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Reduction of Nitric Oxide by Carbon Monoxide on Copper Catalysts[1]

R. T. REWICK AND H. WISE

Solid State Catalysis Laboratory, Stanford Research Institute,
Menlo Park, California 94025

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An experimental study has been carried out of the kinetics and mechanism of the reduction of NO by reaction with CO on unsupported and supported copper catalysts. At low CO concentrations ($3 < CO/NO < 10$), the kinetics of this reaction exhibit an effective reaction order of unity with respect to NO; hence, the fractional conversion is independent of the reactant level. However, relatively high CO concentrations ($CO/NO > 10$) in the gas stream cause reaction inhibition. On the basis of the experimental results a reaction mechanism is proposed involving dissociative chemisorption of nitric oxide. The formation of an isocyanate (NCO) species on the copper surface is responsible for reaction inhibition. This species acts as the precursor for ammonia formation in the presence of water vapor. The dissociative chemisorption step of NO on a copper surface has an activation energy of 9.3 kcal/mole, a value unaffected by such supports as SiO_2 or $CuAl_2O_4$.

INTRODUCTION

The utility of copper-based materials for catalytic oxidation of CO and hydrocarbons in automobile exhaust emissions has been well documented (*1-6*). However, the conversion of NO_x (nitric oxide and nitrogen dioxide) to nitrogen remains a problem of considerable magnitude in view of federal and state restrictions on NO_x emissions. A number of recent engineering studies (*7*) have been concerned with the applicability of copper alloys to the catalytic reduction of NO_x with reducing gases such as CO. Supported Cu-Ni catalysts operating in the temperature range 1000-1600°F have been found to be effective for the removal of NO_x pollutants from a wide range of exhaust gas compositions (*8*).

The reducing atmosphere that prevails under fuel-rich operating conditions of the automobile will favor the reduction of the metal oxides originally deposited on the catalyst supports. It is likely, therefore, that the catalytic activities observed referred to metallic surfaces or metal/metal oxide interfaces. However, the high-temperature interaction of a metal oxide, such as cupric oxide, with an insulator support material, such as alumina, adds considerable complexity to the identification of the catalytically active surface (*9,10*). The present study was undertaken to obtain a better understanding of the catalytic mechanism of the NO/CO reaction on copper catalysts. Preliminary experiments with single crystals of cuprous oxide demonstrated the appearance of high catalytic activity for this reaction after the crystal had become oxygen-deficient to the point of exhibiting macroscopic islands of metallic copper. Thus, we decided to study in more detail the propoerties of metallic copper for the NO/CO reaction.

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EXPERIMENTAL DETAILS

Procedure

The experimental apparatus used in these studies is shown schematically in Fig. 1. The composition of the CO/NO reactant mixture was adjusted by means of calibrated flow meters that controlled the reactant stream (a mixture of 10 vol% CO in helium; a mixture of 10 vol% NO in helium; and helium diluent, purity 99.9%). Other gases, such as O_2 and H_2, were metered into the reactant flow stream when desired. After passing through a mixing chamber, a Pyrex glass trap filled with glass beads, the gas mixture entered the reactor. It consisted of a vertical Pyrex tube (5 cm long, 1 cm i.d.) provided with a medium porosity glass frit for support of the powdered catalyst. The reactor was heated by means of a temperature-controlled electrical furnace. The reaction temperature was monitored by a thermocouple attached to the outside wall of the reactor adjacent to the catalyst bed. For studies of the effect of water vapor, the reactant gas stream could be diverted to pass through a water bubbler (kept at a specified temperature) before being admitted to the reactor.

The composition of the gas stream before and after contact with the catalyst was monitored by subjecting aliquots (1.0 cc gas sampling loops) to gas chromatographic analysis using a Hewlett-Packard Model 5750 gas chromatograph and two 12-ft by 0.125-in. columns. For N_2, NO, and CO, a molecular sieve 5-A column operating at 373 K was employed: for N_2O and CO_2, a Porapak Q column operating at 323 K was used. Analysis for ammonia was conducted by bubbling a known volume of the product stream through standard 0.05 *N* H_2SO_4, and back-titrating with standard 0.05 *N* NaOH solution.

