

Investigation of Interactions between Metals and Adsorbed Organic Compounds by Infrared Spectroscopic Study of Adsorbed CO

I. Infrared Study of CO Adsorption and Desorption on Pt/Cab-O-Sil Catalyst

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The adsorption of CO on a 5% Pt/SiO₂ catalyst has been studied using infrared spectroscopy. Spectra obtained under different conditions showed the presence of two distinct adsorbed CO species. The high-frequency infrared band centered at 2070 cm⁻¹ ($\Theta_{298\text{ K}} = 0.35$) was assigned to the stretching frequency of CO linearly adsorbed on Pt. These *adsorptive* CO molecules were characterized as having a nonordered structure with large dipole-dipole interactions. The low-frequency infrared band centered at 2047 cm⁻¹ ($\Theta = 0.35$) was assigned to the stretching frequency of *desorptive* CO with ordered structure adsorbed on Pt surface sites having a low surface coordination. Dipole-dipole interaction for CO molecules adsorbed on these surface sites was small. Adsorption-desorption hysteresis curves suggested that the CO coverage-dependent shifts were due to an adsorbed disordered-ordered transition when a migration occurred from low Miller index planes to high Miller index planes. By carefully controlling the adsorption-desorption conditions, it was possible to obtain a CO doublet at 2070 and 2049 cm⁻¹ indicating that both ordered and disordered CO could coexist on silica-supported Pt surface. The relative intensities of the adsorbed CO species suggested that the ordered structure had a higher extinction coefficient than the disordered CO structure.

INTRODUCTION

The use of CO as a probe in the study of catalytically important metals has resulted in a wealth of information regarding the nature and disposition of the active metal sites. In particular, the use of infrared spectroscopy as a tool to study the structure of adsorbed CO species on the surface of supported metals has led to important conclusions regarding the factors which influence catalytic activity. Following the initial review of Eischens and Pliskin (1), several other excellent surveys have appeared in the literature through 1970 (2-5). The continuing significance of this research with particular emphasis on the Pt-CO interaction has received considerable attention during the last several years (6-11).

One of the main tasks which we are attempting to accomplish in our current research efforts is the investigation of interactions between various organic compounds

and metals, with the long-term goal of developing new metal-catalyzed reactions. The studies already alluded to in addition to some recent investigations (12-14) have led us to study the infrared spectra of CO adsorbed on metals in the presence of various electron-donor and electron-acceptor organic adsorbates. The results obtained in these studies have been of value in considering additional research in this area (15-18).

In the present paper we report on some novel experimental results relating to the infrared spectra of CO chemisorbed on silica-supported Pt.

EXPERIMENTAL

Materials

The silica-supported Pt samples (5 w% Pt/Cab-O-Sil) used in this study were prepared by impregnation. Initially, the appropriate weight of H₂PtCl₆ · 6H₂O (Reanal,

Budapest) was dissolved in an amount of doubly distilled water to give a solution containing 0.015 g Pt/ml. This solution was mixed with Cab-O-Sil, grade M-5 (BDH Chemicals Ltd.) until a slurry having the consistency of a thin paste was formed. The slurry was stirred at room temperature for 1 hr and subsequently evaporated to dryness in a vacuum evaporator at 373 K over a period of 30 min with constant mixing. Drying was completed by placing the sample in an oven at 393 K for 3 hr. The sample was then ground into a fine powder in an agate mortar and stored in a desiccator until use.

The gases used in this study were subjected to the following purification treatment: H_2 was prepared using a hydrogen generator (Matheson Ltd., model 8326) fitted with a palladium purifier. CO (Matheson Ltd.) had a purity of 99.997% and was used without further treatment. O_2 and CO_2 (Matheson Ltd.) were of commercial purity and were further purified by repeated vacuum distillation.

Apparatus and Procedure

Infrared measurements were made using a Specord 71 ir (Zeiss, Jena) double-beam spectrophotometer, fitted with a NaCl monochromator. Absorption spectra were recorded at rates of $0.63\text{--}5\text{ cm}^{-1}\text{ s}^{-1}$. A continuously adjustable attenuator made by us was used in the reference beam. The apparatus was regularly calibrated with polystyrene film. The experimental accuracy at the slowest scanning speed and an attenuation of $8\times$ was about $\pm 1\text{ cm}^{-1}$.

