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Oxidation of Carbon Monoxide on Copper Catalysts

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The reaction between carbon monoxide and oxygen over both clean and oxygen-poisoned copper has been examined. A low-pressure flow reactor permitted measurement of both adsorption and reaction. In addition, thermodesorption measurements were made; oxygen-18 isotope exchange was studied and infrared absorption spectra were taken. The reaction over metallic copper is fast and limited by the desorption of carbon dioxide. On oxygen-poisoned copper, which amounts to a cuprous oxide covered surface, the reaction is slower and a stable species, "CO_3," is formed on the surface. The mechanisms of the reactions on the two different surfaces are discussed.

I. INTRODUCTION

In the course of studies on the oxidation of carbon monoxide on cuprous oxide, it was discovered that copper metal was an exceedingly active catalyst. Jones and Taylor (*1*) first noticed this effect in 1923. However, this system was not studied further, largely because one of the reactants—oxygen—is also a poison for the catalyst. However, running the reaction at low pressures, it is possible to study the system for long periods of time before the catalyst is poisoned.

II. EXPERIMENTAL

The apparatus and copper samples used in this study are the same as those reported in the paper on carbon monoxide adsorption (*2*).

In order to follow the reaction before the sample became poisoned, and in order to determine both the extent of the reaction and the amount of each gas adsorbed, a low-pressure flow reactor was constructed.

The system was operated in the following way. A gas mixture was prepared and introduced into a gas reservoir. A calibrated Granville-Phillips leak valve admitted gas from the reservoir to the sample tube. The sample tube consists of a 6-mm Pyrex tube wound in a spiral to fit in the Dewar furnace. Copper shot sieved for a uniform particle size of 1 mm, filled the tube to a length of 40 cm. A second calibrated leak let the gas from the sample tube into the omegatron mass spectrometer. Typical pressures in each section were: 10 Torr in the reservoir, 10^{-2} Torr in the sample tube, and 10^{-6} Torr in the mass spectrometer. There is no appreciable back flow through the leaks.

Thermodesorption runs were carried out by closing the inlet valve, opening the valve to the mass spectrometer, and heating the sample at a constant rate as discussed previously (*2*).

In order to measure the composition of gas mixtures accurately, a differentially pumped omegatron mass spectrometer was constructed. This omegatron is based on a design of Wagener and Marth (*3*). Their design was altered by placing the filament in a separate chamber. This chamber consists of a flattened stainless steel tube containing the filament and pumped by a small ion pump. There is a 0.020-inch hole by the filament for the electron beam. This tube is inserted in the omegatron envelope in the normal place of the filament. The whole structure is set on a gold gasket flange so

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that the filament can be replaced without breaking open the tube. The filament is a thorium-coated iridium ribbon. A direct current power supply was constructed after it was discovered that an alternating current caused the filament to vibrate in the magnetic field, seriously shortening its life.

The reason for the differentially pumped filament chamber was to keep the interactions of the gases with the filament from distorting the mass spectra. For example, it is almost impossible to keep carbon from forming on the filament. When oxygen is introduced, a large carbon monoxide peak will also occur in the mass spectra. This effect is completely removed by using the differentially pumped filament.

Isotope exchange studies were carried out with this apparatus, using a sample of 98% O_2^{18} obtained from the Volk Radio Chemical Company.

Infrared absorption measurements were made in the same cell discussed before (*2*).

III. Results

Copper metal which has been activated by several oxidation-reduction cycles using either hydrogen or carbon monoxide for reduction, becomes a very active catalyst. Because oxygen poisons this catalyst, it has been studied here principally with excess carbon monoxide. Carbon dioxide is produced at temperatures down to —130°C. Above this temperature most of the oxygen reacts to form carbon dioxide and the remainder slowly poisons the surface. The amount of carbon dioxide produced in the low-pressure flow reactor remains constant for several hours before the surface becomes poisoned.

Table 1 shows the per cent of the oxygen which was converted to carbon dioxide in a 5:1 carbon monoxide rich mixture. The rest of the oxygen remained on the copper. Thus, the surface is stable in this reaction mixture at +100°C and becomes slowly poisoned at lower temperatures.

TABLE 1
Percentage of Oxygen Converted to Carbon Dioxide

Temperature (°C)	Per cent oxygen converted to carbon dioxide
−100°	75
25°	90
+100°	100

The results of an experiment which illustrates many features of this system are shown in Fig. 1. The omegatron mass spectrometer is an accurate instrument for measuring composition of gas mixtures. However, due to difficulties in maintaining an absolute calibration from day to day, only relative partial pressures are plotted in these results. A reaction mixture was introduced into the flow system at —84°C. The first compound to appear in the mass spectrometer was carbon dioxide. The reaction between carbon monoxide and oxygen was rapid while the surface was still rather bare. As the surface became covered with carbon monoxide, the pressure of this gas in the reactor rose and a quasi-steady state was reached and maintained for the first period of the experiment. During the second period, two features are noted. At the beginning of this period the temperature was decreased. This resulted in increased adsorption of carbon monoxide and a decrease in the production of carbon dioxide. Ordinarily the pressure of carbon monoxide and carbon dioxide would return to nearly their original values as a new quasi-steady state was established. However, at this point the coverage of oxygen had increased to the point where the surface was becoming noticeably poisoned. This was evidenced both by the decreased rate of production of carbon dioxide and by the appearance of oxygen in the gas phase.