The copper catalysts used in the present studies were prepared by reduction of reagent grade (99.8% purity) cupric oxide (J. T. Baker Chemical Co.) with 6 vol% CO in helium. The samples were reduced inside the reactor by exposing a weighed sample of cupric oxide (generally 155 ± 5 mg) to a stream of CO/He at 532 K and a volumetric flow rate of 176 cc/min. The resulting powdered metal exhibited slight

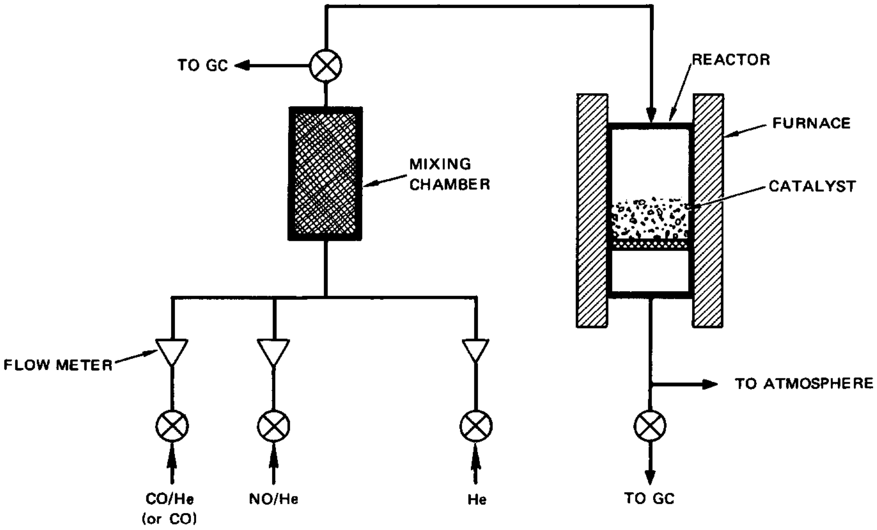

FIG. 1. Schematic diagram of apparatus.

aggregation after reduction; however, it was easily redispersed to powder by vibrating the reactor.

Catalyst surface areas were determined by the BET technique with krypton as the adsorbent. The surface area of the copper powder, prepared by reduction of cupric oxide in 10 vol% CO for more than 3 hr, was found to be 0.54 m^2/g, compared to 0.90 m^2/g for the cupric oxide before reduction. Reduction of CuO in H_2 was reported to produce a copper surface of higher activity toward oxidation (*11*). However, our experiments with H_2 (10 vol%) reduction yielded a copper catalyst of lower surface area (0.35 m^2/g).

Comparison of specific catalyst activity (conversion per unit area) demonstrated little difference between the two methods of catalyst preparation. All the kinetic measurements were carried out with cupric oxide samples reduced in CO for 3 hr at 523 K before exposure to the desired CO/NO/He gas mixture. The reactant flow rate was carefully adjusted at each temperature studied to maintain constant space velocity through the reaction bed (volumetric flow rate = 316 cc/min at reaction temperature, $\text{VHSV} = 1.36 \times 10^6\ \text{hr}^{-1}$), corresponding to a contact time with the catalyst of about 5 msec over the temperature range studied.

RESULTS

1. Reaction Kinetics

Measurements on the catalytic activity of metallic copper for the CO/NO reaction in the temperature range 473–573 K demonstrated rapid conversion of NO to N_2 in accordance with the stoichiometry,

$$\text{NO} + \text{CO} \rightarrow \tfrac{1}{2}\, \text{N}_2 + \text{CO}_2.$$

The formation of nitrous oxide as a minor by-product was also observed over the temperature range studied. Its concentration tended to somewhat higher values with increasing initial NO concentration and lower values with increasing reaction temperature.

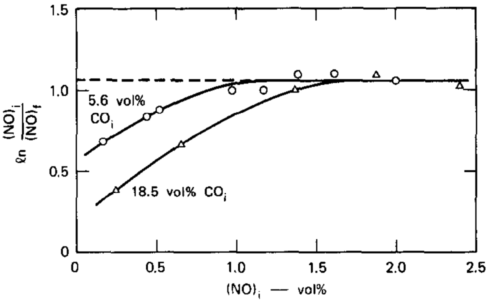

FIG. 2. Activity of metallic copper during CO/NO reaction as a function of $(CO)_i$ and $(NO)_i$.

