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

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The kinetics of NO reduction by H_2–CO mixtures have been investigated over a Rh/SiO_2 catalyst. Nearly 90% of the reduction can be ascribed to H_2. The presence of CO retards the rate of NO reduction, presumably due to competitive adsorption with H_2. The formation of urea is a direct result of NO reduction by H_2 and CO. The catalyst activity is 50% higher when the catalyst is preoxidized rather than prereduced. N_2O, N_2, NH_3, and $(NH_2)_2CO$ are formed over the prereduced catalyst. NH_3 formation is largely suppressed when the catalyst is preoxidized and a product believed to be HNCO is formed instead of urea. *In situ* infrared spectra of the catalyst show that for NO conversions below 70%, the surface is dominated by adsorbed NO. At higher conversions, bands are also observed for adsorbed CO, but none for isocyanate species attached to Rh.

INTRODUCTION

Hydrogen and CO are believed to be the principal reducing agents responsible for the reduction of NO over Rh and other Group VIII metals present in the catalytic convertors used for automobiles. While there have been a few studies (*1–8*) on the reduction of NO over Rh by CO and H_2 alone, relatively little is known about the concurrent interaction of all three species. Kobylinski and Taylor (*3*) have found that for Rh/Al_2O_3, the reduction of NO by an equimolar feed mixture of H_2 and CO proceeds somewhat more rapidly than reduction by CO alone, but significantly more slowly than reduction by H_2 alone. At 755 K and 100% NO conversion, 80% of the NO reduced was attributable to reaction with H_2. Under these conditions 67% of the NO was converted to N_2 and 33% to NH_3.

Working with Rh sponge, Voorhoeve *et al.* (*9, 10*) reported that under certain conditions a solid product was formed from NO, H_2, and CO, in addition to the usually expected gaseous reduction products, N_2O, N_2, and NH_3. When collected at temperatures below 373 K, the solid analyzed as urea, $(NH_2)_2CO$, and when collected at temperatures above 373 K the product analyzed as ammonium cyanate, NH_4OCN. A maximum selectivity of 85% to solid product was obtained for reaction temperatures between 573 and 673 K. Similar results were observed with unsupported Pt, Ru, Os, and Cu-Ni (*9–11*). Attempts were also made to observe solid products over supported Pt (*9–11*). For conditions where Pt sponge produced a high yield of NH_4OCN, Pt/Al_2O_3 produced a low yield of NH_4OCN but a high yield of NH_3. The authors speculated that the failure to produce a high yield of solid product over the supported catalyst might be due to the migration of NCO groups from the metal onto the support, where they are bound very strongly.

This paper is the fourth in a series devoted to NO reduction over silica-supported Rh (*6–8*). The first two papers (*6, 7*) have discussed the kinetics of NO reduction by CO and infrared observation taken under reaction conditions. Similar studies of NO reduction by H_2 were described in the third paper (*8*). The present investigation was aimed at understanding the behavior of Rh when NO is reduced by a mixture of CO and H_2. The results reported here are

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TABLE 1

Range of Operating Conditions for which Rate Data were Collected

System	Pretreatment	T (K)	$P^0_{NO} \times 10^2$ (atm)	$P^0_{H_2} \times 10^2$ (atm)	$P^0_{CO} \times 10^2$ (atm)
$NO/H_2/CO$	Red.	445–503	0.4–2.7	0.5– 7.3	0.6–8.3
$NO/H_2/CO$	Oxid.	445–503	0.5–2.7	0.6– 7.6	0.6–8.3
NO/H_2	Red.	423–483	0.6–2.4	1.2–12.0	—
NO/H_2	Oxid.	423–483	0.6–2.4	1.2–12.0	—
NO/CO	Red.	465–524	0.1–3.6	—	1.2–9.6
NO/CO	Oxid.	465–524	0.9–3.6	—	1.2–9.6

compared and contrasted with those in which only a single reducing agent (i.e., H_2 or CO alone) was used. The formation of products containing H, N, C, and O atoms [viz. HNCO, NH_4OCN, and $(NH_2)_2CO$] is also described.

EXPERIMENTAL METHODS

The experimental apparatus and techniques used in this study are identical to those described in references (*6–8*). Reaction rates were measured using a small reactor with external recycle. Fresh reactants were continuously supplied to the recycle loop and products were withdrawn for analysis by gas chromatography (*12*). The design of the reactor is such that infrared spectra of adsorbed species could be taken under reaction conditions.

The catalyst, 4.6% Rh/SiO_2 (Cab-O-Sil HS-5), was used in the form of a pressed wafer weighing 0.123 g. The Rh dispersion of the reduced catalyst, determined by H_2 chemisorption, is 38%. Mixtures of NO, H_2, and CO diluted in He were supplied from a gas manifold. The procedures used to purify each of the gases are described in Refs. (*6, 8*).