In Period 3 the entrance leak was closed and the gas flow stopped. The fall in the oxygen pressure is rapid, corresponding to removal from the gas space only. Both carbon monoxide and carbon dioxide are more slowly removed from the surface. The actual amounts of each component adsorbed and removed from the surface are given in Table 2. Note that at the end of Period 3, 54 units of carbon monoxide are adsorbed on the surface and 30 units of oxygen (as atoms). The surface at this point was saturated with carbon monoxide,

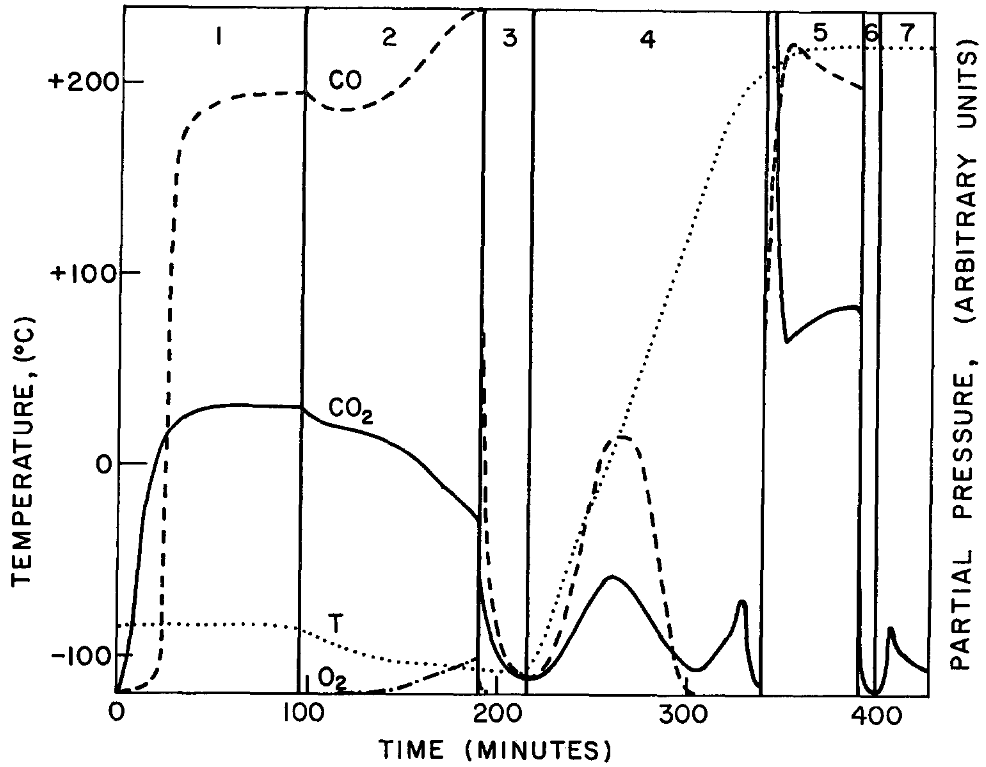

FIG. 1. Partial pressures during reaction and thermodesorption from a copper catalyst.

TABLE 2
Amounts of Gas Components Taken Up or Given Off by Copper Catalysts during Run Shown in Fig. 1

	In		Out					Net	
	CO	O	CO	CO_2	O	CO + CO_2	O + CO_2	CO	O
Periods 1–3	370	138	214	102	6	316	108	+54	+30
Period 4	0	0	31	19	—	50	19	−50	−19
Periods 5–7	112	40	66	48	—	114	48	−2	−8
Total	482	178	311	169	6	480	175	+2	+3

but had not nearly reached saturation with oxygen. Although oxygen adsorbs as a molecule at this temperature (*4*), the data in Table 2 have been listed as atoms of oxygen to simplify the material balance.

Thermodesorption was carried out during Period 4. The results are that carbon monoxide desorbs with a thermodesorption peak at +23°C, and also that the carbon monoxide apparently reacts with adsorbed oxygen to produce a carbon dioxide thermodesorption peak at the same temperature. Above 125°C there is no carbon monoxide left on the surface, but there is some carbon dioxide.

The high-temperature treatment consists of passing a reaction mixture over the sample during Period 5, outgassing during Period 6, and passing a relatively high pressure of carbon monoxide over the sample during Period 7. These treatments were done to clean the surface in order to obtain a material balance. The accuracy of the experiment is shown by the fact that the balance for carbon monoxide agreed to within 0.4% of the total gas adsorbed and for oxygen to within 1.7%.

Note that during the high-temperature treatment a net of 8 units of O was desorbed and 2 units of CO. This could be held as 2 units of "CO_3" and 4 units of "O." The high-temperature thermodesorption peak of carbon dioxide contained about 5 units of carbon dioxide so there could have been 6 to 7 units of "CO_3" on the surface at 125°C. This material balance supports the theory (*5*) that CO_2 desorbing at high temperature is held as a CO_3 complex.

Figure 2 shows the course of this reaction at room temperature. At this temperature the carbon monoxide coverage is small and the pressure of carbon monoxide rises rapidly after the introduction of the reaction mixture. As the carbon dioxide production increases, more carbon monoxide is consumed, and the carbon monoxide pressure goes through a maximum and decreases. This result shows that the rate of carbon dioxide production depends on the amount of oxygen adsorbed and not just on the carbon monoxide alone. At this temperature a second steady state rate is approached by the reaction after the catalyst is poisoned.