To study the details of the reaction mechanism, a series of kinetic measurements were conducted in which the concentration of each reactant was varied over a wide range. At CO/NO < 10, the kinetics of N_2 formation exhibit a simple first-order dependency on NO; at CO/NO > 10 CO inhibition in the conversion of NO is observed (Fig. 2).

2. Effect of Water Vapor

The addition of water vapor (3 vol%) to the reactant stream results in the formation of significant quantities of NH_3 as a reaction product (Table 1). The fraction of NH_3 formed appears to decline with increasing temperature and to increase with increasing CO level in the feed stream. However, the degree of NO conversion remains unaffected by water vapor, although more of the nitrogen is replaced by ammonia as the reaction product (Table 2), an indication of a common reaction intermediate.

3. Effect of Oxygen

The addition of oxygen to the NO/CO reactant mixture hardly affects the degree of NO conversion at 473 K as long as the

TABLE 1

EFFECT OF WATER ON AMMONIA FORMATION DURING COPPER-CATALYZED NO/CO REACTION[a]

Temp (K)	Reactants (vol%)		Products (vol%)			Conversion
	$(NO)_i$	$(CO)_i$	(N_2)	(NH_3)[b]	$\frac{NH_3}{N_2 + NH_3}$	$\frac{\Delta NO}{NO_i}$
423	1.39	11.3	0.019	0.16	0.89	0.15
			0.12	0.63	0.84	0.67
			0.28	0.66	0.70	0.87
			0.42	0.65	0.61	0.99
523	1.54	6.2	0.31	0.70	0.69	0.85
		11.6	0.24	0.81	0.77	0.86
		27.2	0.21	0.96	0.82	0.86
		35.8	0.16	1.0	0.86	0.85
		40.9	0.18	0.97	0.84	0.85

[a] Volumetric gas flow rate = 316 cc/min; VHSV = 1.36×10^6 hr^{-1}; catalyst mass = 0.124 g Cu; water concn = 3 vol%.

[b] Calculated by difference between NO consumed and N_2 formed.

O_2 concentration remains below 0.5 vol% (Table 3). The NO conversion decreases to nearly zero as the concentration of O_2 approaches the stoichiometric amount required for CO oxidation.

4. *Effect of Hydrogen*

In contrast to the effect of water vapor, the addition of hydrogen to the reactant stream generated little NH_3 at temperatures below 573 K (Table 4). Only at higher temperatures, significant NH_3 formation was observed. Total NO conversion remained unaffected by the presence of H_2 over the temperature range studied (523–773 K).

5. *Supported Copper Catalysts*

As suitable support materials for metallic copper dispersions, SiO_2 and $CuAl_2O_4$ were selected for further study. Samples containing 0.3 wt% Cu/SiO_2 and 15 wt% $Cu/CuAl_2O_4$ were prepared by standard wet impregnation techniques. In Fig. 3, we compare their activity with an

TABLE 2

EFFECT OF WATER ON NO CONVERSION TO N_2 AND NH_3 DURING COPPER-CATALYZED NO/CO REACTION[a]

Temp (K)	Without water (vol%)			With water (vol%)			
	$(NO)_i$	Total NO conversion	(N_2)	$(NO)_i$	Total NO conversion	N_2	NH_3[b]
423	1.63	18	0.098	1.32	15	0.019	0.16
473	1.63	60	0.46	1.33	65	0.12	0.63
523	1.68	91	0.72	1.38	88	0.28	0.66
573	1.80	97	0.88	1.51	99	0.42	0.65

[a] Volumetric gas flow rate = 316 cc/min; VHSV = 1.36×10^6 hr^{-1}; catalyst mass = 0.124 g Cu; water concn = 3 vol%.

[b] Calculated by difference between NO consumed and N_2 formed.

TABLE 3

EFFECT OF O_2 ON NO CONVERSION DURING COPPER-CATALYZED NO/CO REACTION AT 473 K[a]

Added O_2 (vol%)	Fractional NO conversion[b]
0	0.89
0.53	0.91
1.1	0.72
2.1	0.30
5.3	~0

[a] Volumetric gas flow rate = 316 cc/min; VHSV = 1.36×10^6 hr^{-1}; catalyst mass = 0.125 g Cu; initial CO concn = 10.7 vol%.