A greaseless vacuum infrared cell similar to that in Ref. (19) was modified in the following way: (a) two 3-arm (stirrup shaped) retaining units were made to facilitate placement of the sample disk in and out of the furnace without damage to the infrared cell. (b) A positioning device was constructed. This consisted of two glass bars located at the bottom of the sample holder designed to fit two depressions located at the bottom of the infrared cell. (c) The sample holder was made from two lengths of

capillary glass tubing appropriately sealed together. The resulting sample holder was then suitably attached to the sampling assembly.

The infrared cell was connected to a conventional vacuum system capable of attaining an ultimate pressure of 10^{-6} Torr (1 Torr = 133.3 N m^{-2}).

Thermal pretreatments and adsorption studies at higher temperatures were carried out in the externally heated portion of the infrared cell. Spectra were recorded at room temperature. However, the sample temperature due to heating by the infrared beam was between 310 and 320 K.

The dried catalyst was pressed into self-supporting tablets at a pressure of 2000 kp cm^{-2} ($1\text{ kp cm}^{-2} = 98.1\text{ kN m}^{-2}$). The optical density of the samples was 10 mg cm^{-2} .

Prior to an adsorption-desorption experiment, a fresh sample was treated as follows: evacuated for 10 min at 298 K, temperature increased at a rate of 20 K min^{-1} to 373 K followed by evacuation at 373 K for 30 min, heated at 20 K min^{-1} to 673 K under vacuum followed by evacuation at 673 K for 30 min, treated in 100 Torr of O_2 at 673 K for 30 min followed by evacuation at 673 K for 30 min, reduced for 1 hr at 673 K in flowing H_2 (50 ml min^{-1}) followed by evacuation at 673 K for 1 hr. A used sample was treated in the same way except that the first two steps in the pretreatment were omitted. Pretreatments other than those described above are indicated in the text.

Pt dispersions were determined: (1) by a Cahn electrobalance (2102 RG, Ventron Inst. Corp.) using O_2 and CO adsorption and (2) by measuring the intensity of the infrared adsorption bands. Dispersions decreased from 0.35 for a fresh sample to about 0.1 following 40 or so experimental measurements.

RESULTS

The Effect of Surface Coverage on the Adsorption and Desorption of CO

The adsorption of CO on a silica-supported Pt sample at 298 K is shown in Fig.

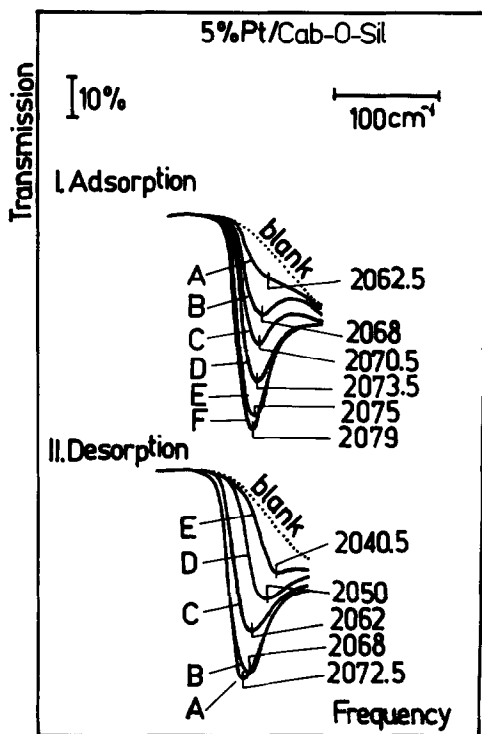


FIG. 1. Infrared spectra of adsorbed CO on reduced Pt/Cab-O-Sil at 298 K.