Figures 3 and 4 are the result of an attempt to assess the activity of adsorbed oxygen versus that of adsorbed carbon monoxide on copper at −90°C. In each experiment the amount adsorbed is the area between the curves labeled "in" and "out," representing the rate of flow of gas into and out of the catalyst chamber. The important observation is that adsorbed carbon monoxide seems to be more reactive toward oxygen than adsorbed oxygen is toward carbon monoxide. Carbon dioxide appeared in the gas phase almost immediately when oxygen was added to adsorbed carbon monoxide. When carbon monoxide was added to adsorbed oxygen, there was quite a period before carbon dioxide appeared. On the other hand, in this run carbon dioxide continued to be produced for a longer time.

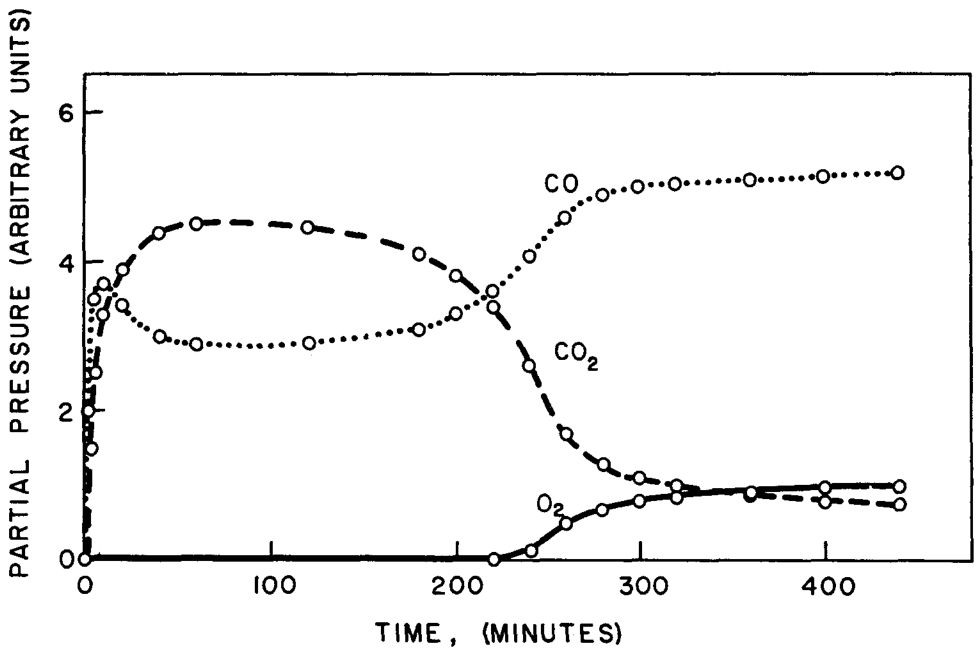

FIG. 2. Rate of carbon monoxide oxidation on active copper catalyst in flow system at room temperature.

The obvious interpretation of these re-

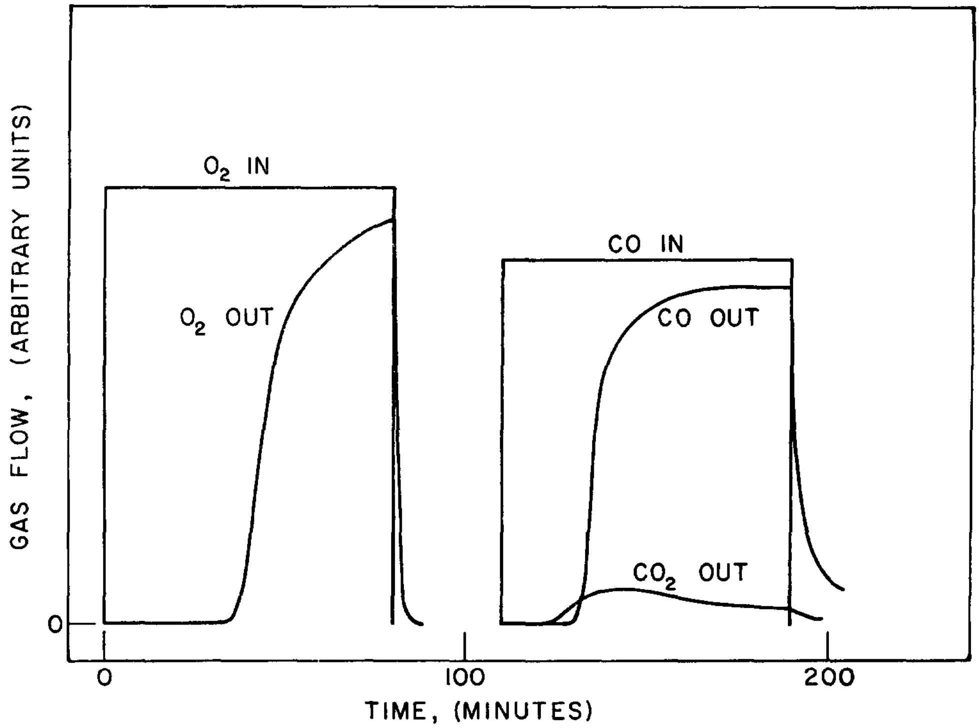

FIG. 3. Adsorption of O_2 followed by adsorption and reaction of CO at —90°C.

sults is that carbon monoxide reacts with adsorbed oxygen to form a complex which decomposes on addition of more carbon monoxide. When there is plenty of carbon monoxide, each oxygen can be converted to carbon dioxide immediately, but with excess oxygen the carbon dioxide is initially tied up in the complex.