Preceding each run, the catalyst was either reduced in H_2 or oxidized in NO. Reduction was typically done at 553–573 K in 100% H_2 for at least 24 hr. Oxidation was carried out for 1 to 2 hr at the temperature of the subsequent run, using a 2% NO mixture in helium. The pretreatment period was ended by purging the reactor loop with helium. Following pretreatment and prior to collecting rate data, the reaction of NO with the mixture of H_2 and CO was allowed to proceed for 15–20 hr. The catalyst activity and selectivity at the end of the break-in period were stable, and for a given pretreatment and set of reaction conditions could readily be reproduced. Measurements of the Rh dispersion after reaction showed no evidence of sintering. Consequently, the initial dispersion was used to determine turnover frequencies.

RESULTS

Rate Measurements

The results obtained in this study for the reduction of NO by mixtures of H_2 and CO bear many similarities to those reported earlier (*6, 8*) for the reduction of NO by H_2 and CO alone. Since the same Rh/SiO_2 catalyst and range of reaction conditions were used in each case (see Table 1), it is easy to compare the effects of reducing agent composition on the kinetics of NO reduction and the distribution of products formed.

Figure 1 illustrates the effects of temperature on NO conversion. It is evident that for the same inlet partial pressure of NO, the extent of NO reduction at a given temperature is much greater when the reducing agent is H_2 rather than CO. When CO and H_2 are present simultaneously, the extent of NO reduction lies between the values observed using either CO or H_2 alone. Estima-

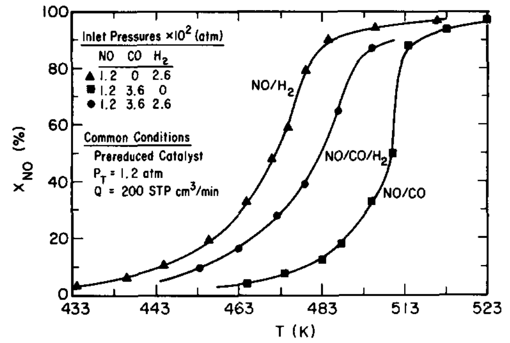

FIG. 1. Effects of temperature on NO conversion for reduction by H_2, CO, and a mixture of H_2 and CO.

tion of the fraction of NO reduced by each reducing agent reveals that 87% of the reduction is due to H_2. Thus, even though CO is present in excess of H_2, H_2 is consumed preferentially.

The manner of catalyst pretreatment affects both the activity and selectivity of Rh. As indicated in Table 2, preoxidation of the catalyst in NO increases the activity of the catalyst by about 50% relative to that observed when the catalyst is prereduced in H_2. The magnitude of this effect is comparable to that observed in the studies of NO reduction by H_2 and CO alone (*6*, *8*).

The selectivities for N_2O, N_2, and NH_3 observed over prereduced catalyst are comparable to those obtained when NO is reduced by H_2 alone. The primary difference is that in addition to these three products a fourth product is formed in the NO/H_2/CO system, which has an N/C ratio of about 2.0. Since this product did not appear on the chromatograms, it was assumed that it might be a solid. Efforts to collect this material from the recycle line were unsuccessful. It was possible, though, to obtain a sample in experiments performed with a quartz microreactor. Elemental analysis and infrared spectra of the solid clearly indicated that it was urea, $(NH_2)_2CO$.

Preoxidation of the catalyst in NO causes a significant increase in the selectivity to N_2 and a decrease in the selectivity to N_2O for both the NO/H_2/CO and the NO/H_2 systems. However, while the manner of catalyst pretreatment has little effect on the selectivity to NH_3 in the NO/H_2 system, the selectivity to NH_3 is strongly affected by pretreatment in the NO/H_2/CO system. As shown in Table 2, preoxidation causes the NH_3 selectivity to decrease to zero at the same time that the selectivity to the fourth product rises to the level of the NH_3 selectivity for the prereduced catalyst. Efforts to collect the unknown product for analysis were completely unsuccessful. By examination of the mass balance around the reactor, it could be determined, though, that the N/C ratio of the unknown product is close to 1.0. One possibility is that the product is isocyanic acid, HNCO, or its trimer, $(HNCO)_3$, which is a solid. This supposition is supported by the work of Voorhoeve *et al.* (*9*, *10*), which has shown that over unsupported Pd and Ir a primary product of

