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Surface Interactions Between Chemisorbed Species on Platinum: Carbon Monoxide, Hydrogen, Oxygen, and Methanol

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By means of ultrahigh vacuum techniques, including thermal flash desorption and residual gas analysis, the surface interactions of single-component and multicomponent adsystems were examined. The gases studied included CO, H_2, O_2, and CH_3OH in contact with a polycrystalline platinum ribbon. Three binding states were observed for CO, each of which exhibited high sticking probability, relative to that of oxygen or hydrogen. Carbon contamination of the Pt surface greatly reduced the adsorption rate of oxygen. Competitive sorption studies revealed displacement of chemisorbed hydrogen by carbon monoxide. Preadsorbed oxygen interacted readily with gaseous carbon monoxide, but very slow reaction was noted in the case of preadsorbed CO interacting with gaseous oxygen. During the methanol decomposition the surface interactions exhibited similar characteristics to those observed for the hydrogen-carbon monoxide. The results are interpretable in terms of the formation of a bound three-atomic intermediate species, such as [HCO], produced by hydrogen abstraction from the methyl group during methanol decomposition, and subsequent reaction with hydrogen adatoms by way of rupture of the H-CO bond to yield H_2 and CO. These surface studies on the molecular level elucidate some of the elementary steps involved in the catalytic reactions involving methanol.

INTRODUCTION

Of special interest to the study of catalytic processes is the influence of the substrate on the short-range and long-range interactions between adsorbates. To investigate reactions between neighboring surface species, it is useful to employ molecular flow sorption techniques involving ultrahigh vacuum flash desorption and constant-flow or constant-pressure adsorption. Under well-defined conditions of surface structure and surface cleanliness, the results of such studies elucidate on a molecular level the kinetics and mechanisms of different adsystems undergoing surface-catalyzed reactions.

In this paper we examine in detail the processes occurring during the decomposition of methanol on a polycrystalline platinum surface. In addition we relate the results so obtained to the properties of single-component and multicomponent adsorbate systems involving carbon monoxide, hydrogen, and oxygen, some of which are the products of methanol decomposition.

EXPERIMENTAL DETAILS

Apparatus and Materials

All the measurements were conducted in an ultrahigh vacuum system (*1*) (base pressure $<1 \times 10^{-9}$ Torr) equipped with a quadrupole mass spectrometer (AEI) and Bayard-Alpert gages for determination of gas composition and gas pressure (Fig. 1). The platinum catalyst in the form of a U-shaped foil ($5.0 \times 0.5 \times 0.013$ cm^3), was

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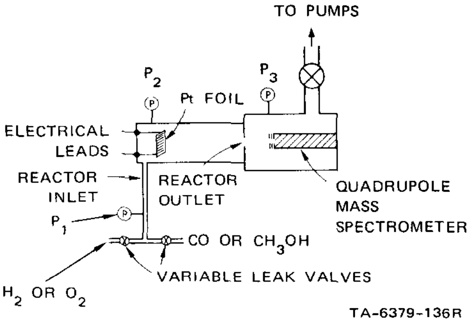

FIG. 1. Schematic diagram of apparatus (*P*-ion gages).

welded to tungsten leadthroughs and was mounted in a cylindrical glass reactor (3.8 cm in diameter and 9.5 cm in length). Variable leak valves and an ion pump were used to establish the desired pressures both upstream and downstream of the flow reactor. The flow rate through the reactor was adjusted by the setting of the leak valve and the inlet conductance at the entrance to the reactor, and a copper disk with a circular orifice (diameter of 0.63 cm) on the outlet of the reactor. Since the pumping speed of the ion pump was large relative to the sorption rates under study, the mass spectrometer signal after suitable calibration was a quantitative measure of the rates of sorption or reaction on the Pt surface.

The polycrystalline platinum foil had a purity of 99.99 wt%. The carbon monoxide (99.5%) was stripped of metal carbonyls by passage over glass beads cooled to liquid nitrogen temperature. Oxygen (99.999%) was used without further purification. Hydrogen was purified by passage through a palladium–silver alloy thimble. Methanol, electronic grade, was degassed by repeated freezings and evacuations and distilled into the glass vessel used as a gas reservoir.

Procedures

Single-Component Sorption Studies

In the adsorption studies the constant-flow method (*2*) was employed predominantly. However, in a number of experiments involving carbon monoxide and hydrogen the constant-pressure technique (*3*) was utilized and a comparison was made between the results obtained by the two experimental procedures. Essentially good agreement was noted. However, since the constant-pressure method is more difficult to apply to multicomponent sorption studies exhibiting different rates of adsorption for the individual components, most of the results to be presented were obtained by the constant-flow procedure.

To remove contaminants from the platinum surface it was found expedient to expose the metal to an oxygen atmosphere at 775 K (exposure at 5×10^{-7} Torr O_2 for 10 to 40 min). The formation of carbon monoxide and dioxide indicates the presence of carbon as the major contaminant on the platinum surface as observed in a number of studies (*4*). Such a pretreatment procedure was used at frequent intervals during the course of the experiments.

In a typical adsorption measurement, the clean platinum foil was heated for 1 min in the gas under study and subsequently cooled to the desired sorption temperature while the gas was flowing past it. During this process the gas pressure was recorded continuously. The initial flashing temperatures were between 775–875 K for hydrogen, near 1075 K for carbon monoxide, and about 1375 K for oxygen. The wall temperature of the reactor was maintained near room temperature by forced air convection over the entire exterior surface. For desorption studies the temperature of the Pt foil was programmed to increase from 15 to 80 K/sec in a temperature range from 300 to 1500 K.