1. During the stepwise adsorption, the pressure was increased from 10^{-4} to 20 Torr. The spectra were recorded after a 5-min adsorption period following the admission of each dose. Only one infrared band in the region $2000\text{--}2100\text{ cm}^{-1}$ of the spectrum was observed. The position of the CO stretching band was observed to increase with coverage at pressures in excess of 100 Torr: a small shoulder centered at 2105 cm^{-1} was observed. However, this band was readily removed by evacuating the sample at 293 K. No bands in the region $1800\text{--}2000\text{ cm}^{-1}$ of the spectrum were observed indicating the absence of bridged CO.

CO desorption was performed under vacuum as the temperature was increased from 298 to 623 K. Prior to recording a spectrum, the sample was evacuated for 5–10 min at each one of the following temperatures: 323, 348, 373, 423, 473, 523, 573, and 623 K. The results (Fig. 2) show infrared bands of equal intensities on the adsorption and de-

sorption portions of the curve, and markedly different frequencies. Frequencies on the desorption branch of the curve were consistently lower than those on the adsorption branch, the difference being particularly noticeable at low surface coverages where $\Delta\nu(\text{CO}) \cong 25\text{ cm}^{-1}$. The adsorption and desorption curves were roughly S shaped. Initially, a large increase in the adsorption frequency occurred as the surface coverage was increased. This was followed by a relatively flat portion of the curve in which the frequency was observed to be rather insensitive to surface coverage. Finally, as monolayer coverage was approached, the frequency was again observed to increase sharply with increasing surface coverage. When the desorption was initiated at monolayer coverage, the absorbance and frequency corresponding to

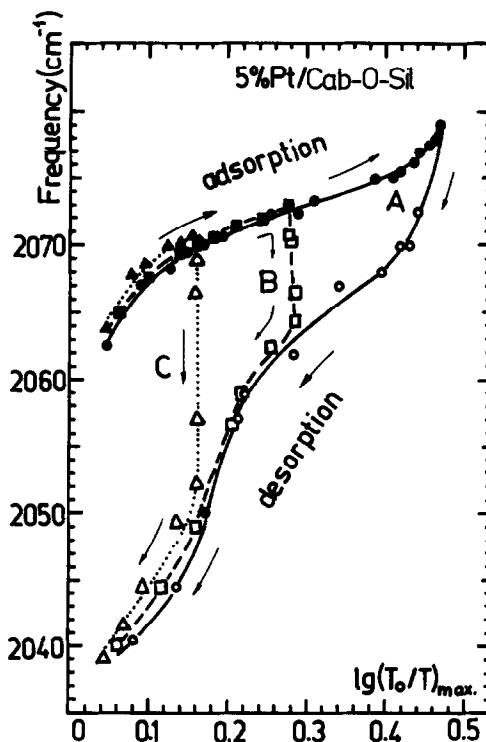


FIG. 2. Frequency shift of adsorbed CO on Pt/Cab-O-Sil as a function of CO absorbance up to (A) $\Theta = 1$, \bullet ; (B) $\Theta = 0.57$, \blacksquare ; (C) $\Theta = 0.35$, \blacktriangle ; after its desorption at increasing temperatures under continuous evacuation: (A) \circ ; (B) \square ; and (C) \triangle .

the band maxima decreased continuously during desorption. On the other hand, when desorption was initiated at lower surface coverages which were less than $\Theta = 1.0$ (i.e., $\Theta = 0.57$ or 0.35), the intensity of the absorption band did not change until the frequency corresponding to the band maxima coincided with a value on the desorption branch of the curve. Subsequently, the frequency was again observed to decrease continuously with decreasing surface coverage.