TABLE 2

Comparison of the Effects of Catalyst Pretreatment on Activity and Selectivity

Reaction system	Pretreatment	T (K)	$N_{NO} \times 10^3$[a] (s^{-1})	S_{N_2O}	S_{N_2}	S_{NH_3}	S_X[b]
NO/H_2/CO	Red.	453	6.5	0.51	0.17	0.19	0.12
NO/H_2/CO	Oxid.	453	9.8	0.40	0.18	0.0	0.42
NO/H_2	Red.	445	6.4	0.64	0.15	0.21	—
NO/H_2	Oxid.	445	8.9	0.50	0.27	0.23	—
NO/CO	Red.	488	10.5	0.83	0.17	—	—
NO/CO	Oxid.	488	17.2	0.79	0.21	—	—

[a] Reaction conditions: $P^0_{NO} = 1.2 \times 10^{-2}$ atm, $P^0_{CO} = 3.6 \times 10^{-2}$ atm, $P^0_{H_2} = 2.6 \times 10^{-2}$ atm.

[b] X is presumed to be $(NH_2)_2CO$ for prereduced catalyst. X is presumed to be HNCO for preoxidized catalyst.

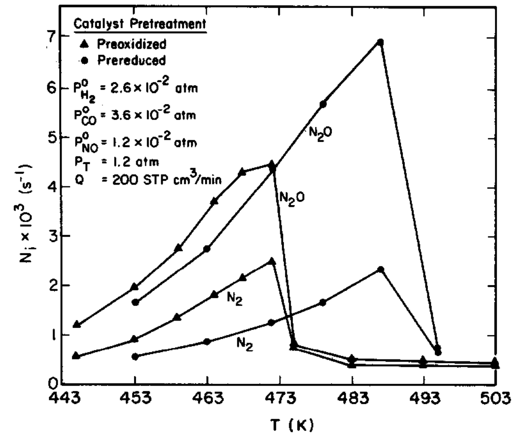

FIG. 2. Effects of catalyst pretreatment on the turnover frequencies for N_2O and N_2 formation as a function of temperature.

NO reduction by H_2/CO mixtures is HNCO.

Catalyst pretreatment also influences the effects of temperature on product distribution. This is shown in Figs. 2 and 3. For both modes of pretreatment, the rates of N_2O and N_2 rise with increasing temperature up to a maximum value and then rapidly decrease to very low values. The point of the maximum corresponds to an NO conversion of roughly 50–60%. Because preoxidation increases the catalyst activity, the temperature for the maximum rates of N_2O and N_2 formation is lower for the preoxidized than for the prereduced catalyst. The rate of NH_3 formation over the prereduced catalyst remains relatively constant at first, then decreases and subsequently increases. The temperature at which the rate of NH_3 formation begins to increase coincides with the attainment of an NO conversion of about 90%. Over the prereduced catalyst, the rate of $(NH_2)_2CO$ formation increases progressively with temperature. Above 487 K, the rate of $(NH_2)_2CO$ formation rises very rapidly and at NO conversions above 90% $(NH_2)_2CO$ is the dominant product. Figure 3 shows that over the preoxidized catalyst, the rate of NH_3 formation is zero until the temperature exceeds 483 K, at which point the rate of NH_3 formation rises rapidly with increasing temperature. Due to difficulties in measuring the low NO partial pressures prevailing at high NO conversions, estimates of the turnover frequency for the formation of the product believed to be HNCO could not be obtained.

The effects of reactant partial pressures on the rates of NO reduction and product formation were investigated at 472 K. Similar experiments were performed for both types of catalyst pretreatment. It was established that the turnover frequency for each species, N_i, is well described by a power-law rate expression of the form

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

where i = 1, 2, 3, 4, and 5 correspond to NO, N_2O, N_2, NH_3, and the solid product, respectively; k_i is the rate coefficient for species i; and l_i, m_i, and n_i are the exponents on the partial pressures of H_2, CO, and NO, respectively. A nonlinear regression technique was used to determine the parameter values, and these are listed in Table 3. The quality of agreement between predicted and observed values of N_i are reasonably good: ±1 to 3% for N_2O and N_2, ±2 to 6% for NO, and ±16% for NH_3. Table 3 shows that for the NO/H_2/CO system, the exponents on the reactant partial pressures are essentially the same regardless of whether the catalyst is prereduced or oxidized. As a result, the differences in N_i observed with changes in the manner of catalyst pretreatment are due almost totally to

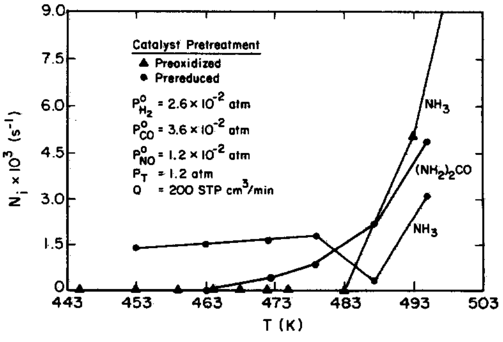

FIG. 3. Effects of catalyst pretreatment on the turnover frequency for NH_3 formation as a function of temperature.

