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Silver and Gold Catalyzed Reactions of Carbon Monoxide with Nitric Oxide and with Oxygen

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The reaction of carbon monoxide with oxygen and with nitric oxide over silver and gold catalysts has been studied in a recirculating system with product removal. Nitrous oxide was the predominant nitrogen containing product of the latter reaction over both catalysts, nitrogen amounting to less than 2%. With gold the two reactions had similar characteristics both proceeding between −30°C and 100°C with identical pressure dependencies and activation energies close to zero. Oxidation by oxygen was about 40 times faster than that by nitric oxide and furthermore the latter reaction poisoned readily above 40°C because of some interaction of nitric oxide with the surface. With silver, both reactions were first order in carbon monoxide pressure. For the CO + NO reaction the rate passed through a maximum as the NO pressure was increased eventually tending to inverse first order. The activation energy was 14 kcal $mole^{-1}$ below 118°C and 4 kcal $mole^{-1}$ above that temperature. These results could be qualitatively explained by a Langmuir–Hinshelwood mechanism in which there is competition for a small number of sites. The $CO + O_2$ reaction was zero order in oxygen and believed to proceed by a quite different mechanism.

INTRODUCTION

Noble metal and transition metal oxides capable of catalyzing reduction of NO by CO are known (*1–6*). However in the presence of excess oxygen it is invariably found that the $CO + O_2$ reaction is catalyzed faster than the CO + NO one, an undesirable situation if the primary aim is removing both CO and NO from automobile exhaust emissions. Thus Shelef *et al.* (*5a*) found that of the transition metal oxides tested only Fe_2O_3 and Cr_2O_3 had intrinsically higher activity for CO + NO than for $CO + O_2$. However, when the former reaction was run in the presence of excess oxygen no NO removal took place. Their conclusions were that either oxygen was adsorbed more strongly than nitric oxide or that in the presence of oxygen the catalyst surface was converted to an oxidized form ineffective for the CO + NO reaction. Somewhat more promising were the findings of Bauerle *et al.* (*6*) for copper chromite where the rate of the $CO + O_2$ reaction was faster but nonetheless essentially complete removal of small quantities of NO could still be achieved provided the pressure of O_2 did not exceed that required for CO removal.

None of these studies attempted to measure pressure dependencies although such determinations are essential if it is to be established whether the $CO + O_2$ and CO + NO proceed by similar or different mechanisms. This paper concerns such a comparison for silver and gold sponges. These metals were chosen because, although controversy exists, there is evidence to suggest that they absorb oxygen less readily than most metals and hence might suffer less from change in surface oxidation state or exclusion of nitric oxide from the surface, the factors suggested by Shelef *et al.* (*5a*) for the inhibition of the CO + NO reaction by O_2. Thus for silver Benton and Drake (*7*) reported a heat of adsorption of 16 kcal mole^{-1} for reversible adsorption of oxygen, Scholten *et al.* (*8*) found oxygen adsorption was slow below 150°C and Sandler and Durigon (*9*), Czanderа (*10*) and Smeltzer *et al.* (*11*) found evidence for both weakly and strongly bound oxygen. In the same vein Trapnell (*12*) stated that oxygen did not adsorb on gold at all, while the results of MacDonald and Hayes (*13*) show a maximum coverage of less than 3% between −100 and 500°C.

The CO + O_2 reaction has been carefully studied over silver by Keulks and Chang (*14*) following earlier work by Benton and Bell (*15*) and Yamada (*16*), and over gold by Daglish and Eley (*17*). No previous report on the catalysis of the CO + NO reaction over silver or gold could be found in the literature.

EXPERIMENTAL METHODS

Kinetic measurements were carried out in a conventional Pyrex recirculating system consisting in turn of the catalyst sample, a cryostat loop, magnetically operated pump, mixing bulb, gas chromatograph loop and pressure gauge (MKS Instruments Type 77 capacitance manometer). The volume of the loop was slightly less than 300 cm^3 and the circulation rate within it was such that the conversion per pass never exceeded 20% and was generally less than 2%. Thus the system could be treated as an approximate differential reactor. The loop was connected to a gas handling and pumping system consisting of a two-stage mercury diffusion pump trapped with liquid N_2. Pressures in the range 10^{-4}–10^{-6} Torr (1 Torr = 133.3 N m^{-2}) were routinely recorded with a Penning gauge.