The half-width ($h_{1/2}$) of the absorption band corresponding to adsorbed CO did not change appreciably with increasing surface coverage (Fig. 3). However, during desorption, an initially large increase in $h_{1/2}$ was observed. As the surface coverage was continually decreased, $h_{1/2}$ was observed to decrease, finally becoming smaller than the

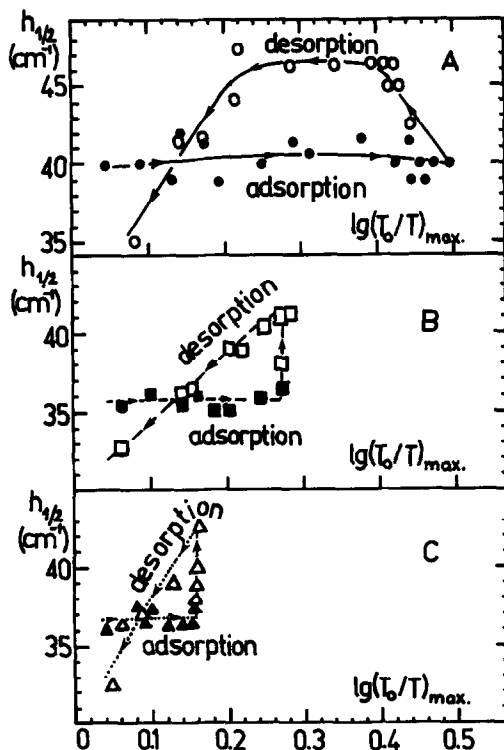


FIG. 3. Change of half-width of ir bands corresponding to adsorbed CO on Pt/Cab-O-Sil during adsorption at 298 K and subsequent thermal desorption (see Fig. 2).

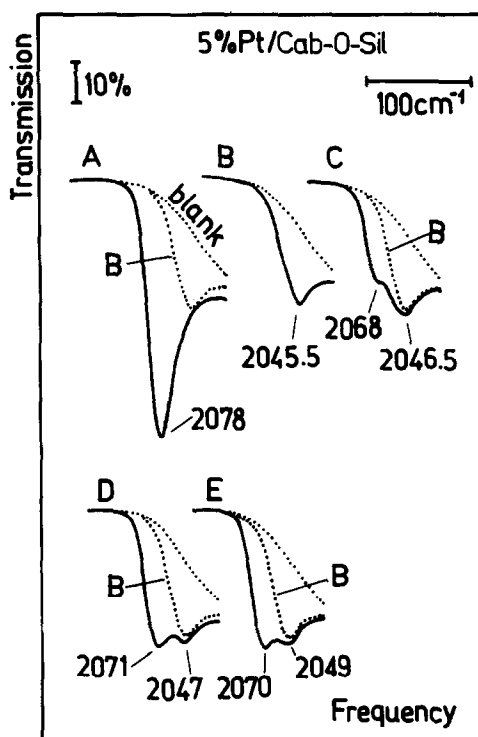


FIG. 4. Production of adsorptive and desorptive CO ir doublet (for notations see Table 1).

corresponding value of $h_{1/2}$ observed during the initial adsorption portion of the curve. The increase in $h_{1/2}$ during the initial desorption stage appeared to be greater when there was a sudden shift in the wavenumber (Figs. 2 and 3).

Production and Properties of the ir Desorption-Adsorption Doublet

When partial desorption ($\Theta_{\text{CO}} = 0.21$) was followed by the readsorption of a small amount of CO at 298 K, a new absorption band was observed. The frequency of this band was about 25 cm^{-1} higher than that corresponding to the desorption band. Some of the properties of this ir doublet are shown in Figs. 4 and 5 and also in Table 1. In addition to the data shown in Fig. 4, it should be mentioned that evacuation caused the doublet to broaden such that the bands became more poorly resolved. If the dose of CO readmitted to the sample fol-

TABLE I
Production of Adsorptive-Desorptive CO ir Bands on Reduced 5% Pt/Cab-O-Sil and the Effect of H₂ on Them