TABLE 3

Power-Law Parameters for NO Reduction by H_2, CO, and Mixtures of H_2 and CO

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

System	T (°C)	Pretreatment	NO				N_2O			
			$k_i \times 10^3$ [a]	l_i	m_i	n_i	$k_i \times 10^3$ [a]	l_i	m_i	n_i
$NO/H_2/CO$	472	Red.	24	0.67	−0.15	−0.34	18	0.52	−0.14	−0.01
$NO/H_2/CO$	461	Oxid.	28	0.60	−0.08	−0.31	16	0.51	−0.22	0.09
NO/H_2	445	Red.	20	0.59	—	−0.22	6.9	0.59	—	−0.19
NO/H_2	445	Oxid.	22	0.58	—	−0.24	7.7	0.54	—	−0.16
NO/CO	483	Red.	4.3	—	0.08	−0.17	1.5	—	0.08	−0.21
NO/CO	483	Oxid.	6.0	—	0.08	−0.20	2.0	—	0.08	−0.23
$NO/H_2/CO$	472	Red.	5.8	0.46	−0.10	0.02	11	0.85	−0.36	−0.07
$NO/H_2/CO$	461	Oxid.	9.7	0.57	−0.17	0.06	1.3[b]	0.67[b]	0.18[b]	−1.15[b]
NO/H_2	445	Red.	1.1	0.40	—	−0.14	3.8	0.71	—	−0.37
NO/H_2	445	Oxid.	2.0	0.46	—	−0.21	3.1	0.82	—	−0.50
NO/CO	483	Red.	0.8	—	0.07	0.0	—	—	—	—
NO/CO	483	Oxid.	1.2	—	0.08	−0.06	—	—	—	—

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

[b] X is presumed to be HNCO.

the effects of pretreatment on the value of k_i.

The rate parameters reported earlier (*6*, *8*) for NO reduction by CO and H_2 alone are also listed in Table 3, for the sake of comparison with the parameter values determined for NO reduction by CO and H_2. For the $NO/H_2/CO$ system, the exponents on H_2 and NO partial pressures are comparable to those for NO reduction by H_2 alone. A similar fractional inverse-order dependence of NO partial pressure was also observed for NO reduction by CO. However, while the CO partial pressure dependence of the turnover frequency for NO reduction is weakly positive for the NO/CO system, it is weakly negative for the $NO/H_2/CO$ system. A similarity is observed in the relationship of the exponent values for N_2O and N_2 formation obtained for the $NO/H_2/CO$ system to those obtained for the NO/H_2 and NO/CO systems. The dependence of the rates of formation of these products on H_2 is essentially the same whether H_2 alone or a mixture of H_2 and CO is used as the reducing agent. As in the case of the turnover frequency for NO reduction, the dependencies of the turnover frequencies for N_2O and N_2 formation on CO partial pressure are weakly positive-order for the NO/CO system, but weakly negative-order for the $NO/H_2/CO$ system. The dependence of the turnover frequencies for N_2O and N_2 formation on NO partial pressure in the $NO/H_2/CO$ system are essentially zero order. For N_2O formation this stands in sharp contrast to what is observed for the NO/H_2 and NO/CO systems, where the NO partial pressure dependence is roughly −0.15 to −0.20. A comparable set of values is found for N_2 formation using H_2 as the reducing agent. However, for N_2 formation during NO reduction by CO, the NO dependence is again nearly zero order.

NH_3 is formed during the reduction of NO by CO and H_2 only when the catalyst is prereduced. The H_2 partial pressure dependence of the NH_3 turnover frequency is

TABLE 4

Comparison of Apparent Activation Energies Determined for NO Reduction by a H_2–CO Mixture with those determined for NO Reduction by H_2 and NO Reduction by CO

Species	System[a]	E_A (kcal/mol)
NO	$NO/H_2/CO$	23
NO	NO/H_2	22
NO	NO/CO	34
N_2O	$NO/H_2/CO$	22
N_2O	NO/H_2	25
N_2O	NO/CO	34
N_2	$NO/H_2/CO$	20
N_2	NO/H_2	25
N_2	NO/CO	34
NH_3	$NO/H_2/CO$	7
NH_3	NO/H_2	27

[a] The temperature ranges over which E_a was determined were: $NO/H_2/CO$—453–479 K; NO/H_2—436–479 K; NO/CO—478–498 K. In each case, the upper limit was chosen so that $X_{NO} \simeq 0.50$. All studies were carried out with a prereduced catalyst.

positive and nearly twice as large as that for NO reduction, or N_2O and N_2 formation. As in the case of N_2O and N_2, the turnover frequency for NH_3 exhibits an inverse dependence on CO partial pressure and is nearly independent of the NO partial pressure. The dependence on H_2 partial pressure for the $NO/H_2/CO$ and the NO/H_2 systems are nearly the same, but the inverse dependence on NO in the latter system is much stronger. The turnover frequency for the unknown product (i.e., the one presumed to be HNCO) formed during NO reduction by CO and H_2 over the preoxidized catalyst also exhibits a positive-order dependence on H_2. The dependence on CO is weakly positive-order, and the dependence on NO is roughly inverse first-order.