The temperature of the Pt specimen above 475 K was determined with the aid of a radiation thermometer focused on the central portion of the specimen, thus measuring its maximum temperature. At temperatures less than 475 K, electrical resistance measurements of the Pt-foil were employed. In analyzing the sorption data we assumed (a) uniform temperature distribution across the entire metal foil thereby neglecting the temperature gradients near the ends connected to the tungsten leadthroughs, and (b) a surface roughness of unity.

Multicomponent Sorption Studies

For study of the interaction of two reactants with the Pt-surface, including displacement reactions, the experimental procedure involved either the simultaneous introduction of the multicomponent gas mixture or preadsorption of one of the gaseous components prior to the admission of the second component to the reactor. Thus the solid was exposed to the first gas for a given period of time at a specified temperature to attain the desired degree of surface coverage as evaluated from previous determinations. Subsequently the reactor was evacuated for 1 to 5 min before introduction of the second component. Continuous sampling of the reactor efflux indicated that in the absence of adsorption or reaction a time interval of nearly 30 sec was required to attain a steady-state flow.

In the constant-flow mode of operation, the rate of adsorption or desorption of a given component present at pressure P_2 was calculated from the observed change in flow rate, using the following expression:

$$R = \frac{dN}{dt} = \left[F_{23}(P_2^0 - P_2) - F_{23}(P_3^0 - P_3) - V\frac{dP_2}{dt} \right] \Big/ A, \quad (1)$$

where

N	number density of adsorbed molecules
R	rate of adsorption (molecules/cm² sec)
$-R$	rate of desorption (molecules/cm² sec)
F_{23}	conductance between the reactor and the chamber where P_3 is located.
P_2, P_3	pressures at the points shown in Fig. 1; P_2^0 and P_3^0 refer to those at the same flow rate in the absence of adsorption
V	the volume of the reactor
A	surface area of the platinum foil.

The mass spectrometer was calibrated against the flow rate $F_{23}(P_2 - P_3)$ measured by the ion gages. The last term in the brackets of Eq. (1) is small enough to be neglected without appreciable error in the analysis.

RESULTS AND DISCUSSIONS

Adsorption of Individual Gases

The adsorption rates of carbon monoxide, hydrogen, and oxygen, measured in the pressure range from 1×10^{-6} to 1×10^{-9} Torr can be expressed in terms of sticking probability S (defined as the ratio of the rate of adsorption to the collision rate with the surface). It is a function of surface coverage and substrate temperature but independent of pressure. Typical results are shown in Fig. 2. The stickling probabilities and the amount of adsorbate as a function of exposure are reproducible within ±15%. For low surface coverages ($N < 1.4 \times 10^{14}$ molecules/cm²), the variation of sticking probability with temperature is shown in Fig. 3. Note that the sticking probability of carbon monoxide is fairly constant up to 425 K, while that of oxygen gradually decreases as the temperature is raised, the rate of change varying

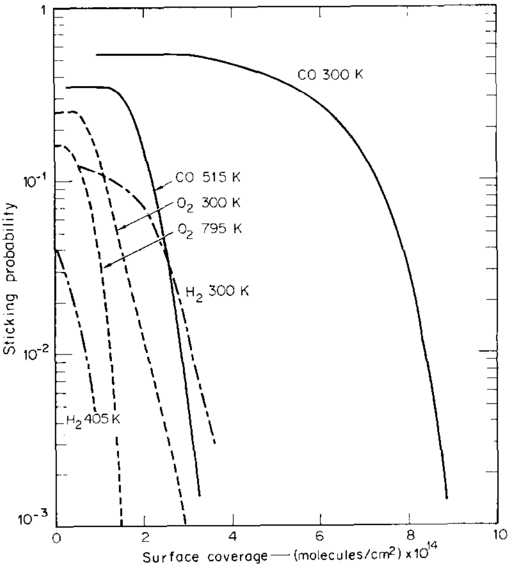

FIG. 2. Sticking probabilities of CO, H_2, and O_2 on Pt.

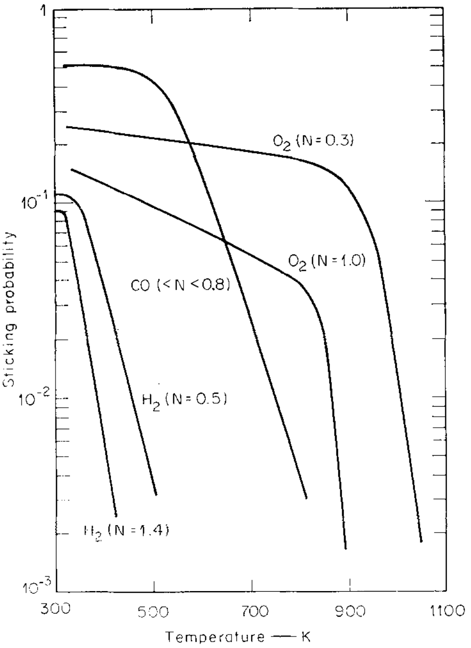

FIG. 3. Variation in sticking probability of oxygen and hydrogen with Pt-surface temperature [N = surface coverage in (molecules/cm^2) $\times$ 10^{14}].

with coverage. The value for the sticking probability of CO, S_{CO}, is considerably higher than reported in an earlier measurement (*5*). Undoubtedly this discrepancy is due to the presence of carbon contamination which was not removed by flash heating at 1475 K in the absence of oxygen, the procedure employed previously.