[b] $(NO_i - NO_f)/NO_i$.

unsupported copper catalyst on the basis of unit mass of copper. These data demonstrate the significant effect of increased copper dispersion of the supported catalysts on the conversion of NO. For quantitative comparison, specific activity data (expressed in terms of conversion per unit surface area of Cu) are required. However, no method is presently available to determine the metal surface area of supported Cu. It is of interest that the slopes of the curves presented in Fig. 3 are the same, indicating a common reaction mechanism for the conversion of NO by reaction with CO and a constant activation energy of 9.3 kcal/mole.

6. *Durability Studies*

The durability of different Cu-catalyst systems under reaction conditions was examined by prolonged exposure of the catalyst to NO/CO mixtures and product analysis at various time intervals. Among the catalysts studied (Cu powder, 15 wt% $Cu/CuAl_2O_4$, and 0.3 wt% Cu/SiO_2), the powdered metal and Cu/SiO_2 exhibited high stability in a 6-hr exposure test at 573 K (Table 5). For the $Cu/CuAl_2O_4$, a 30% decrease in activity was recorded, presumably because of sintering, especially at the high Cu weight-loading employed (15 wt%).

7. *Multicomponent Catalysts*

A comparative study of the catalytic efficacy of powdered Monel[2] and metallic copper for NO/CO reactions has shown that much higher temperatures are required for equivalent NO conversion in the case of Monel (Fig. 4). Also, the activation energy is nearly a factor of three greater for Monel than for copper. A significant effect observed during the Monel-catalyzed reactions is the enhancement in the degree of NO conversion in the presence of water vapor (Table 6). Such a promoting effect of H_2O vapor was absent in the case of the Cu catalyst studied. However, in analogy with Cu metal, the Monel catalyst exhibits strong inhibition in NO conversion with increasing CO concentration (Table 7), a much more pronounced effect than that encountered with metallic Cu. Although operating at higher temperatures, the Monel catalyst exhibited good thermal stability at 848 K over a period of 5 hr. Experimental measurements with copper sponge (Hogen Industries, Willoughby, Ohio) and Raney Cu–Al alloy (Alfa Inorganics, Inc.) indicate that these materials are ineffective as catalysts for the NO/CO reaction. Under conditions comparable to those employed with copper powder, the NO conversion was found to be less than 1%.

DISCUSSION

In providing a mechanism for the Cu-catalyzed reaction between NO and CO, one needs to take into account (a) the high activity of metallic copper compared to its oxides, (b) the reaction order of unity with respect to NO, (c) the inhibition at high ratios of CO/NO, and (b) the formation of NH_3 as a reaction product in the presence of water vapor. The high reactivity of

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[2] Alloy composition: 68.30 wt% Ni, 30.00 wt% Cu, 0.97 wt% Fe, 0.73 wt% Mn, 0.004 wt% S; and 0.003 wt% C (supplied by Glidden-Durkee Division of SCM Corp.).