The apparent activation energies for NO reduction and the formation of N_2O, N_2, and NH_3 determined in this study are given in Table 4. For the sake of comparison, the activation energies reported earlier (*6, 8*) for NO reduction by H_2 and CO alone are also presented. It is apparent that the activation energies for NO reduction, and for N_2O and N_2 formation, fall within the range of 20 to 25 kcal/mol, regardless of whether H_2 or a mixture of H_2 and CO is used as the reducing agent. When CO is the reducing agent the activation energies for all three species are significantly larger, 34 kcal/mol. The activation energy for NH_3 formation is significantly lower when NO is reduced by H_2 and CO than when H_2 is present alone.

Infrared Observations

Infrared spectra taken during NO reduction over prereduced and preoxidized Rh are shown in Fig. 4. These spectra resemble very closely the spectra observed during NO reduction by H_2 and CO alone, reported earlier (*6–8*). The bands at 2300 and 1465 cm^{-1} are due to isocyanate species

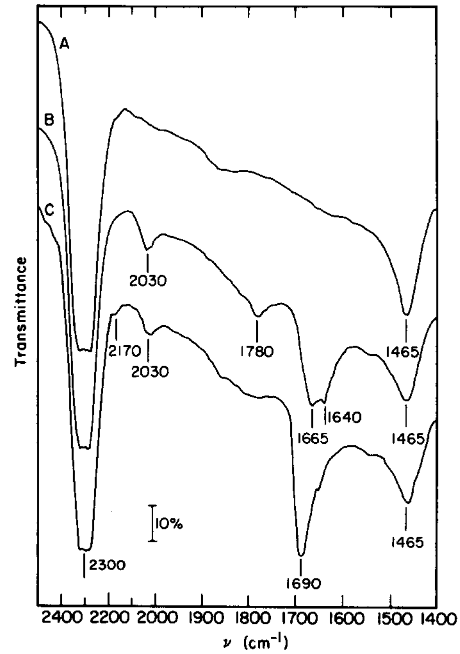

FIG. 4. *In situ* spectra for NO reduction by a mixture of H_2 and CO: (A) baseline spectrum taken after reduction of the catalyst in H_2 at 457 K; (B) spectrum for a prereduced catalyst—T = 472 K, $P_{NO} = 1.7 \times 10^{-2}$ atm, $P_{CO} = 3.5 \times 10^{-2}$ atm, $P_{H_2} = 0.5 \times 10^{-2}$ atm; (C) spectrum for a preoxidized catalyst—T = 461 K, $P_{NO} = 1.6 \times 10^{-2}$ atm, $P_{CO} = 3.5 \times 10^{-2}$ atm, $P_{H_2} = 0.5 \times 10^{-2}$ atm.

bound to the silica support, while the band at 2170 cm^{-1} is due to isocyanate groups bound to Rh. Detailed discussions of the origin of the Rh–NCO and Si–NCO groups have been presented in a separate paper (*7*). The remaining bands are all due to adsorbed NO and CO (*6–8*). The weak band at 1780 cm^{-1} is characteristic of Rh–NO, and the strong bands appearing between 1690 and 1640 cm^{-1} are characteristic of Rh–$NO^{\delta-}$. The band at 2030 cm^{-1} is ascribed to Rh–CO.

Consistent with the infrared observations reported for NO reduction by H_2 over the same catalyst (*8*), the envelope of the bands attributed to Rh–NO is narrower and centered at a higher frequency when the catalyst is oxidized prior to being used for NO reduction. A similar shift in the bands for Rh–$NO^{\delta-}$ was not observed during NO reduction by CO alone over the present catalyst (*6*). It appears, therefore, that when H_2 and CO are both present, CO does not interfere with the effects of catalyst pretreatment on the spectrum of adsorbed NO. This result is somewhat surprising since the band at 2030 cm^{-1} for Rh–CO has roughly the same intensity as that observed during NO reduction by CO alone.