Addition of carbon monoxide and oxygen at —196°C followed by thermodesorption produced a carbon dioxide thermodesorption peak at —90°C, whereas that due to carbon dioxide alone occurred at —110°C. When the surface became poisoned, carbon monoxide and oxygen caused a carbon dioxide thermodesorption peak in the 150° to 200°C region. Adsorption of carbon dioxide plus oxygen caused a thermodesorption peak in the same region.

Further information can be had by introducing oxygen-18 into the reaction mixture. Figure 5 shows the results of such a run. In this run the sample was cooled to —100°C and carbon monoxide passed over it until a steady pressure was reached.

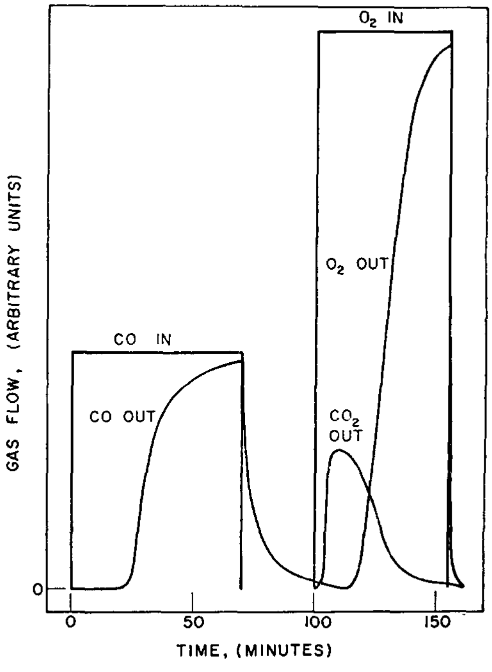

FIG. 4. Adsorption of CO followed by adsorption and reaction of O_2 at —90°C.

Oxygen-18 was then added to the reaction mixture to about 20% of the carbon monoxide. After a steady state was reached, the temperature was increased to about 200°C. The results are shown in Fig. 5. Several important facts can be obtained from these results. At no time is there any mass 30 in the reaction mixture even though adsorption and desorption of carbon monoxide is occurring. At −100°C the carbon dioxide that results from this reaction is completely mixed, isotopically. A careful calibration of the mass spectrometer at this time gave:

mass 44—24.3%
mass 46—50.5%
mass 48—25.1%

Within the accuracy of the instrument this is two parts of mass 46 for one part each of masses 44 and 48.

On heating there is some thermodesorption of carbon monoxide and carbon dioxide. As the temperature increases, the amount of mass 44 in the gas increases with respect to mass 48. (In Fig. 5 CO_2^{I} refers to the isotopic mixture produced by the reaction of CO and O_2^{18}. CO_2^{II} refers to additional CO_2 formed from CO and O^{16}. In all the figures, absence of a superscript indicates oxygen-16.) This indicates that the oxygen-18 is exchanging with oxygen-16 that was not previously removed from the sample by reduction at 200°C.

If the reaction proceeded as

$$CO + O_{ads}^{18} \rightarrow COO^{18} \quad (1)$$

all of the carbon dioxide would be mass 46.

If on the other hand a mechanism such as

$$CO + O_{2(ads)}^{18} \rightarrow COO_{2(ads)}^{18} \quad (2a)$$

$$COO_{2(ads)}^{18} + CO \rightarrow C_2O_2O_2^{18} \rightarrow aCO_2 + bCO_2^{18} + cCOO^{18}, \quad (2b)$$