In addition several measurements were made of CO_2 sorption on platinum. At room temperature the mass sorbed was less than 2×10^{13} molecules/cm^2.

Adsorbed States

A distinction between different binding states for the gases under study can be made from the desorption spectra. In addition two methods are available for analysis of the energetics of adsorption. One deals with an interpretation of the sticking probability, in terms of the Kisliuk isotherm (*6*) which yields the difference in the activation energy of desorption and adsorption. The other approach is based on (a) an analysis of the shape of the desorption spectrum in terms of the theoretical desorption rate expression:

$$-R = -dN/dt = N^x \cdot \nu \cdot \exp(-E_D/kT), \qquad (2)$$

where x is the reaction order for desorption, and ν the frequency factor (*2*), and (b) the temperature T_m at which the maximum in desorption rate occurs (*2*). Of the latter two analyses the evaluation of E_D by the T_m technique is more satisfactory due to the nonuniform temperature distribution of the Pt ribbon.

Carbon monoxide. As shown in Fig. 4 the desorption data for CO depict three binding states (A, B, and C) with energies ranging from 34 kcal/mole at low coverage

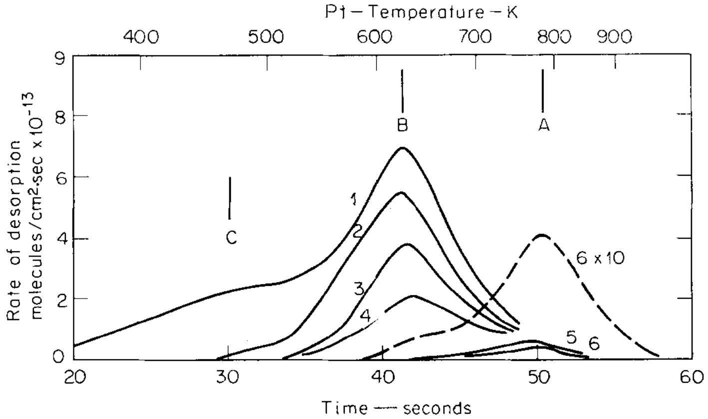

FIG. 4. Flash desorption kinetics of carbon monoxide chemisorbed on Pt [initial surface coverages (molecules/cm^2): 1—8.0$\times$ 10^{14}; 2—5.2 $\times$ 10^{14}; 3—2.9 $\times$ 10^{14}; 4—1.2 $\times$ 10^{14}; 5—0.4 $\times$ 10^{14}; 6—0.2 $\times$ 10^{14}].

TABLE 1
ADSORBED STATES ON PLATINUM

Gas	Binding state	Surface coverage (molec/cm^2) $\times 10^{-14}$	Sticking probability (300 K)	Desorption temp (K)	Kinetic order of desorption	E_D (kcal/mole)	
						Expt	Literature
CO	A	$0 \sim 0.8$	$\geqslant 0.5$	790	1	28 ± 3[a] 34 ± 2[b]	32[c]
	B	$0.8 \sim 6$	$0.5 \sim 0.3$	630	1	19 ± 3[a] 28 ± 2[b]	28–32[d]
	C	$6 \sim 9$	<0.3	470	1	9 ± 4[a] 22 ± 2[b]	—
H_2		$0 \sim 3$	0.12	370	2	10 ± 3[a] 17 ± 3[b]	16[e]
O_2	A	$0 \sim 1.5$	0.25	990	2	44 ± 2[b]	69–36[f]
	B	$1.5 \sim 3$	0.01	800	2	38 ± 8[a] 36 ± 3[b]	58[g]

[a] From Eq. (2).

[b] From max desorption rate temperature P. A. Redhead, *Vacuum* **12,** 203 (1962).

[c] W. J. M. Rootsaert, L. L. Van Reijen, and W. M. H. Sachtler, *J. Catal.* **1,** 416 (1962) (*8*).

[d] R. Lewis and R. Gomer, *Nuovo Cimento Suppl.* **5,** 506 (1967) (*7*).

[e] R. Lewis and R. Gomer, *Surface Sci.* **17,** 333 (1969) (*12*).

[f] D. Brennan, D. O. Hayward, and B. M. W. Trapnell, *Proc. Roy. Soc., Ser. A* **256,** 81 (1961).

[g] B. Weler, J. Fusy, and A. Assut, *J. Chem. Phys.* **66,** 708 (1969).

to 22 kcal/mole at high coverage. The binding energies for the A- and B-states are nearly the same as obtained from field-emission studies (*8*) (Table 1). To estimate the contribution of each state to the surface population, we have resolved the flash desorption spectra by arithmetic addition of the component peaks. Such an analysis yields the data depicted in Fig. 5. It demonstrates that the A-state, the most strongly bound state, represents only 6% of the adsorbate, the B-state 61%, and the C-state 33%. The total surface coverage of 9 × 10^{14} CO molecules/cm^2 indicates a ratio of carbon monoxide to platinum of ¾, assuming an average surface atom density of 1.2 × 10^{15} Pt-atoms/cm^2 (based on a surface area of 8.1 Å^2/Pt-atom averaged for various crystal orientations).