The effects of reactant partial pressures on the absorbances of the bands for adsorbed NO and CO are summarized in Table 5. As the partial pressure of H_2 increases, the intensities of the bands for adsorbed NO decrease somewhat, but the intensity of the CO band is unaffected. Decreasing the partial pressure of CO has little effect on the band for Rh–$NO^{\delta-}$ but does cause an increase in the band for Rh–NO. The band for Rh–NO is also seen to decrease strongly in intensity with decreasing NO partial pressure. Decreasing the NO partial pressure brings about a modest decrease in the absorbances of the bands for Rh–$NO^{\delta-}$ and Rh–NO, and a strong increase in the absorbance of the band for Rh–CO.

Figures 5 and 6 illustrate the effect of increasing temperature on the spectra obtained during the steady-state reduction of NO by H_2 and CO. The four spectra shown in Fig. 5 were obtained for a prereduced

TABLE 5

Absorbances for Rh–$NO^{\delta-}$, Rh–NO, and Rh–CO as a Function of H_2, CO, and NO Partial Pressures

$P_i \times 10^2$ (atm)[a]			Maximum absorbance				
H_2	CO	NO	Preoxidized catalyst		Prereduced catalyst		
			Rh–$NO^{\delta-}$	Rh–CO	Rh–$NO^{\delta-}$	Rh–NO	Rh–CO
0.5	3.5	1.7	0.84	0.09	0.49	0.16	0.12
1.3	3.5	1.6	0.83	0.09	0.49	0.14	0.12
3.4	3.5	1.5	0.78	0.09	0.47	0.13	0.13
7.3	3.4	1.2	0.72	0.09	0.46	0.11	0.13
3.5	8.3	1.5	0.78	0.12	0.46	0.10	0.16
3.4	3.5	1.5	—	0.09	0.49	0.14	0.13
3.3	1.5	1.5	0.81	0.06	0.49	0.15	0.09
3.3	0.6	1.4	0.80	0.05	0.50	0.16	0.07
3.5	3.5	2.7	0.80	0.07	0.51	0.15	0.10
3.4	3.5	1.5	0.79	0.09	0.49	0.14	0.11
3.3	3.5	0.8	0.72	0.11	0.48	0.13	0.14
2.9	3.4	0.4	0.69	0.12	0.47	0.09	0.18

[a] $T = 472$ K.

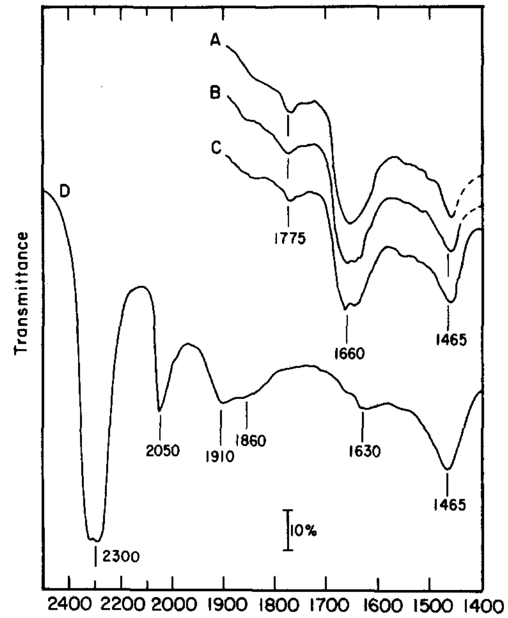

FIG. 5. Effects of temperature on the spectra obtained with a prereduced catalyst: $P^0_{NO} = 1.2 \times 10^{-2}$ atm, $P^0_{CO} = 3.6 \times 10^{-2}$ atm, $P^0_{H_2} = 2.6 \times 10^{-2}$ atm; (A) $T = 453$ K, $x_{NO} = 0.10$; (B) $T = 472$ K, $x_{NO} = 0.28$; (C) $T = 487$ K, $x_{NO} = 0.65$; (D) $T = 495$ K, $x_{NO} = 0.87$.

catalyst, while the six spectra shown in Fig. 6 were obtained for a preoxidized catalyst. As indicated in the legend of each figure, the feed composition was maintained constant as the temperature was raised.

A number of interesting trends are observed in Figs. 5 and 6. Figure 5 shows that as the temperature of the prereduced catalyst is increased from 453 to 487 K there is little change in the spectrum, even though the NO conversion increases from 10 to 65%. However, when the temperature is raised to 495 K, the spectrum undergoes several dramatic changes. The nitrosyl bands are strongly attenuated leaving only a weak feature at 1630 cm^{-1}, and the carbonyl band intensifies and shifts from 2030 to 2050 cm^{-1}. In addition, bands appear at 1910 and 1860 cm^{-1}, characteristic of bridge-bonded CO.

The effects of temperature on the spectra obtained, starting with a preoxidized catalyst, are shown in Fig. 6. Spectra A–C, obtained at 453, 464, and 472 K are virtually identical. An increase in temperature to 475 K, though, produces a radical change in the spectrum, which then remains virtually the same as the temperature is further increased. The general appearance of spectra D–F in Fig. 6 is very similar to spectrum D in Fig. 5. Thus, it is evident that at temperatures sufficiently high to achieve NO conversions in excess of ~70%, the spectra of adsorbed species are very similar for prereduced and preoxidized Rh.

