k_3 is the rate coefficient for reaction 3, and θ_{NO} and θ_H are the fractional surface coverages for adsorbed NO and H_2, respectively. The coefficient α can vary between 1 and 3 as the selectivity to NH_3 varies from 1 to zero. For the conditions of this study, α lies between 2.4 and 2.6 and does not change strongly with temperature or reactant partial pressure. If it is assumed that the coverages by adsorbed NO and H_2 are described by Langmuir isotherms, then

$$\theta_{NO} = K_1 P_{NO} \theta_v \tag{2}$$

and

$$\theta_H = K_2^{0.5} P_{H_2}^{0.5} \theta_v, \tag{3}$$

where P_{NO} and P_{H_2} are the partial pressures of NO and H_2, and K_1 and K_2 are the equilibrium constants associated with reactions 1 and 2. Substitution of Eqs. (2) and (3) into Eq. (1) and imposition of a steady-state balance on Rh surface sites yields the expression for N_{NO}:

$$N_{NO} = \frac{\alpha k_3 K_1 K_2^{0.5} P_{H_2}^{0.5} P_{NO}}{(1 + K_1 P_{NO} + K_2^{0.5} P_{H_2}^{0.5})^2}. \tag{4}$$

Implicit in the formulation of Eq. (4) is the assumption that the surface coverage by species other than NO and H atoms is small, and hence that the contributions to the denominator of Eq. (4) arising from these species can be neglected.

The infrared spectra obtained in the course of this study indicate that for the range of NO and H_2 partial pressure considered, the coverage by adsorbed NO is independent of reactant partial pressures. Under such circumstances θ_{NO} is assumed to be close to unity and the turnover frequency for NO reduction can be approximated by

$$N_{NO} = \alpha \frac{k_3 K_2^{0.5} P_{H_2}^{0.5}}{K_1 P_{NO}}. \tag{5}$$

The partial pressure dependencies appearing in Eq. 5 can be compared with those determined from the observed rates of NO reduction, given in Table 3. Good agreement is seen for the partial pressure dependence on H_2. However, the inverse first-order dependence on NO partial pressure predicted by Eq. (5) is considerably stronger than that observed experimentally, which is approximately inverse 0.2 order. A similar level of disparity between the predicted and observed dependence on NO partial pressure has recently been reported by Hecker and Bell (*7*) in a study of NO reduction by CO over the same silica-supported Rh catalyst used in this study. The authors suggested that the problem was due to the assumption that NO adsorption obeys a Langmuir isotherm. It was shown that by using an isotherm based on the observed variation in the infrared band intensity for adsorbed NO, an expression for N_{NO} could be derived which was in good agreement with that obtained from experimental data. In view of this, it seems likely that the overly strong inverse dependence on NO partial pressure predicted by Eq. (5) is due to the assumption of a Langmuir isotherm for NO.

Based on the proposed mechanism, formation of N_2O, N_2, and NH_3 can be written as

$$N_{N_2O} = k_4 \theta_{NO} \theta_N \tag{6}$$

$$N_{N_2} = k_5 \theta_{NO} \theta_N \tag{7}$$

$$N_{NH_3} = k_8 \theta_N \theta_H. \tag{8}$$

If it is assumed that $\theta_{NO} \propto 1.0$, as would be indicated by our infrared observations, the steady-state coverage by N atoms, θ_N, is given by

$$\theta_N = \frac{k_3 \theta_H}{(k_4 + k_5) + k_8 \theta_H}. \tag{9}$$

Substitution of Eq. (3) into Eq. (9) and further substitution of the resulting equation into Eqs. (6) through (8) yields

$$N_{N_2O} = \frac{k_3 k_4 K_2^{0.5} P_{H_2}^{0.5}}{K_1 P_{NO}[(k_4 + k_5) + k_8 K_2^{0.5} K_1^{-1} P_{H_2}^{0.5} P_{NO}^{-1}]} \tag{10}$$

$$N_{N_2} = \frac{k_3 k_5 K_2^{0.5} P_{H_2}^{0.5}}{K_1 P_{NO}[(k_4 + k_5) + k_8 K_2^{0.5} K_1^{-1} P_{H_2}^{0.5} P_{NO}^{-1}]} \tag{11}$$

$$N_{NH_3} = \frac{k_3 k_8 K_2 P_{H_2}}{K_1^2 P_{NO}^2[(k_4 + k_5) + k_8 K_2^{0.5} K_1^{-1} P_{H_2}^{0.5} P_{NO}^{-1}]}. \tag{12}$$