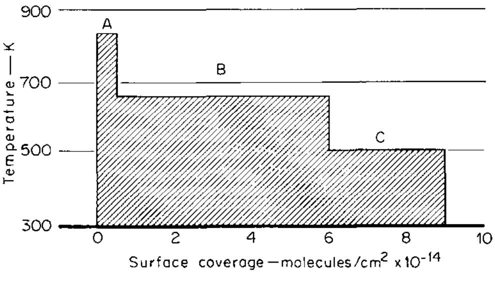

FIG. 5. Distribution of binding sites occupied by CO on Pt.

These results are similar to those reported for the interaction of CO with Pt(100), as measured by LEED (*9*). Three adsorption states were found for Pt(100) with desorption temperatures in the same range as observed in our measurements (*10*). Also the LEED data indicated on an atomic scale the ratio CO/Pt = ¾. The observed surface structures were found to be (1 × 1)-CO for the strongly bound states (A) and (B), and (4 × 2)-CO for the less strongly bound C-state (*9*). These results may reflect a bridged CO molecule for the A- and B-states and a linear species for the C-state. In view of the predominant surface coverage with the B- and C-carbon monoxide, a CO/Pt < 1 would be expected to prevail.

Hydrogen. For this system only one binding state was observed during sorption measurements at room temperature (Fig. 6). Earlier studies on evaporated Pt films (*11*) and on Pt field emitters (*12*) indicated the existence of two types of adsorbates. The one predominating at low surface coverage was interpreted to represent atomic hydrogen, while at high surface coverage a molecular hydrogen component held by charge transfer forces was proposed (*7*). It is apparent that under our experimental conditions of low surface coverage and 300 K the adsorbed state of hydrogen was in the atomic form, as evidenced by the desorption measurements which followed second-order kinetics (Fig. 6).

Assuming a nonactivated adsorption process, one would expect the energetics of desorption to exhibit a value of E_D comparable to the heat of adsorption (*7, 12*) (16 kcal/mole) in fair agreement with the experimental results (Table 1).

The maximum surface coverage at 298 K corresponds to less than a complete monolayer (H/Pt $\simeq 0.5$), indicative of the δ-state postulated by Tsuchiya, Amenomiya and Cvetanovic (*13*). Recent LEED experiments (*9*) on hydrogen adsorption on Pt(100) have been interpreted in terms of a (2 × 2) surface structure. Similar measurements on "stepped" surfaces (*14*) of Pt(111) have indicated a structure with a (2 × 2) unit cell. Such an atomic arrangement of the adsorbate would result in surface coverages with H/Pt < 1, as observed for the Pt specimen employed in our measurements.

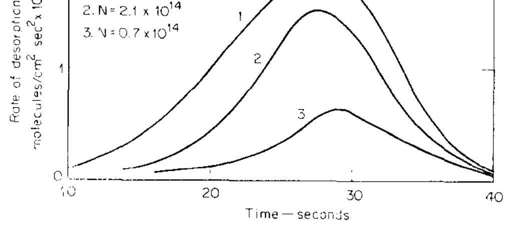

FIG. 6. Flash desorption kinetics of hydrogen chemisorbed on Pt (numbers refer to different initial surface coverages).

Also the relatively low sticking probability of hydrogen on Pt (Table 1) is reflected in the weak interactions exhibited by the low-index planes of Pt surfaces (*9, 14*). They appear to require crystal imperfections, such as steps and terraces, to effect chemisorption.

Oxygen. The initial sticking probability of oxygen on Pt at 300 K is of the magnitude estimated in an earlier publication (*15*), and exhibits a much higher value than observed in the case of hydrogen (Fig. 2). It is of interest that for Pt(100) the absence of any oxygen chemisorption has been noted (*9*), while for Pt(111) a sticking probability of $S_0 < 10^{-3}$ has been reported (*16*). Since the presence of a carbon contaminant on the surface of the Pt has been proposed as the source of a high sticking probability, we have examined in some detail the role of such a surface contaminant on oxygen adsorption. By exposing platinum at elevated temperatures (1300 K) to oxygen (exposure 10^{-3} to 10^{-4} Torr min) and monitoring the mass of CO and CO_2 evolved during flashing, we were able to demonstrate by subsequent adsorption-rate studies that the removal of a carbon residue leads to higher sticking probabilities. Thus the value of $S_0 = 0.25$ shown in Fig. 1 refers to a Pt surface cleaned by repeated exposures to oxygen at elevated temperatures, a process which has been shown to remove carbon from the Pt surface (*17*). It is likely that the high sticking probabilities observed in our studies with a polycrystalline surface† are more closely akin to the oxygen sorption measurements on stepped surfaces (*18*) of Pt(S)(111) which demonstrated more rapid chemisorption of oxygen and hydrogen as compared to the nonterraced Pt(111) or Pt(100).

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† After prolonged use the X-ray diffraction pattern revealed predominance of the (111) orientation of the polycrystalline ribbon.

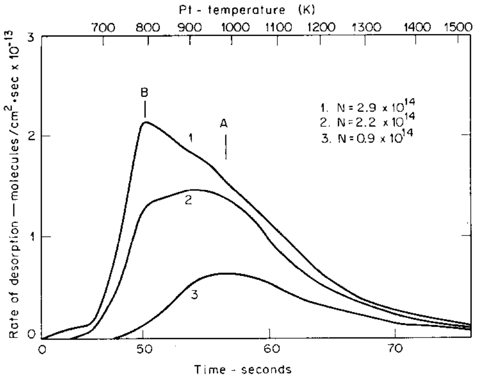

FIG. 7. Flash desorption kinetics of oxygen chemisorbed on (Pt numbers refer to different initial surface coverages).