The changes in the infrared spectra with increasing temperature reported here for NO reduction by CO and H_2 show some similarities and some difference to the patterns noted during the reduction of NO by H_2 or CO alone (*6–8*). The influence of temperature on the bands for Rh–NO$^{\delta-}$ seen in Fig. 5 are essentially the same as those observed during the reduction of NO by H_2 or

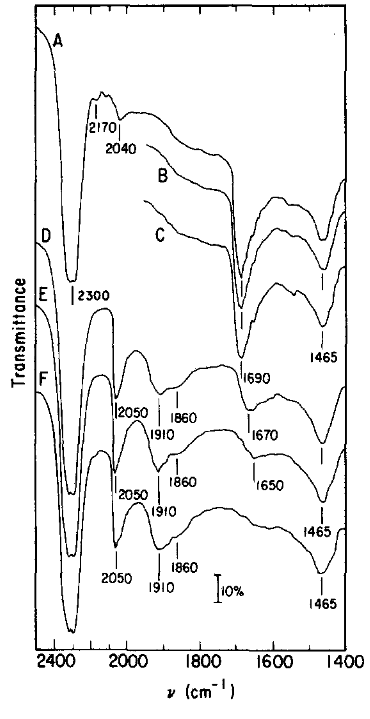

FIG. 6. Effects of temperature on the spectra obtained with a preoxidized catalyst: $P^0_{NO} = 1.2 \times 10^{-2}$ atm, $P^0_{CO} = 3.6 \times 10^{-2}$ atm, $P^0_{H_2} = 2.6 \times 10^{-2}$ atm; (A) $T = 453$ K; (B) $T = 464$ K; (C) $T = 472$ K; (D) $T = 475$ K; (E) $T = 483$ K; (F) $T = 503$ K.

CO. The sharp increase in the intensity of the band for linearly adsorbed CO is comparable to that reported for NO reduction by CO. A significant difference between the NO/H_2/CO and NO/CO systems is the absence of any evidence in the former system for a sudden increase in the intensity of the Rh–NCO band (2170 cm^{-1}), at high temperature. Another difference is the appearance at high temperatures of a band at 1810 cm^{-1} for Rh–NO in the NO/CO system instead of the bands at 1910 and 1860 cm^{-1} for bridge-bonded CO in the NO/H_2/CO system.

DISCUSSION

The results presented here clearly illustrate the similarities and differences in NO reduction by mixtures of H_2 and CO, and by H_2 and CO alone. It is apparent from Fig. 1 that for a fixed inlet partial pressure of NO, and specified temperature and space velocity, the rate of NO reduction proceeds much more rapidly with H_2 than with CO as the reducing agent. The use of an H_2/CO mixture results in an intermediate rate of reduction, but even when the CO partial pressure exceeds the H_2 partial pressure, roughly 87% of the reduction occurs through the consumption of H_2. These results are in qualitative agreement with those reported by Kobylinski and Taylor (*3*), for NO reduction over Rh/Al_2O_3.

The preferential participation of H_2 in NO reduction from mixtures containing NO, H_2, and CO is also evidenced by the similarity of the distribution of N_2, N_2O, and NH_3 to that observed during NO reduction by H_2 (see Table 2). Additional indications of the similarities between the NO/H_2/CO and NO/H_2 systems is given by the equivalence of the activation energies for NO reduction, and for the formation of N_2 and N_2O (see Table 4), which are roughly 10 kcal/mol lower than the corresponding values for NO reduction by CO. Finally, it is noted that for both the NO/H_2/CO and NO/H_2 systems, preoxidation of the catalyst results in a decreased selectivity to N_2O, an effect which occurs to a much smaller degree for the NO/CO system.

The observed differences in the rates of NO reduction by H_2, CO, and H_2/CO mixtures can be rationalized in terms of the mechanisms recently proposed to explain the kinetics of NO reduction by H_2 and CO alone over the present catalyst (*6, 8*). When CO is the only reducing agent,

$$NO_a + S \rightarrow N_a + O_a \qquad (1)$$

is believed to be the rate-limiting step. If H_2 is present without CO, then

$$NO_a + H_a \rightarrow NH_a(N_a) + O_a(OH_a) \qquad (2)$$

is believed to be the rate-limiting step. For NO conversions below ~50%, *in situ*, infrared spectral reveal that the catalyst surface is nearly saturated by adsorbed NO, independent of whether CO or H_2 is used as the reducing agent. Since the reduction of NO by H_2 proceeds much more rapidly than by CO, it must be assumed that reaction (2) is faster than reaction (1). When CO and H_2 are both present, H_2 reacts preferentially with the NO, but at a rate which is less than that when CO is absent. The infrared data reported in Table 5 indicate that CO competes for adsorption sites with NO only weakly, and certainly not to the extent needed to retard the rate of NO reduction by the degree observed. This then suggests that what is impeded is the adsorption of H_2. Unfortunately, though, there is no way to confirm the inhibition of H_2 adsorption by CO under reaction conditions.