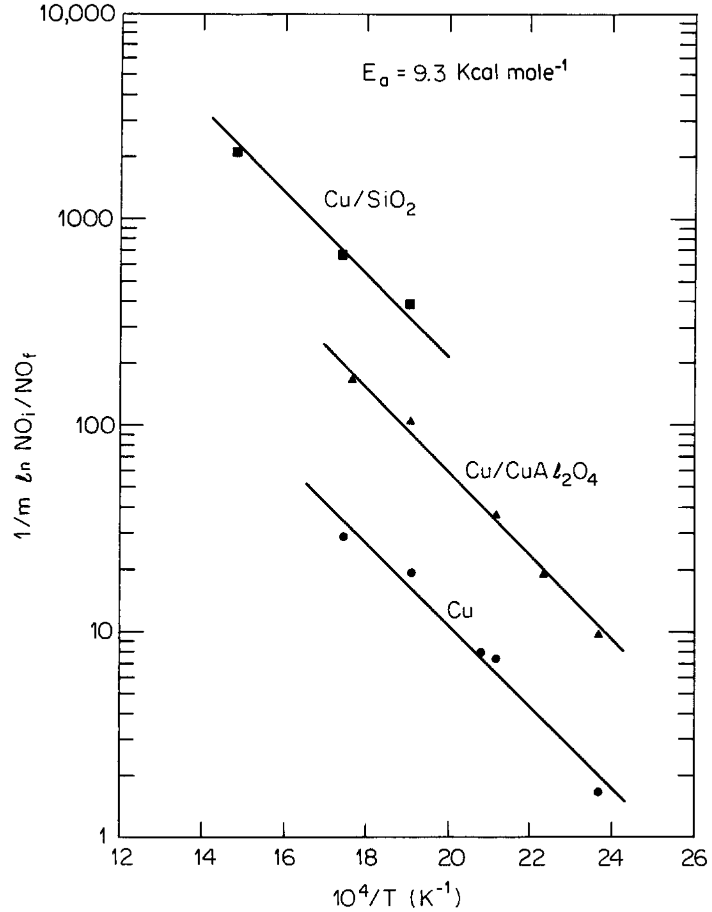

FIG. 3. Kinetic Analysis of Copper Catalysts as a function of temperature.

TABLE 4

EFFECT OF H_2 ON NO CONVERSION TO N_2 AND NH_3 DURING COPPER-CATALYZED NO/CO REACTION[a]

	Without H_2 (vol%)			With H_2 (vol%)			
Temp (K)	$(NO)_i$	Total NO conversion	N_2	$(NO)_i$	Total NO conversion	N_2	NH_3[b]
523	1.47	79	0.50	1.40	73	0.41	0.042
573	1.25	83	0.43	1.34	82	0.46	0.012
623	1.25	92	0.49	1.29	90	0.44	0.12
673	—	—	—	1.26	96	0.37	0.30
723	1.28	99	0.58	1.34	99	0.37	0.47
773	—	—	—	1.30	100	0.28	0.74

[a] Volumetric gas flow rate = 316 cc/min; VHSV = 1.36 × 10^6 hr^{-1}; catalyst mass = 0.124 g Cu; Hydrogen concn = 2 vol%; initial CO concn = 10.5 vol%.

[b] Calculated by difference between NO consumed and N_2 formed.

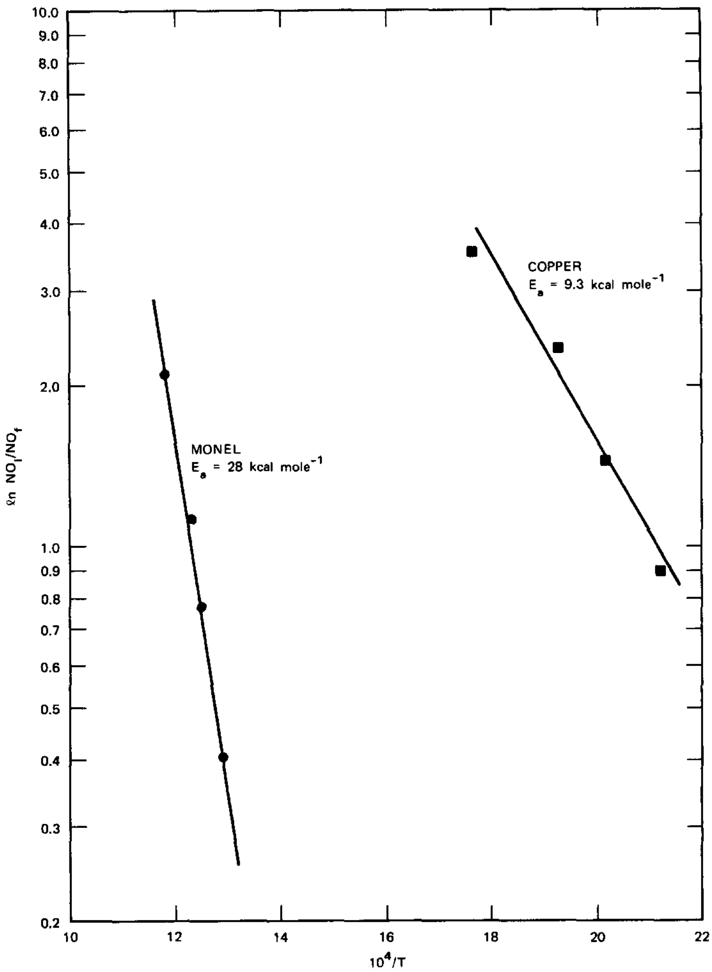

FIG. 4. Comparison of catalytic activity of Monel and Cu for NO/CO reaction.