Our desorption spectra (Fig. 7) follow second-order kinetics, indicative of an adsorbate in the atomic state (*2*). Also the results are interpretable in terms of two binding states of oxygen on Pt. At surface coverages exceeding 3×10^{14} atoms/cm^2 or 25% of the available surface sites ($N_{\max} = 1.2 \times 10^{15}$/cm^2), one calculates a desorption energy of 36–38 kcal/mole (Table 1). At lower surface coverage another binding state prevails. However its temperature of desorption (990 K) is near that of metal oxide formation so that the binding energy calculated may be inaccurate. It should be noted that for this adsystem the maximum oxygen surface coverage corresponds to a O/Pt = ½, in agreement with the upper limit of sorbed oxygen reported by other investigators (*15*, *19*, *20*).

Interactions Between Carbon Monoxide and Hydrogen

The competitive adsorption of hydrogen and carbon monoxide from a two-component gas mixture (40 vol% H_2/60 vol% CO) is demonstrated by the data presented in Fig. 8. The high sticking probability of CO relative to H_2 and their respective temperature coefficients offer a suitable explanation of the behavior observed during the initial stages of adsorption of these two gases. Thus hydrogen exhibits an "induction period" for the sorption process associated with cooling of the flashed Pt surface to temperatures below 475 K, while CO is capable of bonding to the surface at much higher temperature. However it is to be noted that the calculated sticking probabilities of H_2 and CO from the gas mixture are somewhat lower than those observed at comparable surface coverage for the individual gases (Table 2).

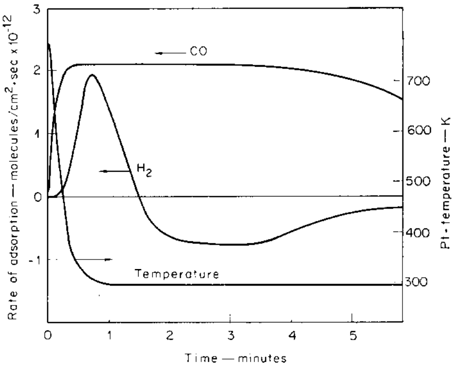

FIG. 8. Adsorption kinetics on Pt from a gas mixture containing 40 vol% H_2 and 60 vol% CO.

Of special interest is the displacement of the hydrogen adsorbate by CO during the later stages of the experiment.‡ To examine in more detail this aspect of the sorption process, a number of experiments were carried out in which hydrogen was preadsorbed on Pt, and CO admitted subse-

TABLE 2

MIXED STICKING PROBABILITIES[a] OF CO AND H_2 ON PLATINUM AT 300 K

	Surface coverage (molecules/cm^2) $\times 10^{-14}$	Sticking probability	
		Individual gas	Gas mixture
CO	0.8	0.5	0.3
H_2	0.3	0.1	0.02

[a] Composition of gas mixture: 40 vol% H_2, 60 vol% CO.

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‡ During the relatively long time interval (~6 min) of this experiment, back diffusion of hydrogen from the Vac-Ion pump contributed to an anomalously large value of the total concentration of hydrogen detected by the mass spectrometer.

quently. The experimental results shown in Fig. 9 (sets A and B) differ only in the exposure time to CO. In each case the initial mass of preadsorbed hydrogen was nearly the same. In set A the CO was allowed to pass through the reactor during the entire course of the experiment, while in set B the CO supply was cut off after 60 sec of exposure in order to examine the response of the hydrogen desorption rate to the removal of CO from the gaseous environment. In both runs the evolution of hydrogen is delayed as the surface becomes populated with CO. Also as shown by the data (set B), hydrogen continues to desorb for some time after cessation of CO adsorption, indicative of changes in the binding sites occupied by CO. This observation is further substantiated by measurements of the hydrogen displacement reaction for varying initial surface coverages with hydrogen (Fig. 10). At low initial hydrogen coverage the desorption of hydrogen is appreciably delayed compared to the desorption rate at higher initial surface coverage.

The mole ratio of molecular hydrogen desorbed to CO adsorbed approaches the value of 0.5, indicative of a process which leads to the removal of one adatom of hydrogen for each molecule of CO adsorbed (Fig. 11). Also the mass of hydrogen initially adsorbed is recovered quantitatively during the displacement process, so that on a Pt surface no new stable compounds are formed by interaction of H and CO.

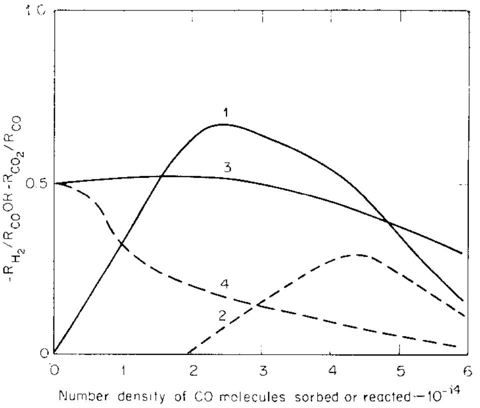

FIG. 10. Comparison of interaction between gaseous carbon monoxide and (a) adsorbed hydrogen (1 and 2); and (b) adsorbed oxygen (3 and 4) [initial surface coverage: 1—5.2 × 10^{14} H/cm^2; 2—1.7 × 10^{14} H/cm^2; 3—4.8 × 10^{14} O/cm^2; 4—1.0 × 10^{14} O/cm^2].