Spectra of Figs. 4 and 5	Experimental conditions	Adsorptive ir band		Desorptive ir band	
		Absorbance	Wavenumber (cm ⁻¹)	Absorbance	Wavenumber (cm ⁻¹)
A	10 Torr CO ads. at 298 K, 1 hr, then evacuation at 298 K for 30 min	0.6430	2078	—	—
B	Evacuation at 523 and 573 K ($\Theta_{CO} = 0.21$)	—	—	0.1375	2045.5
C	10 ⁻³ Torr CO ads. at 298 K, 5 min	0.1298	2068	0.1500	2046.5
D	2.5 × 10 ⁻³ Torr CO ads. at 298 K, 5 min	0.2081	2071	0.1594	2047
E	Evacuation at 298 K, 30 min	0.2144	2070	0.1603	2049
F	10 ⁻³ Torr H ₂ (after treatment D) at 298 K, 5 min	0.2162	2067	—	—
G	5 × 10 ⁻³ Torr H ₂ at 298 K, 5 min	0.2152	2059	—	—
H	Evacuation for 15 min at 373 K	0.2181	2066	0.1730	2044.5
I	10 ⁻³ Torr CO ads. at 293 K, 5 min	0.2530	2071	—	—
K	10 ⁻¹ Torr CO ads. at 293 K, 5 min	0.4914	2076.5	—	—

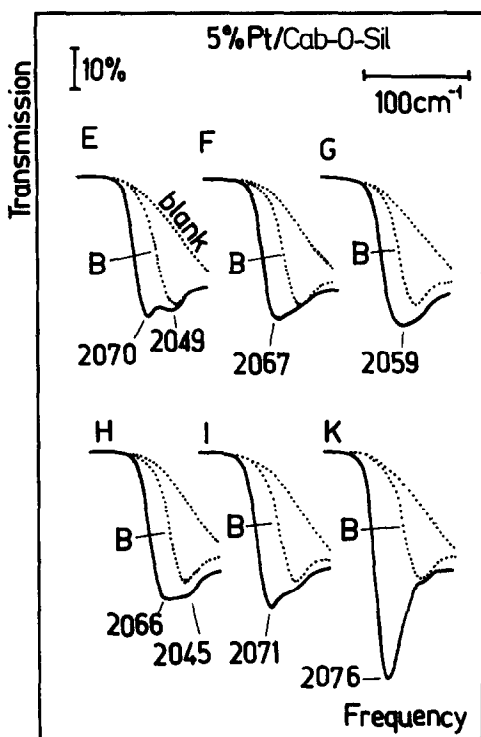


FIG. 5. Effect of H_2 on frequencies and intensities of adsorptive and desorptive CO ir bands (for notations see Table 1).

lowing partial desorption was too large, the doublet was not observed.

The ir desorption-adsorption doublet could also be produced as follows: following CO adsorption made at 523 K a low-intensity desorption ir band was obtained by thermal desorption. Subsequent re-adsorption at a CO pressure of 10^{-4} Torr at 298 K resulted in the formation of the ir doublet.

The addition of $H_2(g)$ to a sample with a well-defined ir doublet at 298 K resulted in a decrease in the frequency of the adsorptive CO but no change in its intensity. The adsorptive-desorptive doublet was observed to broaden and finally became poorly defined. Subsequent evacuation at 373 K for 15 min resulted in the *reappearance of the doublet*, however the bands were not nearly as well defined as they had been prior to the H_2 treatment. Further ad-

dition of CO resulted in an increase in both the intensity and the frequency of the adsorptive CO band. The desorptive CO band could no longer be observed in the infrared spectra.

The addition of $O_2(g)$ to a sample with a well-defined ir doublet at 298 K, resulted in the *irreversible decrease of both the adsorptive and desorptive bands*. The adsorptive band appeared to be more directly affected, disappearing at an oxygen pressure of 10^{-2} Torr O_2 . The desorption band did not disappear until the O_2 pressure was increased to about 3 Torr. We will report in detail on these results in the next paper.

Effect of Temperature on the Adsorption and Desorption of CO

CO was adsorbed onto the silica-supported Pt sample at the following temperatures: 298, 523, and 623 K. At 298 K, the spectrum was recorded 5 min following the addition of each CO dose. At the higher temperatures, a 10-min period was allowed to elapse prior to recording the infrared spectrum. Following a 10-min exposure to each CO dose, the sample was evacuated for 1 min at the adsorption temperature and then lowered into position for the recording of the infrared spectrum. All spectra were recorded under vacuum at room temperature. The CO pressure was varied from 10^{-4} to 100 Torr. Desorption was carried out under vacuum as before, the temperature being increased from 298 to 623 K.