copper toward NO is undoubtedly associated with the formation of a strong bond between copper and oxygen adatoms formed as a result of dissociative chemisorption of NO. This fact is born out by qualitative studies of NO decomposition on copper metal. In these measurements, we noted the formation of molecular nitrogen on a copper surface accompanied by the gradual loss in activity for NO decomposition because of progressive oxygen coverage of the copper surface. Cuprous oxide, on the other hand, chemisorbs NO very slowly (*12*). Therefore, one may conclude that the catalytic reaction between NO and CO involves as

TABLE 5

STABILITY OF COPPER CATALYSTS FOR NO CONVERSION DURING NO/CO REACTION AT 573 K[a]

Time (hr)	Fractional NO conversion/g of copper[b]		
	Cu	$Cu/CuAl_2O_4$	Cu/SiO_2
0.25	8.2	43	295
1.0	8.2	41	210
2.0	8.2	40	330
4.0	8.1	35	350
6.0	7.9	30	350

[a] Volumetric gas flow rate = 192 cc/min; initial CO concn = 10.4 vol%; initial NO concn = 1.5 vol%.

[b] $(NO_i - NO_f)/(NO_i \cdot \text{mass Cu})$.

TABLE 6

Effect of Water on NO/CO Reaction Catalyzed by Monel[a]

	Without water (vol%)			With water (vol%)			
Temp (K)	$(NO)_i$	NO conversion	N_2	$(NO)_i$	NO conversion	N_2	NH_3[b]
773	1.36	50	0.32	1.36	72	0.37	0.23
798	1.45	70	0.45	1.44	85	0.41	0.40
823	1.64	88	0.65	1.56	100	0.47	0.63
848	1.38	100	0.64	1.36	100	0.44	0.49

[a] Volumetric gas flow rate = 316 cc/min; VHSV = 1.36×10^6 hr^{-1}; catalyst mass = 0.156 g; water concn = 3 vol%; initial CO concn = 10.8 vol%.

[b] Calculated by difference between NO consumed and N_2 formed.

a primary step the decomposition of NO with the formation of O and N adatoms (designated as O* and N*). Subsequently, the chemisorbed oxygen reacts with CO and the chemisorbed nitrogen reacts with NO, thereby making available the Cu surface sites for further reaction with NO. Hence, for efficient catalysis, the removal of O* and N* by CO and NO must be more rapid than their production by surface-catalyzed decomposition of NO.

A clue to CO inhibition may be found in recent observations in which the formation of an isocyanate intermediate during the NO/CO reaction was reported on Al_2O_3-supported noble metal catalysts (*13*). Thus, CO inhibition, as noted in our experimental work, could result from the production of NCO species by a side reaction involving the interaction of a nitrogen adatom with CO, thereby blocking the formation of molecular nitrogen by interaction with NO.

TABLE 7

Effect of CO on NO Conversion during Monel-Catalyzed NO/CO Reaction[a]

	Total NO conversion (vol%)	
Temp (K)	10.8 vol% CO	21.8 vol% CO
773	50	34
798	70	53
823	88	68
848	100	83

[a] Volumetric gas flow rate = 316 cc/min; initial NO concn = 1.7 vol%; mass of Monel = 0.156 g.

In line with these concepts, a reaction mechanism is proposed that includes the following elementary steps,

$$NO \rightarrow N^* + O^*, \qquad (1)$$

$$O^* + CO \rightarrow CO_2, \qquad (2)$$

$$N^* + NO \rightarrow N_2 + O^*, \qquad (3)$$

$$N^* + CO \rightarrow NCO^*, \qquad (4)$$

$$CO \rightleftarrows CO^*, \qquad (5)$$

where the asterisk refers to adsorbed species. Reaction (1) involves the dissociative chemisorption of NO on a copper surface. It is followed by the interaction of an oxygen adatom with CO [Reaction (2) to form the stable product CO_2] possibly by way of a Hinshelwood mechanism involving reversibly adsorbed CO (*11*). The nitrogen adatom N* further reacts with NO to product a nitrogen molecule [Reaction (3)] and an additional oxygen adatom that can interact further by Reaction (2). Most likely, Reaction (3) is the source of N_2O seen as a minor component in the product gas stream. It is to be noted that the nitrogen adatom may undergo another reaction (Step 4), leading to the formation of the isocyanate surface intermediate. At high surface coverage, its presence interferes with the initiation reaction involving chemisorption of nitric oxide on a bare copper surface [Reaction (1)].