The experimental results indicate that, irrespective of the initial hydrogen coverage, the displacement ceases when the mass of CO adsorbed reaches a value of 6 × 10^{14} molecules/cm^2 corresponding to complete filling of the A- and B-states. The fact that the displacement is complete before type C adsorption of carbon monoxide begins suggests that the energetics are unfavorable for filling the C-state occupied by hydrogen. Indeed the binding energies of CO in the C-state and of hydrogen are nearly the same (Table 1), making the displacement of H by CO less probable.

Several studies of this adsystem (*21–24*)

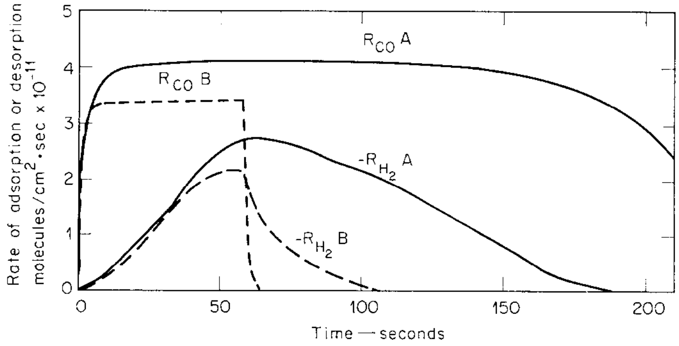

FIG. 9. Displacement of chemisorbed hydrogen by carbon monoxide on Pt [initial surface coverage (H-atoms/cu^2): A—5.2 × 10^{14}; B—5.4 × 10^{14}].

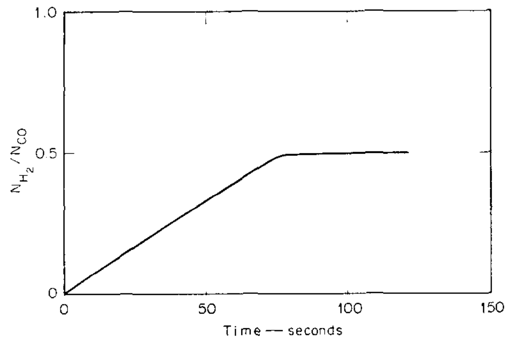

FIG. 11. Number ratio of hydrogen molecules desorbed to carbon monoxide molecules adsorbed during surface interaction on Pt at 300 K.

have dealt with the interaction between the chemisorbed species on the surface of Pt and the displacement of chemisorbed hydrogen by carbon monoxide. Our experimental observations of the time lag between hydrogen desorption and CO adsorption are interpretable in terms of the formation of a third species associated with a specific binding state during the displacement process. The following mechanism is proposed:

$$H(a) + CO(g) \rightarrow CO(a) + H^*(a), \qquad (3)$$

$$H^*(a) + H(a) \rightarrow H_2(a) \rightarrow H_2(g), \qquad (4)$$

$$H^*(a) + \square \rightarrow H(a). \qquad (5)$$

In this schema, $H^*(a)$ denotes a binding state of hydrogen different from $H(a)$ observed in the absence of CO. The symbol $\square$ indicates a vacant surface site. As a matter of fact, flash desorption studies suggest the presence of a weak shoulder centered near 320 K, possibly due to $H^*(a)$. Such a change in binding energy may be the result of: (a) variation in the electron density of the substrate brought about by the adsorption of CO, (b) decrease in the polarization of the hydrogen adlayer due to CO sorption, and (c) lateral van der Waals interaction between surface-sorbed hydrogen atoms and CO molecules leading to the formation of a [H–CO] complex. This intermediate could react subsequently by interaction with another H-adatom as follows

$$H(a) + [H\text{–}CO](a) \rightarrow H_2(g) + CO(a) + \square. \qquad (6)$$

The formation of such an intermediate was suggested by Baldwin and Hudson (*24*) in their study of CO and H_2 coadsorption on and formaldehyde desorption from Pt(111).

Interactions Between Carbon Monoxide and Oxygen

In an extension of earlier work from this laboratory (*15*) two types of experimental measurements were performed, one dealing with preadsorbed oxygen, the other with preadsorbed carbon monoxide. In the case of preadsorbed oxygen the formation of CO_2 was detected immediately upon the admission of CO to the reactor containing the Pt surface at room temperature. (Fig. 10) As shown by the results presented in Table 3 the rate of CO_2 production is a function of the degree of oxygen surface coverage N_{O_2} and the carbon monoxide collision frequency Z with the Pt surface. Since the maximum surface coverage with O-atoms is 6×10^{14} atoms/cm² (or O/Pt

TABLE 3

INTERACTION BETWEEN GASEOUS CARBON MONOXIDE AND CHEMISORBED OXYGEN ON PLATINUM AT 300 K

Initial surface coverage (molecules/cm²) $\times 10^{-14}$		Oxygen fract. coverage	CO pressure (Torr $\times 10^8$)	Surface collision frequency (molecules/cm² sec) $\times 10^{-12}$	CO_2 formation rate (molecules/cm² sec) $\times 10^{-11}$	Reactive collision factor
O_2	CO	θ_O	p_{CO}	Z_{CO}	$-R_{CO_2}$	γ
2.0	0.7	0.67	4.2	17.8	17.5	0.15
1.9	0.3	0.62	2.7	11.4	8.7	0.12
1.75	0.6	0.58	4.0	16.9	12.7	0.13
1.55	1.0	0.52	5.4	22.8	14.4	0.12
1.1	2.8	0.37	4.2	17.8	10.0	0.15