Comparison of Eqs. (10) through (12) with the empirically obtained rate expressions given in Table 3 is facilitated by recognizing that at 445 K, the selectivity to NH_3 is only 15 to 20%. Because of this $(N_{N_2O} + N_{N_2}) > N_{NH_3}$, and Eqs. (10) through (12) can be approximated roughly by

$$N_{N_2O} = \frac{k_3 k_4 K_2^{0.5} P_{H_2}^{0.5}}{(k_4 + k_5) K_1 P_{NO}} \tag{13}$$

$$N_{N_2} = \frac{k_3 k_5 K_2^{0.5} P_{H_2}^{0.5}}{(k_4 + k_5) K_1 P_{NO}} \tag{14}$$

$$N_{NH_3} = \frac{k_3 k_5 K_2 P_{H_2}}{(k_4 + k_5) K_1^2 P_{NO}^2}. \tag{15}$$

The half-order partial pressure dependence on H_2 appearing in Eqs. (13) and (14) is in good agreement with that found empirically (see Table 3). Equation (15) predicts a first-order dependence on H_2 for the rate of NH_3 formation. The agreement with the data in this case is not as close, since Table 3 shows that m_4 is between 0.7 and 0.8. Nevertheless, the proposed mechanism properly predicts that the H_2 dependence of NH_3 formation should be stronger than that for N_2 and N_2O formation. As with the expression for N_{NO} (Eq. 5), the NO partial pressure dependencies predicted by Eqs. (13) through (14) are significantly higher than those found empirically. Here again, the most likely reason for the discrepancy is the assumption that NO adsorption follows a Langmuir isotherm. It is noted, though, that consistent with experimental observation the order in NO for NH_3 formation is twice that for N_2O or N_2 formation.

The rate expressions given by Eqs. (13) through (15), as well as those found empirically, clearly indicate that the relative rates of N_2O and N_2 formation are unaffected by reactant partial pressures. On the other hand, the rate of NH_3 formation relative to N_2 and N_2O formation is a function of the reactant partial pressures, with high NH_3 selectivity being favored by high H_2 and low NO partial pressures. These patterns are a direct reflection of the reaction pathways leading to each product.

Catalyst pretreatment was found to affect both the activity and selectivity of the catalyst. The rate of NO reduction was 30 to 50% higher following preoxidation of the catalyst with NO than it was following prereduction with H_2. Most of this increase came from a 100 to 150% increase in the rate of N_2 formation. The infrared spectra taken under reaction conditions also exhibited differences reflecting the mode of catalyst pretreatment. The band corresponding to the Rh–$NO^{\delta-}$ species was more intense and the band corresponding to the Rh–NO species was less intense following preoxidation as compared to prereduction. It was also observed that the position of both bands shifted to higher wavenumbers following preoxidation as compared to prereduction.

It is of interest to compare the effects of catalyst pretreatment on the reduction of NO by H_2 with those reported earlier by Hecker and Bell (*7*) for NO reduction by CO. Both studies were carried out using the same Rh/SiO_2 catalyst. As in the present case, Hecker and Bell (*7*) observed that using CO as the reducing agent, preoxidation of the catalyst with NO at 423 K increased the rate of NO reduction by 50% relative to that measured when the catalyst was prereduced with H_2 at 523 K. However, the nature of the pretreatment had little effect on product selectivity and no significant effect on either the positions or intensities of the NO bands. In both cases the major feature associated with NO was a strong band at 1685 cm^{-1} due to Rh–$NO^{\delta-}$ and a weaker band at 1750 to 1850 cm^{-1}, associated with Rh–NO. The position and intensity of both features are nearly equivalent to those seen in Fig. 6 for NO reduction by H_2 over the preoxidized catalyst.