A striking difference between the NO/H_2/CO system and either the NO/H_2 or the NO/CO systems is the formation of products above and beyond those normally expected (i.e., N_2O, N_2, NH_3, CO_2, and H_2O). Over the prereduced catalyst this product is identified to be $(NH_2)_2CO$. Conclusive identification of the product formed over the preoxidized catalyst is not possible, but there is evidence to suggest that it might be HNCO.

Voorhoeve *et al.* (*9–11*) have proposed that NH_4OCN is formed via the reaction

$$HNCO_a + NH_3 \rightarrow NH_4OCN \quad (3)$$

The presence of urea, $(NH_2)_2CO$, is postulated to result from the isomerization of NH_4OCN. The results obtained in this study, combined with those reported earlier for NO reduction by CO and H_2 alone (*6*, *8*), support the idea that the precursors to urea are HNCO and NH_3. To begin, we note that the formation of urea is strongly favored at temperatures above which the NO conversion exceeds ~50%. When NO is reduced by H_2 alone, these conditions lead to the formation of NH_3 as the principal product. When the reduction is carried out with CO, the band at 2170 cm^{-1} for Rh–NCO becomes very intense. The absence of an equally intense Rh–NCO band during the reduction of NO with H_2/CO mixtures (see Figs. 4–6) may be due to removal of the NCO group as HNCO. While HNCO was never detected as a gas-phase species, it seems reasonable to suggest that ammonium cyanate is formed via the reaction of HNCO and NH_3. This reaction quite possibly takes place on the walls of the recycle loop, which are much cooler than the reactor itself.

The change in composition of the solid product with catalyst pretreatment is difficult to explain. The decrease in the N/C ratio of the solid from 2.0 to 1.0 upon preoxidation of the catalyst suggests that the solid is the cyclic trimer of HNCO. The absence of any NH_3 formation for temperatures below 483 K (see Fig. 3) may imply that over the preoxidized catalyst, the formation of NH_3 is less favored than the formation of HNCO. This interpretation must be regarded as speculative, though, in view of the limited amount of data on the effects of pretreatment on the formation of solid products.

CONCLUSIONS

The characteristics of NO reduction by H_2 and CO over silica-supported Rh are similar in many respects to those for NO reduction by H_2 alone. While the presence of CO appears to retard the rate of NO reduction somewhat, nearly 90% of the reduction can be ascribed to H_2. The activity of the catalyst and the distribution of products depend on the manner of catalyst pretreatment. Preoxidation in NO results in a catalyst activity 50% higher than that observed following catalyst reduction. The products formed over the prereduced catalyst are N_2O, N_2, NH_3, and $(NH_2)_2CO$. When the catalyst is preoxidized, no NH_3 is observed unless the NO conversion exceeds 90% and a product believed to be HNCO is observed instead of $(NH_2)_2CO$.

The kinetics of NO reduction by H_2 and CO can be described by a power-law rate expression. This expression is positive-order in H_2, negative-order in NO, and weakly negative-order in CO. The magnitudes of the powers on the partial pressures are comparable for NO reduction by H_2 and CO and those observed for NO reduction by H_2 and CO alone, irrespective of catalyst pretreatment. The activation energy for NO reduction by H_2 and CO is 23 kcal/mol, which is in good agreement with that reported for NO reduction by H_2 but 11 kcal/mol lower than that for NO reduction by CO.

Infrared spectra of the catalyst indicate that under reaction conditions the Rh surface is dominated by Rh–$NO^{\delta-}$. For NO conversions below about 90%, the surface is nearly saturated by this species. At higher NO conversions, bands are seen for linearly and bridge-bonded CO. In strong contrast to what has been observed during NO reduction by CO, there is no band for an adsorbed isocyanate structure of the form Rh–NCO.

The higher rate of NO reduction by H_2 and H_2/CO mixtures than by CO is ascribed to the participation of adsorbed H atoms in the dissociation of adsorbed NO. This latter step is believed to be rate-limiting. It is proposed that the formation of $(NH_2)_2CO$ can be ascribed to the reaction NH_3 with adsorbed HNCO to form ammonium cyanate which then isomerizes. This interpretation parallels that proposed originally by Voorhoeve *et al.* (*9–11*).

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