During kinetic runs the cryostat was maintained at 118 K, sufficient to freeze out N_2O and CO_2 to residual pressures of approximately less than 0.1 and 0.01 Torr, respectively. The pressure drop accompanying reaction was continuously followed on a recorder connected to the electrical output of the capacitance manometer. Partial pressures of the individual components of the gas phase were determined prior to, and following reaction, by diverting the contents of the g/c loop to the chromatograph. The relative quantities of CO_2 and N_2O formed were determined by similar measurements on an aliquot of the gas mixture formed by vaporization of the condensed products in the cryostat. The column used was 6 ft × 3/16 in. Porapak Q maintained at 195 K for N_2, O_2, CO and NO analyses and at 273 K for N_2O and CO_2 separations.

The nitric oxide was Mathieson CP grade. Various cylinders were found to contain up to 1.5% of N_2 and 0.5% each of N_2O and NO_2. Circulation through the cryostat at 118 K prior to reaction removed all NO_2 and reduced the N_2O pressure to that prevailing during reaction. No attempt was made to remove N_2. Carbon monoxide was Mathieson CP grade containing 0.1% N_2. Oxygen, hydrogen and helium were obtained from cylinders and showed no impurities detectable by the gas chromatograph. Mixtures of gases were prepared by admitting individual gases to various calibrated volumes in the line, measuring the pressures and then mixing by circulation. Helium was used as a diluent to bring the total pressure up to 150 to 250 Torr in each experiment.

The gold catalyst was prepared as described by Kulifay (*18*), the silver catalyst as described by Keulks and Chang (*14*). The starting metal salts were gold chloride (Fisher Scientific Co.) and silver nitrate (Unilab, analytical grade), respectively. Initial catalyst reductions were carried out over a 7 hr period in recirculating hydrogen at steadily increasing pressures and temperatures concluding with 3 hr in 300

Torr of H_2 at 300°C. At 77 K trap was used to remove water. To minimize sintering, rather milder conditions were applied to catalysts previously used in $CO + O_2$ and CO + NO reactions. Reduction for 1 hr at 200°C for Ag and 150°C for Au followed by 0.5 hr evacuation to a pressure of $< 10^{-4}$ Torr was typically employed.

Surface areas were determined by the BET method using N_2 as adsorbate at the temperature of liquid N_2.

RESULTS

$CO + O_2$ reaction over silver. This reaction was studied first since the results of others were available for comparison. Initial experiments showed that the silver catalyst gave reproducible results provided it was freshly reduced before each reaction. However, it did decline in activity during the course of each reaction since repeat reactions carried out without intervening reduction gave initial rates 10 to 40% lower than the previous one. These declines in rate were especially pronounced if the oxygen pressure was in excess of stoichiometric. Under these conditions the use of integrated rate expressions to obtain pressure dependencies was not satisfactory and we therefore used initial rates obtained from the slope of the pressure–time curves over the first 10% of reaction.

The dependence of rate, measured in this way, on CO pressure with constant initial O_2 pressure of 21.0 Torr, and on O_2 pressure with initial CO pressure of 35 Torr is shown in Table 1. The rate was strictly first order in CO and approximately zero order in O_2, since a 15-fold change in the pressure of the latter changed the rate by less than a factor of two.

TABLE 1

VARIATION IN RATE OF $CO + O_2$ REACTION OVER Ag WITH REACTANT PRESSURE

Effect of CO pressure[a]		Effect of O_2 pressure[b]	
P_{CO} (Torr)	Initial rate[c]	P_{O_2} (Torr)	Initial rate[c]
4.2	0.0096	11.9	0.188
9.6	0.0148	21.0	0.189
18.4	0.024	34.2	0.217
22.2	0.036	65.8	0.291
47.4	0.0652	101.0	0.332
68.2	0.1016	185.0	0.307
106.3	0.140		
138.4	0.1708		

[a] Measured at 53°C with initial $P_{O_2} = 35.0$ Torr.

[b] Measured at 99°C with initial $P_{CO} = 21.0$ Torr.

[c] In cm^3 (CO_2) min^{-1} g^{-1}.

The temperature dependence of reaction was measured over 1.25 g of Ag in the temperature range 90 to 126°C using a stoichiometric mixture with initial pressures of 53.3 and 26.7 Torr for CO and O_2, respectively. The activation energy was 9.3 ± 1 kcal $mole^{-1}$. Over the entire series of $CO + O_2$ and CO + NO reactions the surface area of Ag remained unchanged at 0.26 ± 0.02 m^2 g^{-1}.