TABLE 4

Interaction Between Gaseous CO with Chemisorbed Oxygen on Platinum at 300 K

Initial surface coverage (molecules/cm²) × 10^{-14}		CO pressure (Torr × 10^8)	(molecules/cm² sec) × 10^{-11}		
O_2	CO	p_{CO}	CO ads. rate $-R_{CO}$	CO_2 des. rate R_{CO_2}	$-R_{CO_2}/R_{CO}$
2.0	0.7	4.2	32	17.5	0.55
1.1	2.8	4.2	32	10	0.31
1.0	1.4	5.8	53	27	0.51
0.3	0.1	1.7	86	4.2	0.49
0.2	6.5	2.2	7.0	4.5	0.64

= ½), we may calculate the reactive collision factor γ $(0 < \gamma < 1)$ for CO_2 formation. According to this model the rate of CO_2 desorption is given by

$$-R_{CO_2} = \gamma \cdot Z_{CO} \cdot \theta_O, \tag{7}$$

where θ_O represents the fractional oxygen surface coverage. Evaluation of γ indicates an average value of $\bar{\gamma} = 0.13 \pm 0.01$. Thus 1 in nearly 10 CO collisions results in the formation of a CO_2 molecule. In addition the relative rates of CO_2 formation to CO adsorption (Fig. 10) demonstrated that, for every CO_2 molecule formed, two molecules of CO disappeared from the gas phase. The same conclusion may be drawn from the data presented in Table 4. Therefore the occupied oxygen site vacated by the formation of a CO_2 molecule is taken over by a CO molecule, as follows

$$CO(g) + O(a) \rightarrow CO_2(g) + \square, \tag{8}$$

$$CO(g) + \square \rightarrow CO(a). \tag{9}$$

The CO adsorbate thus formed appears to be strongly bound at low surface coverage (Table 1), and unable to interact with chemisorbed oxygen at 300 K. Thus the presence of small quantities of CO initially present on the Pt surface has no demonstrable effect (Table 3) on the reaction rate relative to reaction (8) leading to CO_2. The experiments clearly demonstrate a rapid interaction between gas phase CO and adsorbed oxygen by way of a predominant Rideal-type mechanism.

In the presence of high fractional CO surface coverage ($N_{CO} > 5 \times 10^{14}$ molecules/cm²), a relatively slow reaction occurs with gaseous oxygen, as long as some sites are available for oxygen coadsorption.

TABLE 5

Interaction Between Chemisorbed Carbon Monoxide and Gaseous Oxygen on Platinum at 300 K

Initial surface coverage (molecules/cm²) × 10^{-14} CO	O_2 pressure (Torr × 10^8)	(molecules/cm² sec)			
		Surface coll. freq. $Z_{O_2} \times 10^{-12}$	O_2 ads. rate $R_{O_2} \times 10^{-11}$	CO_2 des. rate $-R_{CO_2} \times 10^{-11}$	$-R_{CO_2}/R_{O_2}$
5.1	3	11.9	—	2.5	—
5.6	10	39.6	—	4.5	—
5.2	28	107	—	8.0	—
6.0	5.0	19.8	2.9	2.7	0.93
6.5	4.9	19.4	3.1	3.3	1.1
7.0	4.8	19.0	3.2	3.5	1.1
7.4	6.3	25.0	1.0	1.3	1.3
9.0	7.0	27.8	0	0	0

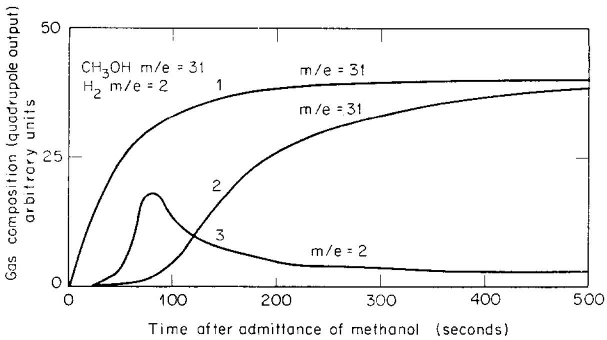

FIG. 12. Methanol decomposition kinetics on Pt surface at 298 K (1—inactive Pt-surface; 2,3—clean Pt-surface).

For a given degree of CO surface coverage, the rate of CO_2 formation appears to be proportional to the square root of the oxygen pressure (Table 5). Thus two empty surface sites are required for the dissociative chemisorption of oxygen, a prerequisite and controlling process for CO_2 formation. In addition the data in Table 5 indicate that in the reaction one molecule of oxygen is consumed for each molecule of CO_2 formed, an indication that one of the oxygen atoms occupies the site emptied by the CO molecule reacted. These results are in general agreement with those presented by Bonzel and Ku (*25*) for CO oxidation on Pt(110), although our data show no evidence for an interaction between sorbed molecular oxygen O_2(a) and CO(a).