The frequency corresponding to the adsorption at higher temperatures was considerably lower than that observed at 298 K (Fig. 6). In the case of adsorption at 523 and 623 K the intensity of the infrared band was considerably greater than that observed at 298 K. The frequencies of the desorption curves for CO adsorbed at 523 and 623 K were lower than those observed at 298 K. Desorption curve C in Fig. 6 differs from the other two curves in that the frequency increased rather than decreased with decreasing band intensity during the initial stages of the evacuation (333 to 420 K).

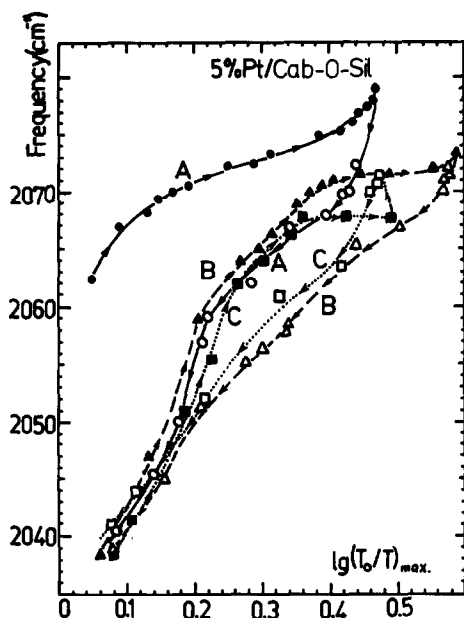


Fig. 6. Effect of temperature on adsorptive and desorptive properties of CO (Pt/Cab-O-Sil pretreated at 673 K, and CO adsorbed at (A) 298 K, ●; (B) 523 K, ▲; and (C) 623 K, ■; desorption under continuous evacuation at increasing temperatures).

This result was reproduced several times, too.

Effect of Temperature on the *ir* Desorption-Adsorption Doublet

Following the formation of the *ir* adsorptive-desorptive doublet at 298 K as previously described, the sample was left in contact with 5×10^{-3} Torr of CO for 1 hr. The frequency corresponding to the adsorptive CO was observed to decrease by about 5 cm^{-1} . When the sample was evacuated at 373 and 423 K, the frequency of the *adsorptive band continually decreased* and a single CO band was observed with larger absorbance (Fig. 7 and Table 2).

DISCUSSION

From the foregoing result, we can conclude the following:

(1) The infrared absorption frequency, $\nu(\text{CO})$, changes during the adsorption-desorption cycle according to a hysteresis

curve. At a given surface coverage Θ , the position of the CO band corresponding to maximum absorbance has a higher wavenumber for the adsorption branch than for the desorption branch.

(2) At 298 K, CO is adsorbed in a random manner on silica-supported Pt. This random adsorption leads to a disordered CO ad-layer. This implies that at 298 K, CO is adsorbed with a high sticking probability with little or no surface rearrangement following adsorption.

(3) On thermal treatment of the adsorbed layer a rearrangement of the ad-layer results. CO appears to migrate from its original adsorption sites to form a new structure. We will refer to this process as ($\text{CO}_A \rightarrow \text{CO}_D$), where CO_A represents the adsorptive CO and CO_D , the desorptive CO. During this rearrangement process, a *CO coverage-dependent shift* is observed.