The effects of pretreatment on the catalyst activity and selectivity for NO reduction have also been reported by Taylor *et al.* (*30*). They found that preoxidation enhanced the activity of Pt/Al_2O_3 and Pd/Al_2O_3, but did not alter the product selectivity. By contrast, preoxidation did not alter the activity of Ru/Al_2O_3 but did increase its selectivity for the formation of N_2.

The influence of pretreatment on the activity and selectivity of Rh/SiO_2 for NO reduction reported here cannot be readily explained. Since the Rh dispersion is unaffected by the manner of catalyst pretreatment, the higher NO reduction activity occurring when the catalyst is preoxidized cannot be ascribed simply to an increase in Rh dispersion. It seems more likely that the differences in activity and selectivity between the prereduced and preoxidized forms of the catalyst are due to differences in the composition of the Rh particles under steady-state reaction conditions. One possibility is that the properties of the preoxidized catalyst are modified by the presence of subsurface oxygen. Studies by a number of authors (*25, 27, 31*) have shown that oxygen can exist on Rh in multiple forms, and that the most strongly bound oxygen resides below the metal surface. Moreover, Gorodetskii *et al.* (*31*) noted that such subsurface oxygen is not removed by reduction in H_2 unless the temperature is raised to between 600 and 900 K. The presence of subsurface oxygen would be expected to modify the surface structure of Rh crystallites, as well as the electronic properties of the exposed Rh atoms. One or both of the modifications could be responsible for the observed changes in the activity and selectivity of Rh upon preoxidation. Since virtually nothing is known about the manner in which subsurface oxygen might influence the adsorption and dissociation of NO or the adsorption of H_2, further speculation is unwarranted at this time.

CONCLUSIONS

The activity and selectivity of silica-supported Rh for NO reduction by H_2 are sensitive to the manner of catalyst pretreatment. Preoxidation in NO increases the specific activity for NO reduction by about 50% over that observed when the catalyst is prereduced. The effect of pretreatment on product selectivity is complex and depends on the reaction temperature. In general, though, it is observed that preoxidation causes a significant increase in the selectivity to N_2 and a corresponding decrease in N_2O selectivity, relative to the selectivities for a prereduced catalyst. A significant increase in selectivity to NH_3 is seen at low temperatures.

The kinetics of NO reduction, and N_2O, N_2, and NH_3 formation, were determined for conditions where the NO conversion is less than 50%. The rates for all species exhibit a positive order dependence on H_2 partial pressure and a negative-order dependence on NO partial pressure. Neither the reaction orders, nor the activation energy for NO reduction is a strong function of the manner of catalyst pretreatment.

Infrared spectra of the catalyst taken under reaction conditions where the NO conversion is less than 50% indicate that the surface is saturated by adsorbed NO. The principal species observed is $Rh\text{–}NO^{\delta-}$, but small amounts of Rh–NO can also be seen. The concentrations of these species are not influenced by the partial pressures of NO or H_2 over the range of values examined.

A mechanism for the reduction of NO by H_2 is postulated in order to explain the observed reaction kinetics. NO and H_2 are both assumed to adsorb reversibly. The rate-limiting step is taken to be the dissociation NO, which is postulated to occur with the assistance of an attack on the oxygen end of the molecule by an adsorbed H atom. It is assumed that N_2O and N_2 are formed via parallel processes, both of which involve the reaction of adsorbed NO with an adsorbed N atom. NH_3 and H_2O are formed by the stepwise hydrogenation of N and O atoms. The rate expressions derived on the basis of this mechanism are qualitatively consistent with those obtained from experimental data. The greatest discrepancy is between the predicted and observed dependences on NO partial pressure. It is proposed that the excessively high inverse-order dependence predicted theoretically is due to the assumption that NO adsorption follows a Langmuir isotherm.

The dispersion of Rh is unaffected by catalyst prereduction or preoxidation. Consequently, the influence of catalyst pretreatment on the activity and selectivity of Rh cannot be ascribed to changes in Rh dispersion. It is suggested that preoxidation may lead to the introduction of a small amount of tightly bound oxygen below the Rh surface. These species could possibly alter the adsorption of NO and H_2 in a manner which favors the dissociation of adsorbed NO and the subsequent reactions of the dissociation products.

ACKNOWLEDGMENT

This work was supported by the NSF under Grant CPE-7826352.

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