One could consider the presence of chemisorbed CO on the metal surface to be responsible for the observed inhibition at high CO concentrations, as in Eq. (5). However, studies of CO adsorption on copper (*11*) indicate an exothermic heat of adsorption of 28 kcal/mole and rapid desorption of this adsorbate at temperatures above 500 K. Thus, the moderate binding energy of this adsorbate would not contribute to any significant degree to catalyst deactivation in the temperature range of interest for the NO/CO reaction.

Using the conventional steady-state assumption for the reaction intermediates (O* and N*), we can derive an expression for the rate of disappearance of nitric oxide in accordance with the reaction sequence,

$$-d(\mathrm{NO})/dt = k_1(\mathrm{NO})\,\{1 + k_3(\mathrm{NO})/[k_3(\mathrm{NO}) + k_4(\mathrm{CO})]\}, \quad (6)$$

where the quantities in parentheses refer to gas-phase concentrations.

One may consider two limiting conditions. At low values of CO, so that $k_4(\mathrm{CO}) \ll k_3(\mathrm{NO})$, Eq. (6) reduces to

$$-d(\mathrm{NO})/dt = 2\,k_1(\mathrm{NO}). \quad (7)$$

On the other hand, at high values of the CO/NO ratio, so that $k_4(\mathrm{CO}) \gg k_3(\mathrm{NO})$, one obtains:

$$-d(\mathrm{NO})/dt = k_1(\mathrm{NO})\,\{1 + [k_3(\mathrm{NO})/k_4(\mathrm{CO})]\}. \quad (8)$$

In accordance with Eq. (7) the rate of disappearance of NO at relatively low CO levels is of first order in NO. At high CO concentrations, one obtains on integration of Eq. (8) between the limits $(\mathrm{NO})_i$ and $(\mathrm{NO})_f$, which represent the initial and final concentrations of NO:

$$\frac{(\mathrm{NO})_i}{(\mathrm{NO})_f}\left[\frac{1 + K(\mathrm{NO})_f}{1 + K(\mathrm{NO})_i}\right] = e^{k_1 t}, \quad (9)$$

where K is defined by

$$K = k_3/k_4(\mathrm{CO})_i. \quad (10)$$

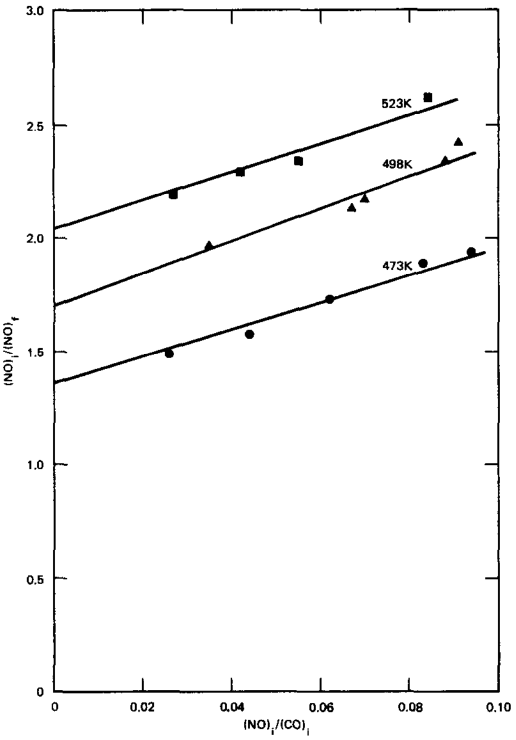

FIG. 5. Kinetic analysis of experimental results at high CO levels.