CO + NO over silver. This reaction was studied over Ag using the initial rate method. Gas chromatographic analyses of residual reactants and products showed that the nitrogen containing products were N_2O 99 ± 0.5% and N_2 1 ± 0.5%. Thus the stoichiometry was effectively

$$CO + 2NO \rightarrow N_2O + CO_2 \qquad (1)$$

and this was always consistent with mass balance calculations.

Figure 1 shows how the initial rate depended on CO and NO pressures. The reaction was first order in CO but the rate passed through a maximum with increase in NO pressure eventually tending to inverse first order.

The temperature dependence of the CO + NO reaction over freshly reduced Ag was investigated in the range 87 to 156°C with initial pressures of CO and NO of 12.5 Torr each. The results, which are plotted in the Arrhenius form in Fig. 2, indicated an apparent activation energy of

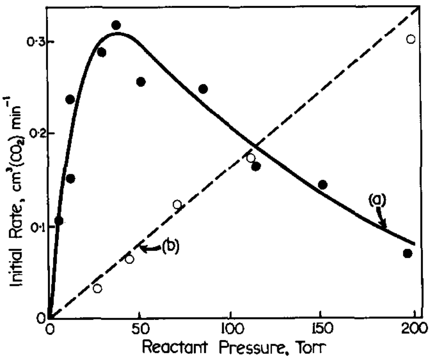

FIG. 1. Dependence of rate of NO + CO reaction over silver on pressure of: (a) NO at 166°C and initial $P_{CO} = 14.5$ Torr; (b) CO at 62°C and initial $P_{NO} = 14.4$ Torr.

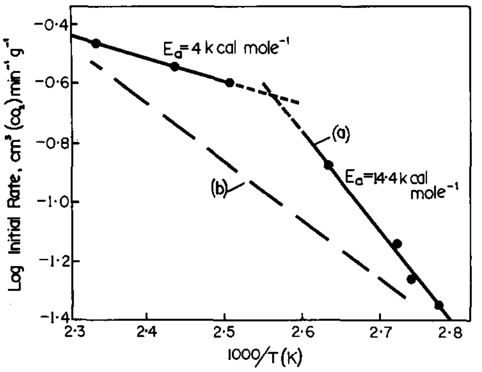

FIG. 2. Effect of temperature on rate of reaction over Ag: (a) measured for CO + NO with initial pressures of 12.5 Torr each; (b) calculated for CO + O_2 with initial pressures of 12.5 Torr each.

14 kcal mole^{-1} below 120°C and 4 kcal mole^{-1} above that temperature. The experimental pressure versus time curves, from which the data plotted in Fig. 2 were obtained, are shown in Fig. 3. At the higher temperatures, the rate fell off continuously with time as reactants were depleted. However, at the lower temperatures, the initial fall was linear, then the rate accelerated for some time before finally showing the fall off apparent at high temperatures.

CO + N_2O over Ag. A single experiment was carried out to test when N_2O would react to form N_2. Since the cryostat could not be used and no pressure drop accompanied reaction, repeated chromatographic sampling was used to follow the course of reaction. At 185°C and initial pressures of both reactants = 38 Torr, the reaction was found to proceed to completion in 2 hr with an initial rate of approximately 0.13 cm^3 (STP) CO_2 min^{-1}. This is approximately 4% of the rate of the CO + NO reaction under the same conditions (as estimated from extrapolation of the Arrhenius plot and assuming first order dependence on both CO and NO).

Adsorption of NO on Ag. An attempt was made to measure the amount of NO adsorbed on a freshly reduced 2.5 g sample of Ag at 100°C. Within an experimental error of ± 0.01 cm^3 (STP) no adsorption was detected. This indicates a surface coverage of less than 3%.

CO + NO over Au. The gold catalyst had a surface area of 0.86 ± 0.02 m^2/g which remained unchanged during the full series of experiments. After reduction in the standard way (in circulating H_2 at 150°C for 1 hr followed by evacuation for

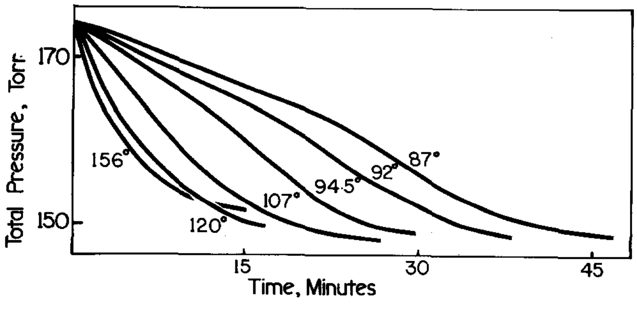

FIG. 3. Pressure–time curves for CO and NO reaction over Ag at various temperatures.