(4) If the desorption process is discontin-

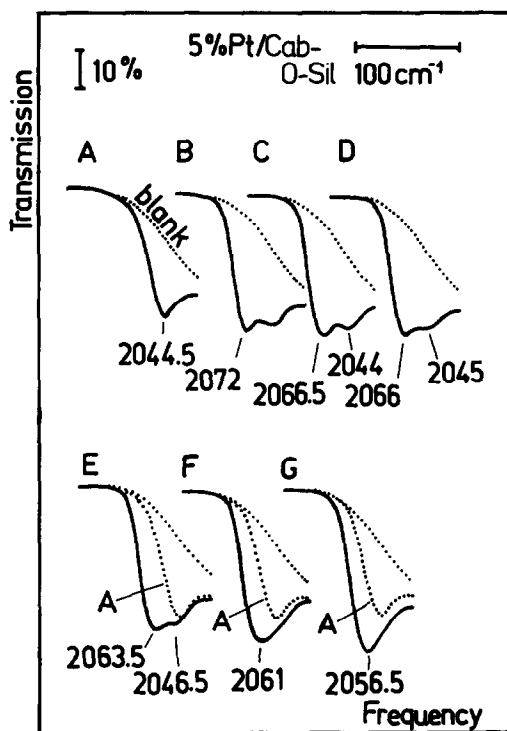


Fig. 7. Effect of time and temperature on the *ir* desorption-adsorption doublet (see Table 2).

TABLE 2
Effect of Time and Temperature on the Absorbances and Frequencies of Adsorptive-Desorptive CO ir Doublet on 5% Pt/Cab-O-Sil

Spectra of Fig. 7	Experimental conditions	Adsorptive ir band		Desorptive ir band	
		Absorbance	Wavenumber (cm ⁻¹)	Absorbance	Wavenumber (cm ⁻¹)
A	Desorptive ir band as in Fig. 5	—	—	0.1467	2044.5
B	5 × 10 ⁻³ Torr CO pulses at 298 K, twice	0.2081	2072	0.1505	2048.5
C	In the same gas at 298 K, 1 hr	0.2041	2066.5	0.1487	2044.5
D	Evacuation at 298 K, 15 min	0.2098	2066	0.1518	2045
E	Evacuation at 373 K, 3 min	0.2105	2063.5	0.1518	2046.5
F	Evacuation at 373 K, 2 hr	0.2307	2061	—	—
G	Evacuation at 423 K, 1 hr	0.2460	2056.5	—	—

ued following the formation of a medium-size desorption peak, the addition of a small CO dose results in the formation of an *ir doublet*. This *ir doublet* can be interpreted by the coexistence of both the adsorptive and desorptive CO on the Pt surface.

(5) The half-width of the $\nu(\text{CO})$ infrared band is invariant during adsorption. However, during desorption, band broadening results in a 5- to 6-cm⁻¹ increase in $h_{1/2}$. This band broadening must be ascribed to the process $\text{CO}_A \rightarrow \text{CO}_D$.

The first two points reinforce conclusions in the published literature. However, points 3-5 represent new information in the study of CO adsorption on supported Pt.

From a comparison of our experimental results with earlier findings on this topic (11, 20-22) the experimental data provided by the different methods for CO adsorption on supported Pt can be interpreted as follows.

It should be stressed that the structure of supported polycrystalline metals is a complex subject and unfortunately one which has not received much attention. Very little is known regarding the orientation and the distribution of Miller planes exposed for a given set of preparation techniques. It should be a function of several intervening variables such as: support, pretreatment conditions, crystallite size, metal-support interactions, and metal salt used. Probably lower Miller index planes predominate on the supported Pt surface. However, higher Miller index planes having lower surface coordinations are also present, with smaller surface area, which are located at corners, edges, steps, kinks, and dislocations. These low-coordination member sites are structurally and energetically more heterogeneous than the high-coordination sites.

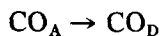
CO is adsorbed on Pt at small coverages with a high sticking probability at room temperature. For this reason, initially adsorbed CO is expected to be randomly distributed. Low infrared stretching frequency is expected for two reasons: (1) initially adsorbed CO is strongly backbonded and,

(2) adsorbed CO molecules are sufficiently separated from one another so that dipole-dipole interactions practically do not occur. Back-donation of electrons from the d orbitals of the metal to the π^* molecular orbitals of CO bond so that the stretching vibration occurs at a lower frequency (15).

As the surface coverage increases, the number of electrons available for back-bonding decreases with a resulting shift in the position of the CO stretching vibration to higher frequency. An additional shift to higher frequency is also due to an increase in the number of dipole-dipole interactions which occur at higher surface coverages. For these reasons and because of the surface heterogeneity of supported Pt the heat of chemisorption of CO decreases with increasing surface coverage.