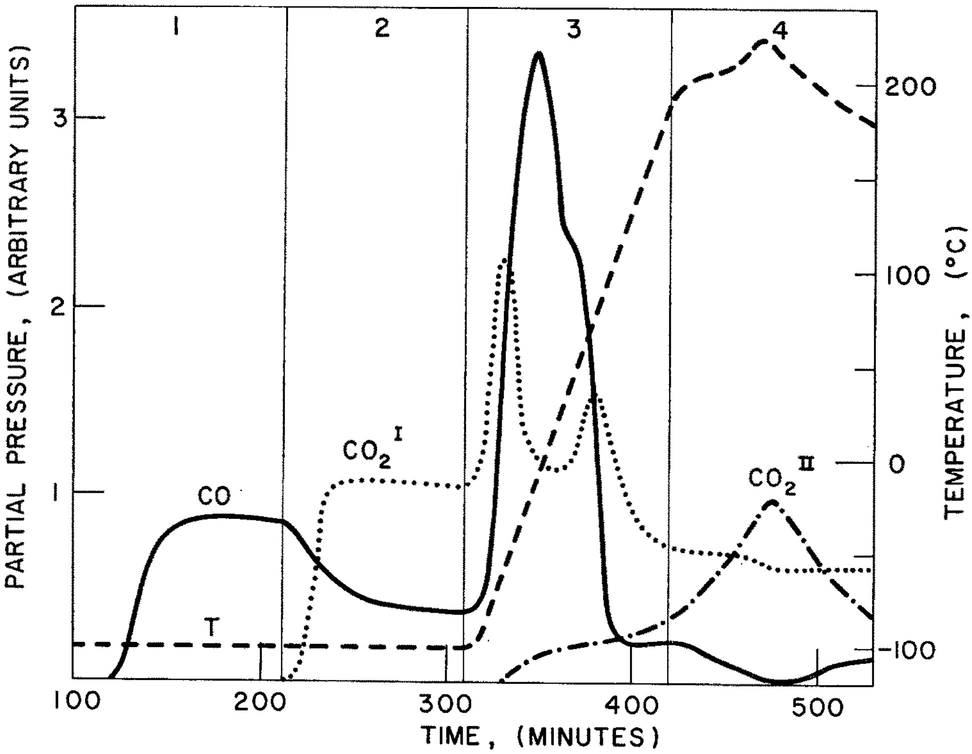

FIG. 5. Partial pressures over copper metal catalyst during low-temperature reaction and heat treatment. CO_2^{I} is isotopic mixture derived from $CO + O_2^{18}$ CO_2^{II} is derived from $CO + O^{16}$. Period 1, carbon monoxide only. Period 2, oxygen-18 added. Period 3, steady heating rate. Period 4, nearly constant temperature.

with random extraction of oxygen isotopes, would give

$$[COO^{18}] = 4[CO_2] = 4[CO_2{}^{18}].$$

If there is an equilibrium

$$CO_2{}^{18} + CO_2 \longleftrightarrow 2COO^{18},$$

the concentration can be obtained from the equilibrium constant. Assuming no difference in energy between the two sides of the equation, random mixing would give

$$[COO^{18}] = 2[CO_2] = 2[CO_2{}^{18}]$$

or

$$\frac{[COO^{18}]^2}{[CO_2][CO_2{}^{18}]} = 4.$$

During the reaction shown in Fig. 5, as oxygen-16 was obtained from the interior of the catalyst at higher temperatures, the ratio of mass 44 to mass 48 changed from 1 to more than 15 while the equilibrium constant remained equal to 4.0 ± 0.2. Thus the reaction intermediate in the carbon monoxide oxidation reaches complete isotopic equilibrium.

A carbon dioxide, oxygen-18 mixture was passed over the catalyst. It was a nearly one-to-one mixture. Only a small amount of mass 46 appeared. After 10 hr, oxygen was appearing in the gas phase, but the amount of mass 46 was about the same. Mass 46 was 14% of mass 44 at 14°C and 2% at —100°C. Thus oxygen and oxygen in the gaseous carbon dioxide exchange under these conditions to a slight amount. These results give an activation energy for this exchange of 1.5 kcal/mole. There is doubt that a true steady state was reached, however, so this activation energy cannot be treated as very accurate.

While the sample was still at —100°C, the carbon dioxide and oxygen-18 were removed from the system and replaced with carbon monoxide. After saturating the surface with carbon monoxide, it was removed and a thermodesorption run was carried out. This treatment is shown in Fig. 6. Initially mass 44 was in larger concentration than mass 48. This indicates that $CO_2 + O_2$ on the surface were only partially mixed, and that carbon monoxide caused the desorption of carbon dioxide rather than reacting with oxygen. During the thermodesorption the ratios changed until mass 48 was larger than mass 44. This indicates an attack of carbon monoxide on the adsorbed oxygen.

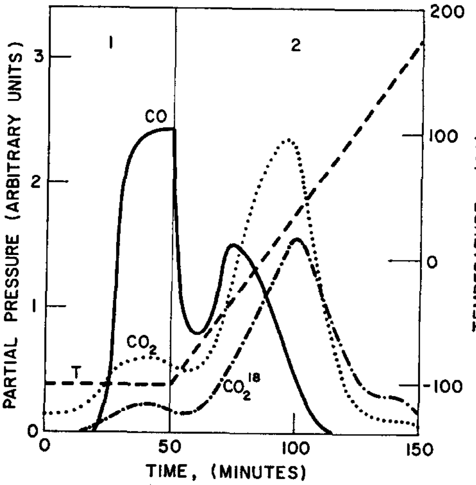

FIG. 6. Addition of carbon monoxide at —100°C and thermodesorption from a copper metal catalyst pretreated with $CO_2{}^{16} + O_2{}^{18}$. Period 1, carbon monoxide being added. Period 2, carbon monoxide shut off and temperature raised.