TABLE 2
EFFECT OF TEMPERATURE ON INITIAL RATE OF REACTIONS OVER GOLD

72 Torr CO + 36 Torr NO		38 Torr CO + 38 Torr O_2	
Temp (°C)	Initial rate[a]	Temp (°C)	Initial rate[a]
−20.8	0.10	−26.5	0.56
0	0.18	0	0.55
24	0.28	0	0.52
41	0.33	21.5	0.63
56	0.28	39.5	0.70
70	0.25	60.0	0.95
91	0.16		
96	0.12		

[a] In cm^3 (CO_2) min^{-1} g^{-1}.

0.5 hr) it was found to catalyze the CO + NO reaction to produce solely $CO_2 + N_2O$ at a convenient rate in the temperature range −20 to 80°C. The results of a series of such experiments, run in random order, are shown in Table 2. Below 41°C, the apparent activation energy was calculated to be about 3 kcal $mole^{-1}$ but above this the rate fell with increasing temperature and indeed no reaction at all was detectable above 140°C. Furthermore, reactions run at temperatures above 40°C slowed to an almost negligible rate before complete reaction had taken place. That these odd results resulted from changes in catalyst activity due to its reaction with NO, was shown in the following way.

Firstly, a reaction was commenced at 22°C and then the temperature rapidly raised to 140°C in 1 to 2 min. The reaction ceased immediately and did not restart again when cooled to 22°C. Standard pretreatment restored activity. Secondly, the initial rate (with $P_{CO} = P_{NO} = 40$ Torr) was measured on a freshly reduced surface at 22°C, the partly reduced mixture pumped out and replaced with 40 Torr of NO for 3 min at 200°C. After evacuation and cooling to 22°C, the catalyst was inactive for the CO + NO reaction but H_2 reduction did restore activity. However, when this second procedure was carried out with CO rather than NO, a subsequent CO + NO reaction proceeded at a rate identical to the initial one, i.e., CO did not poison the catalyst as NO did.

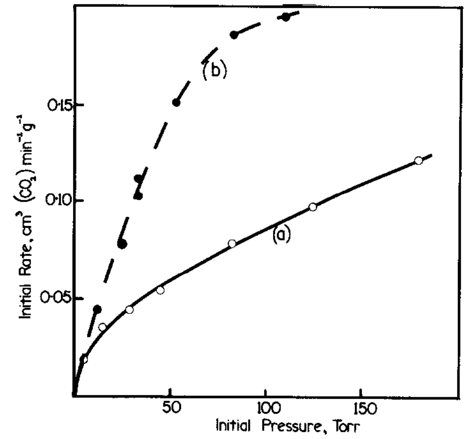

FIG. 4. Dependence of initial rate of CO + NO reaction over Au on: (a) P_{CO} at 22°C with initial $P_{NO} = 33.5$ Torr; (b) P_{NO} at 22°C with initial $P_{CO} = 82.5$ Torr.

Figure 4 shows the results of series of experiments in which freshly reduced catalyst was used and different initial pressures of CO and NO were employed. For both reactants, the initial rate was close to first order at low pressures but tended to a limiting value at the higher pressures.

CO + O_2 over Au. The dependence of the initial rate of this reaction on the individual reactant pressures over gold freshly reduced in the standard manner prior to reaction, is shown in Fig. 5. The curves have a very similar shape to the corresponding ones for the CO + NO reaction. During these series of experiments, the activity of the catalysts was quite reproducible except that slight increases were found to occur after prolonged exposure to the higher pressures of oxygen. A determination of the effect of temperature on initial rate carried out subsequent to the pressure dependencies gave the rather scattered results shown in Table 2. The apparent activation energy was not much greater than zero.

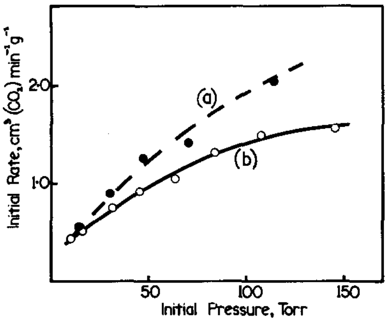

FIG. 5. Dependence of initial rate of CO + O_2 reaction over Au on: (a) P_{CO} at 0°C with initial P_{O_2} = 36 Torr; (b) P_{O_2} at 0°C with initial P_{CO} = 36 Torr.