The structure of adsorbed CO layer changes with increasing surface concentration. Although the surface mobility of adsorbed CO on Pt is large enough we can expect a little surface diffusion only on low Miller index planes at room temperature and there is almost no ordering on higher Miller index planes because of the higher diffusion energy.

As we increase the temperature the CO ad-layer undergoes surface rearrangement such that CO molecules adsorbed on the lower Miller index planes migrate in the direction of the higher Miller index planes, steps, kinks, and other surface irregularities. This rearrangement can be expressed as



where the adsorptive CO has now been transformed into desorptive CO. This transformation should be accompanied by a shift to lower frequency. It is for this reason that hysteresis is observed during the adsorption-desorption cycle.

When the ad-layer is heated prior to the formation of a monolayer, extensive surface rearrangement can take place due to the large number of vacant sites. It is for this reason that the thermal treatment of the

ad-layer for the partially covered surface migration has occurred. During this surface rearrangement, a large frequency shift was observed but the absorbance of adsorbed CO did not decrease and a small desorption was detected only by Pirani pressure gauge. From these observations we concluded that the ordered CO structure has a higher extinction coefficient than the disordered structure. We view this large shift in the frequency as a result not only of the increase in backbonding but also due to the decrease in dipole-dipole interactions. Since the high Miller index planes are energetically much more heterogeneous and the surface atom distances are larger, the dipole-dipole interactions are drastically reduced. It is well known that dipole-dipole interactions are maximized when CO stretching frequencies for adjacent molecules are identical (1). When the frequency corresponding to the CO stretching vibration was equal to that observed for the desorption.

Following partial desorption, the addition of a small dose of CO resulted in the formation of both adsorptive and desorptive CO. This was evidenced by the formation of the infrared doublet. When we added CO to the desorptive CO, it did not change to adsorptive CO, its absorbance did not decrease, rather it increased a very little, and a little increase was observed only in the frequency, too. The intensity of the adsorptive CO increased with the surface coverage.

These suggest that not only the structures of adsorptive CO and of desorptive CO are different, but they are also in different positions on the surface. They are sites on the supported Pt surface on which the CO adsorption will occur primarily. These are probably the lower Miller index planes which have larger surface area and on which the dipole-dipole interactions are larger.

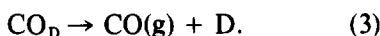
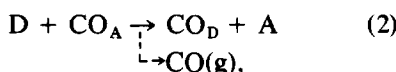
When CO desorption is initiated at monolayer surface coverage, surface migration is limited as all surface sites are occupied.

Under these conditions, desorption occurs first from the low Miller index planes, after it from the higher Miller index planes, steps, and kinks.

When stepwise CO adsorption was carried out at higher temperatures, the adsorbed CO molecules could migrate on the Pt surface resulting in a more ordered overlayer with lower infrared adsorption frequency.

CONCLUSIONS

In conclusion we can summarize our results using the following adsorption-desorption scheme:



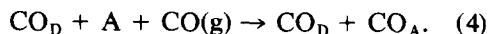
In steps (1) adsorption occurs predominantly on lower Miller index planes (A, adsorption sites). The dipole-dipole interactions are large as evidenced by the relatively high CO stretching frequency on adsorption. The structure of the ad-layer is largely disordered. However, there may be some ordering due to the formation of patches induced by preferential adsorption.

In steps (2), a disordered-ordered transition from low Miller index planes to high Miller index planes, steps, and kinks is a result of surface migration (A sites to D sites). During this transition very little desorption was observed to occur. At low surface coverages a large CO frequency shift was accounted for by considering a decrease in backbonding in addition to a large decrease in dipole-dipole interactions.

In steps (3), CO desorption depends at a given catalyst on the coverage and on the temperature rise with time. At low surface coverages the desorption occurs after steps (2) preferentially from the high Miller index planes, steps, and kinks (D, desorption sites). At high CO coverages the desorption begins from the low Miller index planes

(high-coordination member sites) and after it from the low-coordination sites.

The adsorptive and desorptive CO could coexist on the Pt surface at lower temperatures:



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