About four monolayers of oxygen-18 were adsorbed and incorporated at room temperature to produce a cuprous oxide surface. Incidentally the rate of adsorption was measured and was found to be first order in oxygen for this amount taken up. Carbon

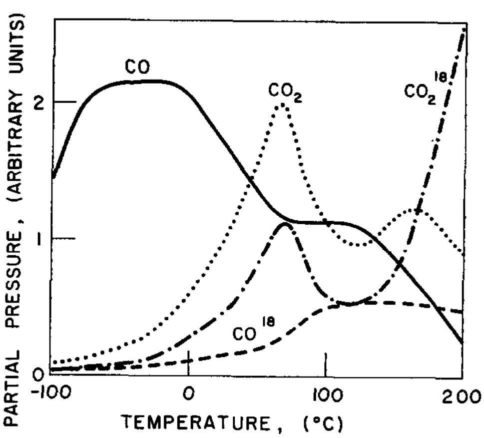

FIG. 7. Reaction between CO and O_2 on an O^{18} covered surface during temperature rise.

monoxide and oxygen-16 were passed over this surface at −100°C, and then the sample was gradually heated to +200°C with the gases still flowing. The results during the heating are shown in Fig. 7. The formation of cuprous oxide reduces the activity of the catalyst. This treatment also left the surface more or less saturated with oxygen. At −100°C considerable carbon monoxide is adsorbed but little oxygen. As the temperature increases, thermodesorption of both carbon monoxide and carbon dioxide is noticed as well as reaction. In addition mass 30 becomes noticeable and is actually greater than mass 28 at the highest temperatures. Thus carbon monoxide exchanges with oxygen on cuprous oxide while on copper it only reacts with it to produce carbon dioxide. The exchange actually occurs before reaction takes place. The ratio of mass 44 to mass 48 starts high, indicating reaction with oxygen-16 from the gas as well as the pretreated oxygen-18. Later this ratio decreases as oxygen-18 comes into play exchanging with the carbon monoxide as well as reacting. Later than shown in this figure, while holding the temperature at 200°C, this ratio increases again as the available oxygen-18 becomes used up.

The exchange of oxygen with carbon monoxide and carbon dioxide on an oxygen-covered catalyst agrees with the results obtained by Winter (*6*) on cuprous oxide in that he found exchange over this temperature range.

It has been shown (*7, 8*) that when carbon dioxide and oxygen or carbon monoxide and oxygen adsorb on nickel or nickel oxide, infrared absorption bands due to

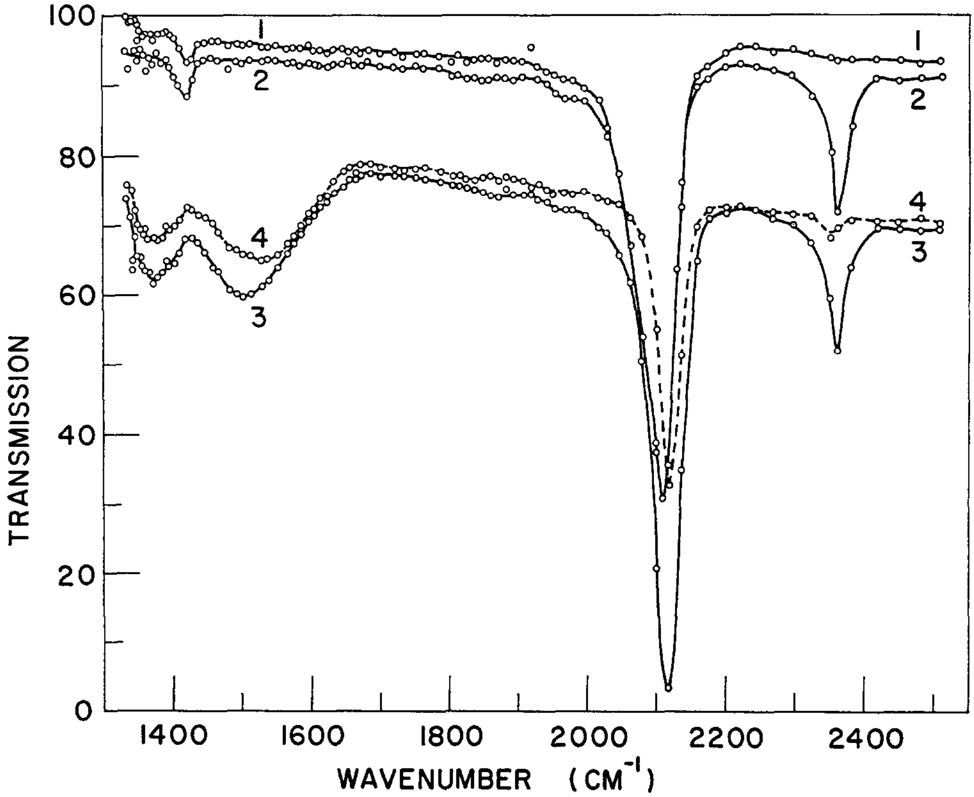

FIG. 8. Infrared spectra during reaction of carbon monoxide and oxygen at 25°C and 110 Torr (20% copper on Cabosil). 1. In pure CO, 1 hr; 2. ½ hr after adding O_2; 3. 14 hr after adding O_2; 4. 1 hr after gas removed.

surface complexes occur in the 1300 to 1600 cm^{-1} region. Also, the formation of a surface "CO_3 complex" has been postulated as a part of the mechanism of oxidation of carbon monoxide on cuprous oxide (*5*). An attempt was therefore made to observe such a complex on copper or cuprous oxide by infrared absorption. A 20% copper-silica sample (*2*) was used.

Because of the background atmospheric water spectrum below 1900 cm^{-1} and because the transmission of the silica decreases rapidly below 1400 cm^{-1}, it is necessary to divide the transmission of the sample with adsorbent by the transmission of the sample before adsorption. Figure 8 shows spectra of a sample after addition of carbon monoxide and oxygen at room temperature. The first spectrum was taken after carbon monoxide alone was added. This shows the characteristic band at 2110 cm^{-1}. There is also a weaker band at 1420 cm^{-1}.