CO + N_2O over Au. A reaction between N_2O (70 Torr) and CO (70 Torr) was followed chromatographically as the temperature was slowly raised from a starting value of −73°C. At 100°C a small amount ($\simeq 4\%$) of the N_2O was converted to N_2 with equivalent consumption of CO but the reaction then ceased and further temperature increases culminating in 4 hr at 300°C produced no further reaction. Subsequent H_2 reduction did not reactivate the catalyst but pretreatment with 80 Torr O_2 at 200°C followed by H_2 reduction did restore the original activity (as judged by the rate of the CO + NO reaction at 22°C).

DISCUSSION

Our results for the silver catalyzed oxidation of CO by O_2 agree with those of Benton and Bell (*15*) and Keulks and Chang (*14*) in that the reaction is first order in carbon monoxide and zero order in oxygen. We believe that the apparent slight deviation from strict zero order behavior implied by our results for the latter (Table 1) is an artifact arising because our measurements span the region from excess carbon monoxide to excess oxygen. This latter regime is known to give substantially higher rates (*15*). A different choice of conditions is also the probable reason why our value of 9.3 kcal mole⁻¹ for the activation energy with a stoichiometric CO/O_2 ratio is slightly lower than the 13 and 11 kcal mole⁻¹ reported previously for excess CO (*14,15*) and excess O_2 (*15*), respectively. In summary, there is nothing in our measurements to suggest that the mechanism over our catalyst differs from that suggested by Keulks and Chang (*14*), namely, that the kinetics are best interpreted in terms of the weak adsorption of CO on top of a strongly adsorbed oxygen layer.

However, the mechanism of the CO + NO reaction can not be interpreted in terms of an analogous model. The dependence of the rate on NO pressures passes through a maximum before tending to inverse first order, a situation readily interpreted only in terms of competition between NO and CO for the same surface sites. In fact, both the pressure and temperature dependencies are in qualitative accord with a Langmuir-Hinshelwood model (*19*), in which CO is weakly adsorbed and the strength of NO adsorption is moderate. Under these conditions, the full rate expression would be

$$\text{rate} = k\theta_{CO}\theta_{NO} = \frac{ke^{-E_T/RT}\, a_{NO}\, P_{NO}\, e^{Q_{NO}/RT} a_{CO}\, P_{CO}\, e^{Q_{CO}/RT}}{(1 + a_{NO}\, P_{NO}\, e^{Q_{NO}/RT})^2}, \tag{2}$$

where the a's represent adsorption coefficients, Q's heats of adsorption, P's pressure, k is a constant and E_T the true activation energy. At low P_{NO}, the second term in the denominator is small compared to 1 and the rate will be first order in both reactants. For large P_{NO}, the second term will dominate and the rate will become inverse order in NO. At high temperature, the second term is small and we have

$$\ln \text{rate} = -(E_T - Q_{NO} - Q_{CO})/RT + \text{const.}$$

At low temperature, the second term dominates and

$$\ln \text{rate} = -(E_T + Q_{NO} - Q_{CO})/RT + \text{const.}$$

Hence the apparent activation energy will be numerically larger at lower temperatures than at higher ones as observed. In fact, the difference will be $2Q_{NO}$. This provides an estimate of 5.2 kcal $mole^{-1}$ for the heat of adsorption of NO on silver.

There is one further piece of qualitative evidence in favor of this explanation. The stoichiometry of the reaction is such that during reaction consumption of nitric oxide is twice that of carbon monoxide. Hence in experiments with initial $P_{CO} = P_{NO}$ and at low temperature, the inverse order in NO would be expected to overwhelm the first order dependence on CO and the rate should increase for some part of reaction. The relevant pressure–time curves of Fig. 3 show just this behavior. As expected at the lower temperatures, the slope does change in the direction of increased rate; whereas at the higher temperature it falls off rapidly, as expected for a positive order dependence on both reactants.