Similar differences between the reactivity of an adlayer of oxygen and of carbon monoxide have been reported recently in a study of CO oxidation on a Pd(110) surface (*26*, *27*). LEED measurements indicated the rapid disappearance of the oxygen surface structure on admission of carbon monoxide to the Pd surface. On the other hand, during the chemisorption of oxygen on the Pt(110) surface partially covered by CO, the coexistence of the individual surface structures characteristic of carbon monoxide and oxygen was noted.

Decomposition of Methanol

The same experimental technique was applied to the study of methanol decomposition including cleaning of the Pt surface by exposure to oxygen at elevated temperature and flash desorption at 1000 K at a background pressure of $<5 \times 10^{-9}$ Torr. Methanol (pressure 10^{-6} to 10^{-8} Torr) was introduced after the Pt foil had cooled down to room temperature. A representation of the changes in gas phase composition due to surface reaction as monitored by the quadrupole mass spectrometer is found in Fig. 12.* Curve 1 exhibits the response characteristics of the system in the absence of catalytic reaction. For this purpose the Pt surface had been poisoned by prolonged exposure to methanol vapor (*vide infra*). Note that a relatively long time is required to reach steady-state flow (~200 sec), undoubtedly due to adsorption of methanol on various portions of the reactor and inlet system. Curve 2 represents the transients in composition which prevail in the presence of a Pt surface cleaned by flash heating under vacuum and cooling to 300 K preceding the admission of methanol. Thus the difference between curves 1 and 2 is a measure of the methanol interacting with the Pt surface. Also shown in Fig. 12 is the curve for hydrogen production during catalytic methanol decomposition; CO is conspicuously absent from the gas phase during this period. However flash desorption at various stages of the methanol adsorption and decomposition process indicates the evolution of CO as the main desorbing species. A measure of the

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* For methanol the predominant species in the cracking pattern of the mass spectrometer corresponds to the nominal mass $m/e = 31$.

TABLE 6

DECOMPOSITION OF METHANOL

Temp (K)	Fractional decomposition[a]	Steady-state surface coverage CO (molecules/cm^2) $\times 10^{-14}$
358	0.34	7.1
393	0.51	6.2
423	0.78	5.1
773	1.00	0

[a] Fractional decomposition relative to that observed at 773 K.

mass of CO retained on the Pt surface during steady-state decomposition of methanol was obtained by raising the temperature of the Pt surface in a constant flow of methanol. After steady-state decomposition had been obtained, as manifested by the constant gas composition leaving the reactor, the flow of methanol was interrupted and the temperature of the Pt surface raised to 1000 K. The amount of CO desorbed during the flash heating was determined by integration of the CO signal output from the mass spectrometer. The results are tabulated in Table 6. Extrapolation of these data indicated that at room temperature under steady-state condition the CO surface coverage would be complete ($\sim 9 \times 10^{14}$ molecules/cm^2) and cause severe inhibition of methanol decomposition.

Assuming that the adsorbed methanol molecule decomposes to hydrogen and CO and that the latter species stays on the surface at room temperature, we expect the measured rates of decomposition to be a function of the coverage of CO as shown in Fig. 13. At room temperature, the rate of adsorption of methanol is assumed to be equal to the rate of decomposition so that the ordinate of Fig. 13 may be interpreted to represent the sticking probability of methanol on Pt.

It is well known that the catalytic decomposition of methanol over transition metals produces mainly hydrogen and carbon monoxide (*28*) and that the latter species inhibits the CH_3OH decomposition (*28–30*). The rate equation is usually written in the form

$$\text{Rate} = cP_{\mathrm{MeOH}}/(1 + bP_{\mathrm{CO}}),$$

where both b and c are temperature dependent (*28*, *29*).

From the present study, it can be concluded that on clean platinum the probability of adsorption and decomposition of methanol is near unity even at 300 K. Notable inhibition by CO is observed only at higher coverages; possibly type C adsorption of carbon monoxide is responsible for inhibiting the adsorption and decomposition of CH_3OH. The temperature dependence of the kinetic parameters is associated with the equilibrium concentration of adsorbed carbon monoxide, which at high surface densities interferes with the adsorption of methanol on the surface. One may conclude that methanol decomposition on Pt occurs by hydrogen abstraction from the methyl group and the

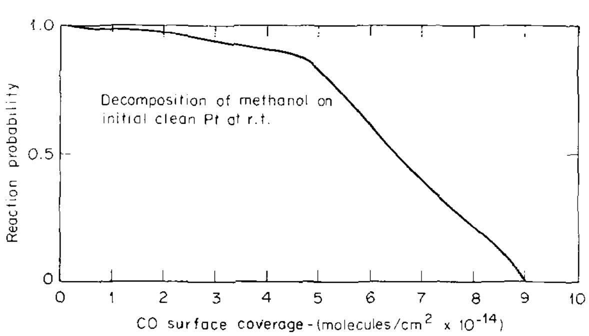

FIG. 13. Reaction probability of methanol on Pt at 300 K as a function of surface coverage with carbon monoxide.

formation of a [HCO] intermediate similar to that observed during the interaction of CO with chemisorbed hydrogen. The interaction of this intermediate with another H-atom leads to the desorption of a hydrogen molecule and, at room temperature the retention of the CO molecule on the surface.

These surface studies on the molecular level demonstrate (a) the close relationship between catalytic mechanisms at high and low reactant pressures, and (b) the feasibility of elucidating such reactions by the analysis of elementary reaction steps.

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