When oxygen is added to the carbon monoxide gas, the transmission decreases over the whole range. This is due to the oxidation of the copper. The same effect is seen whenever oxygen is added to a copper sample. Almost immediately a band appears at 2350 cm^{-1}. This is due to physically adsorbed carbon dioxide and is evidence that oxidation of the carbon monoxide is taking place.

In the spectrum taken after 14 hr, two bands appear at about 1375 cm^{-1} and 1520 cm^{-1} similar to those observed in the nickel system. The whole spectrum has decreased due to further oxidation of the

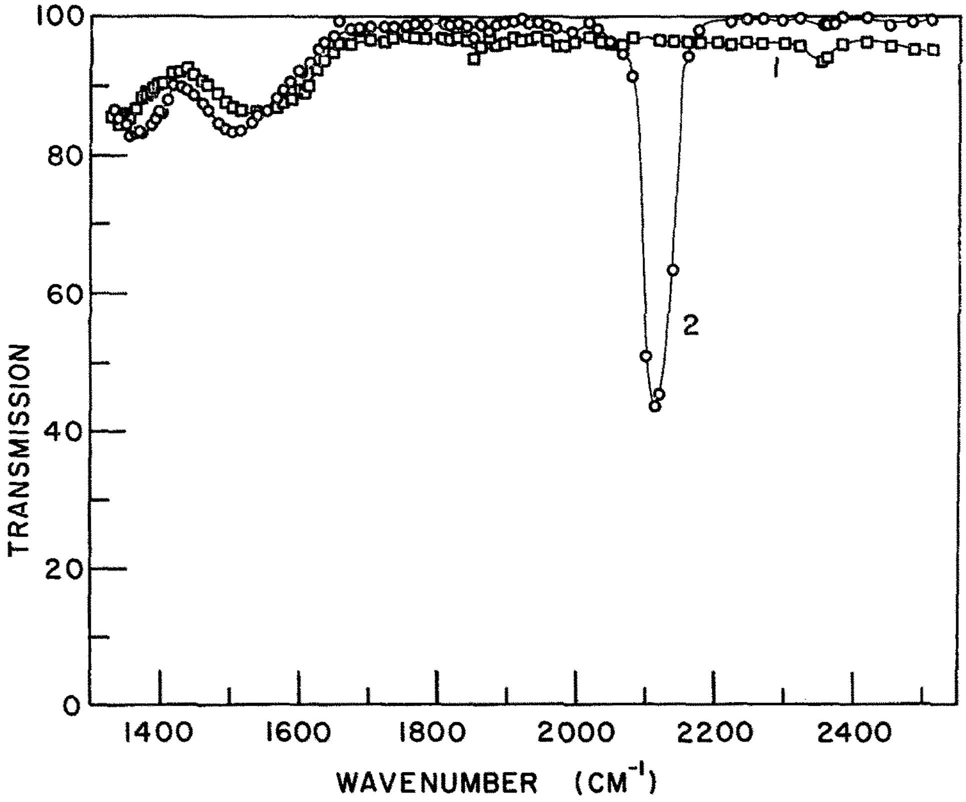

FIG. 9. Infrared spectra during reaction of carbon dioxide and oxygen with carbon monoxide. (20% copper on Cabosil); 1. 75 torr O_2 + 75 torr CO_2 added 4 hr then removed ½ hr. 2. CO added 14 hr then removed ½ hr.

copper. The carbon monoxide band at 2110 cm^{-1} has become stronger and now appears at 2115 cm^{-1}. The increase in the carbon monoxide absorption band indicates a slow adsorption. After evacuating the cell the physically adsorbed carbon dioxide disappears and the band due to carbon monoxide has decreased and moved to 2120 cm^{-1}. The bands at 1375 and 1520 decrease by a small amount.

To determine whether these bands are due to a "CO_3 complex," the same as is formed with carbon dioxide and oxygen, and to see whether carbon monoxide removes this complex as it has been suggested (*5*), the following experiment was carried out. Carbon dioxide and oxygen were added to the sample. This is shown in Fig. 9. The reason the transmission is high compared to that in Fig. 8 is that the blank was already oxidized copper. After 4 hr the carbon dioxide was removed and a spectrum obtained. This showed evidence for two bands which were at somewhat different frequencies than those determined with carbon monoxide and oxygen. These occur at less than 1350 cm^{-1} and at 1550 cm^{-1}. After this carbon monoxide was added, left 14 hr, and then removed. The spectrum shows the normal carbon monoxide band at 2115 cm^{-1} and the appearance of the bands at 1375 cm^{-1} and 1520 cm^{-1}. It is apparent that carbon monoxide and carbon dioxide both form surface complexes with oxygen. These complexes have somewhat different character. Carbon monoxide reacts with the carbon dioxide complex leaving a spectrum characteristic of the carbon monoxide complex.