Table 3 provides a comparison between the observed rates for the CO + NO reaction with those calculated by fitting Eq. (2) to the experimental points. The average difference of 22% (reducing to 15% if the values corresponding to the highest NO pressure are excluded) is not greatly different from the estimated experimental error (±15%), although the deviations are systematic. Attempts were made to describe the experimental results by other equations, the only one giving a significantly better fit having the unusual form, rate $= k\theta_{CO}\theta_{NO}^2$

$$= \frac{k'e^{-E\ /RT}\, a_{NO}^2\, P_{NO}^2\, e^{2Q_{NO}/RT} a_{CO}\, P_{CO}\, e^{Q_{NO}/RT}}{(1 + a_{NO}\, P_{NO}\, e^{Q_{NO}/RT})^3}. \tag{3}$$

This equation will similarly explain the results shown in Figs. 1, 2 and 3 on a qualitative basis and fits the rate data (Table 3) with an average error of 16% (reducing to 11% if data for the highest NO pressure are excluded). Equation (3) followed from the suggestion of Shelef *et al.* (*5a*) that the formation of N_2 (or N_2O) might require pairing of NO molecules. The accuracy obtainable in measurements described here is not sufficient to distinguish Eqs. (2) and (3) but we are currently carrying out measurements on the kinetics of the CO + NO reaction over silver supported on silica in the hope of distinguishing between them.

TABLE 3

EXPERIMENTAL AND CALCULATED RATES OF CO + NO REACTION OVER SILVER AS A FUNCTION OF NO PRESSURE

NO pressure (Torr)	Rates (cm³ (CO_2) min^{-1} g^{-1})		
	Observed	Calcd,[a] Eq. (2)	Calcd,[b] Eq. (3)
6.5	0.103	0.120	0.093
12.3	0.146	0.181	0.175
14.4	0.238	0.196	0.197
29.0	0.289	0.248	0.258
38.2	0.316	0.255	0.261
51.5	0.257	0.252	0.250
75.3	0.247	0.233	0.220
111.8	0.170	0.201	0.180
149.5	0.143	0.174	0.149
195.5	0.070	0.147	0.123

[a] Rate $= 0.0248\, P_{NO}/(1 + 0.0243\, P_{NO})^2$.

[b] Rate $= 0.00564\, P_{NO}{}^2/(1 + 0.0565\, P_{NO})^3$.

Our results for the CO + O_2 reaction over gold agree with those of Daglish and Eley (*17*) in showing a near zero activation energy but disagree somewhat in the pressure dependencies. Those workers found zero order dependence on both reactants even at pressures below 1 Torr, whereas ours only tend to that behavior at pressures over 100 Torr. The discrepancy may be due to the different temperature and catalyst forms employed, Daglish and Eley (*17*) using wires at 200–300°C, in contrast to this work with sponge below 100°C. The similarity in pressure dependencies and activation energies for the CO + O_2 and CO + NO reactions over gold in our work suggest that they proceed by similar mechanisms. (By this we mean that they involve corresponding surface sites and have analogous rate-determining steps.) The shape of the pressure dependence curves conforms approximately to a Langmuir shape in the regime where adsorption of neither reactant approaches saturation. Thus it is not possible to decide if the two reactants compete for sites or adsorb on separate sites. There is some old evidence (*20*) to suggest that gold does have two classes of sites.

Our measurements definitely show that the pronounced self-poisoning of the $CO + NO$ reaction over gold is attributable to some reaction of NO with the surface. In fact, the prime cause may be product N_2O since, while the catalyst did show slight initial activity for the $CO + N_2O$ reaction, this poisoned even more readily than the $CO + NO$ one. This result is perhaps not surprising since MacDonald (*21*) has found the decomposition of N_2O itself over gold is self-poisoned by product oxygen.

On the other hand, silver does catalyze the $CO + N_2O$ reaction effectively albeit at a much lower rate than the $CO + NO$ one. It is quite possible that the small amount of N_2 produced during the latter may have come via N_2O.

Although this work was not intended to assess the possible use of Ag or Au as catalysts for control of NO emissions from automobiles, it is worthwhile to briefly discuss our findings in this context. Under the conditions we employed with gold, $CO + NO$ was always at least one order of magnitude slower than $CO + O_2$ and furthermore, the catalyst poisoned rapidly. To facilitate a comparison with silver, the observed pressure dependencies for the $CO + O_2$ reaction was used to convert our temperature dependence results to the same pressures employed with the $CO + NO$ reaction. The results are shown as the broken line in Fig. 2, which predicts that $CO + NO$ should be faster than $CO + O_2$ over the temperature range 80 to 162°C. However, since the kinetics of the latter reaction indicate strong chemisorption of O_2, it is unlikely that this situation would be sustained if CO, NO and O_2 were reacted simultaneously. Hence our results suggest that neither Ag nor Au is suitable for selective reduction of NO by CO in the presence of O_2. However, our results are not necessarily relevant to the very much higher temperatures usually used for automotive tests.

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