Here the assumption is made that the CO level is sufficiently high to remain unaffected by the reaction, a valid approximation under our experimental conditions with large excess of CO. Equation (9) can be rearranged to:

$$(\mathrm{NO})_i/(\mathrm{NO})_f = e^{k_1 t} + (\mathrm{NO})_i/(\mathrm{CO})_i\,[(k_3/k_4)\,(e^{k_1 t} - 1)] \quad (11)$$

To test the applicability of the proposed mechanism, we have plotted the experimental results as the function,

$$(\mathrm{NO})_i/(\mathrm{NO})_f \text{ vs } (\mathrm{NO})_i/(\mathrm{CO})_i,$$

in accordance with Eq. (11). Indeed the experimental data obtained at CO/NO > 10 are described by Eq. (11). From the intercept of the resulting straight line at a given temperature (Fig. 5) $k_1 t$ may be evaluated; from the slope one finds the ratio k_3/k_4 (Table 8). Also the value of $k_1 t$ may be derived at low CO levels by applying Eq. (7) to the experimental results. A

TABLE 8
Kinetic Data for Carbon Monoxide/Nitric Oxide Reaction Catalyzed by Copper[a]

Temp (K)	k_1t (a)	k_1t (b)	k_1[b] (sec^{-1})	k_3/k_4
473	0.31	0.27	58	16.4
498	0.53	0.53	106	10.1
523	0.71	0.67	138	6.1

[a] (a) CO/NO > 10; (b) CO/NO < 10.

[b] Based on a contact time of $t = 5 \times 10^{-3}$ sec.

comparison of these data shows good agreement between the data obtained at different levels of CO (Table 8), including the activation energy for reaction (1), $E_1 = 9.3$ kcal/mole. Evaluation of k_3/k_4 at several temperatures allows the determination of the difference in activation energy for Reactions (3) and (4). By means of an Arrhenius plot one finds $E_4 - E_3 = 10.1$ kcal/mole.

After prolonged exposure of the catalyst to a reactant gas mixture with high CO/NO ratio (>10) the formation of the isocyanate species (–NCO) on the catalyst was detectable by infrared absorption spectroscopy. For these studies catalyst samples were selected whose activity for NO reduction had diminished by a factor of nine or more from their initial activity. A disc was pressed under anhydrous conditions from a well-dispersed mixture of the spent copper catalyst and optical-grade potassium chloride (12.5% weight loading) and placed in a special optical cell designed to exclude moisture. The infrared analysis with the aid of a Perkin-Elmer spectrometer (Model 457) detected the presence of two absorption bands located near 2380 and 2220 cm^{-1}. These bands were not observed with copper catalyst samples which had not been deactivated by exposure to CO/NO mixtures. A reference sample of cupric isocyanate, prepared in accordance with a procedure for silver isocyanate (*14*), showed a strong infrared absorption at 2270 cm^{-1} characteristic of the isocyanate frequency (*15*). The absorption frequencies measured in our studies were close to those reported by London and Bell (*16*) in their work of the NO/CO reaction on a cupric oxide catalyst.

Unland (*17*) has observed the formation of the same species on supported noble-metal catalysts and suggests the participation of isocyanate adsorbate as a reaction intermediate in the formation of molecular nitrogen, Our data for a copper catalyst indicate no such role for the NCO species. Rather the strongly bound and thermally stable NCO adspecies on the copper surface has primarily the function of a catalyst inhibitor (Reaction 4).

The validity of the NH_3-producing step is further substantiated by the observation that water vapor does not affect the degree of conversion of nitric oxide in the case of the copper catalyst. Rather, its presence causes an alternate path for the removal of the N adatoms by way of hydrolysis of the NCO* intermediate. Such an effect would be expected to become more pronounced with increasing CO concentration, as is borne out by the experimental data presented in Table 1. It may be concluded, therefore, that both N_2 and NH_3 originate from the same precursor, an N adatom.

Of further interest is the absence of ammonia as a reaction product in the presence of hydrogen, except at much higher temperatures than those employed in the experiments with water vapor. At such high temperatures, the reverse water–gas shift reaction may be involved, yielding the same surface intermediates as found on water addition. Thus, NH_3 formation may occur by way of a mechanism identical to that in the presence of added water vapor.

In the case of Monel as a catalyst, the introduction of water vapor into the reactant stream causes not only a shift in the product distribution from N_2 to NH_3, as observed in the case of Cu, but also an enhancement in the total conversion of

NO. These results suggest the possibility of an alternate mechanism (*18,19*) for NH_3 formation involving chemisorbed hydrogel in the presence of transition metals, as contained in the multicomponent Monel alloy.

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