IV. DISCUSSION

Oxidation of Carbon Monoxide on Copper Metal

These results lead to a plausible reaction mechanism as expressed by the following equations

$$CO(g) \rightarrow CO^+ + e^- \qquad (1)$$

$$O_2(g) + 2e^- \rightarrow O_2^{2-} \qquad (2)$$

$$CO^+ + O_2^{2-} \rightarrow CO_3^- \qquad (3)$$

$$CO_3^- + CO^+ \rightarrow C_2O_4 \qquad (4)$$

$$C_2O_4 + O_2^{2-} \rightarrow 2CO_3^- \qquad (5)$$

$$C_2O_4 \rightarrow 2CO_2 \rightarrow 2CO_2(g) \qquad (6)$$

$$O_2^{2-} \rightarrow 2O^- \qquad (7)$$

All of the species written above are surface species unless specified as gaseous species.

The basis of these reaction equations is provided by the following considerations.

1. The adsorption of CO has been discussed fully in a previous paper (*2*). Carbon monoxide adsorbs in both a positive state and a negative state. Since the positive state adsorbs first, it is assumed to be reactive towards oxygen since reaction occurs at low coverages. The formal charge of +1, as given in Eq. (2), is not to indicate that the bonding is entirely ionic, but to signify the sign of the ionic component. Adsorption of carbon monoxide is fast at —196°C and would not have limited the rate of the reaction.

2. The adsorption of oxygen is also fast at low temperatures, and occurs as molecular oxygen (*4*). The formal charge of —2, as given in Eq. (2), is written primarily because the surface potential due to oxygen is twice that for carbon monoxide (*9*) and because the surface potential due to one part of O_2 and two parts of CO approaches zero (*9*).

3. Oxygen dissociates to oxidize copper above —30°C (*10*). Under conditions of the catalytic reaction there is a slow poisoning of the surface at —100°C. It is suggested that dissociation of oxygen, as given in Eq. (7), occurs to a small extent at —100°C. At room temperature copper may be oxidized to several layers (*4*).

4. Carbon dioxide does not chemisorb on clean copper metal. It does have a heat of adsorption of about 10 kcal/mole in the physically adsorbed state. The desorption of carbon dioxide after CO and O_2 have been adsorbed at —196°C gives only a slightly higher activation energy than for thermodesorption of adsorbed CO_2. This suggests that Reaction (6) is the rate-limiting step in the reaction and that the

decomposition of C_2O_4 takes only 1 or 2 kcal/mole.

5. The isotope exchange results lead to the conclusion that there is complete mixing in the intermediate state, but that there is no exchange with adsorbed CO. (There could be exchange with adsorbed O_2 since it does not desorb and hence exchange would not be detected.) The series of reactions (3) to (5) will result in this mixing, especially if reaction (6) is rate limiting. A chain reaction provides the isotope mixing in the product without any isotope exchange with the reactants.

6. These series of chain reactions also provide an explanation of the results that on an oxygen-covered surface the reaction is slowed down, whereas it is fast on a carbon-monoxide–covered surface. On an oxygen-covered surface the intermediate CO_3^- would pile up until sufficient CO^+ were present to complete the series of reactions.

7. The intermediates CO_3^- and C_2O_4 should be observable by infrared absorption spectra at low temperatures. Unfortunately, at room temperature, reaction (6) is fast enough so that there is only a low coverage of CO_3^- or C_2O_4. A higher coverage of CO_3^- could be obtained in excess oxygen. However, the surface would also poison rapidly, and the presence of CO_3^- on clean copper could not be observed.

8. At room temperature the amount of CO adsorbed is small. Thus it was possible to note that the reaction using up CO increases as the O_2^{2-} coverage increases. This indicates that oxygen adsorbs before it reacts. At —90°C oxygen reacts with adsorbed CO^+ as does carbon monoxide with adsorbed O_2^{2-}. Thus it appears that the likely reaction at all temperatures is between adsorbed molecules as given in reaction (3).

9. This reaction scheme provides a mechanism whereby very strong bonds, those holding both the oxygen and carbon monoxide molecules together, can be broken by providing complexes, CO_3^- and C_2O_4 in which the bonds may shift to new partners with little activation energy. Once an oxygen molecule is broken by reaction with the copper, a higher temperature is required for carbon monoxide to react.

Oxidation of Carbon Monoxide on Oxygen-Poisoned Copper (Cuprous Oxide)

An oxygen-poisoned copper catalyst is indistinguishable from cuprous oxide as far as the present studies go. When the catalyst is poisoned, the reaction proceeds at a reasonable rate only near room temperature where a definite layer of cuprous oxide will eventually form. Reaction Eqs. (8) to (13) comprise a reaction scheme for carbon monoxide oxidation on a cuprous oxide surface.

$$CO(g) + h^+ \rightleftarrows CO^+ \tag{8}$$

$$O_2(g) \rightarrow 2O^- + 2h^+ \tag{9}$$

$$O^- + CO^+ \rightarrow CO_2 \tag{10}$$

$$CO_2 + O^- \rightarrow CO_3^- \tag{11}$$

$$CO_3^- + CO \rightarrow 2CO_2 \tag{12}$$

$$CO_2 \rightleftarrows CO_2(g) \tag{13}$$

The oxidation of carbon monoxide on cuprous oxide has been discussed in detail by Stone (*5*). Most of the data presented here are in agreement with the mechanism presented by him. His reaction scheme is similar to that shown in reactions (8) through (13) except that steps (10) and (11) are combined, forcing all the reaction to go through the CO_3 complex. The thermodesorption and infrared results are further evidence for a CO_3 complex. However, it is felt that the reaction scheme presented here is preferable to his since no evidence has been found that the reaction goes only through the CO_3 complex.

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