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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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THE STRUCTURE OF SURFACE COMPOUNDS OF CARBON MONOXIDE ON PALLADIUM ACCORDING TO ADSORPTION MEASUREMENTS AND INFRARED SPECTRA

(Presented by Academician V. I. Spitsyn on 30 XII 1960)

The adsorption of CO was studied at temperatures from −195° to 100° and pressures from 10^{-6} to $2–4 \cdot 10^{-2}$ mm Hg on palladium films condensed at $1–2 \cdot 10^{-7}$ mm Hg, and on palladium deposited on Aerosil. The design of the apparatus used, the method for preparing the films, and the measurement of pressure and adsorption have been described previously ([1]). Samples for spectral study were prepared by impregnating Aerosil with an aqueous solution of $PdCl_2 \cdot 2H_2O$ ([2]). Weighed portions of Aerosil powder of 150 mg were then pressed into disks 28 mm in diameter under a pressure of 50 kg/mm^2. The disks were placed in a special vacuum cell ([3]), evacuated at 300° in a vacuum of 10^{-5} mm Hg, and reduced at 300° in a hydrogen atmosphere at a pressure of 100 mm Hg. Final cleaning of the palladium surface was achieved by training the object at 300° in a vacuum of 10^{-5} mm Hg for 5 hr. The transmission of disks of composition 10% Pd and 90% SiO_2 in the region of 2000 cm^{-1} reached 10%.

Fig. 1. Adsorption of CO at −195° on a Pd film 1160 Å thick: 1 –admission to an empty reactor; 2 –total adsorption; 3 –reversible adsorption; 4 –strong adsorption

X-ray examination showed that the palladium prepared in this way is distributed in the Aerosil in the form of crystals with a normal face-centered cubic lattice, with an average crystal size of 140 Å. Spectra were recorded at 25° on a single-beam IKS-12 infrared spectrometer with a NaCl prism.

Figure 2

Figure 2: Figure 2

The study of CO adsorption on Pd showed that its qualitative features are similar to those characteristic of hydrogen adsorption on Cr, Fe, Ni, Pd ([1]). Even at −195° carbon monoxide is adsorbed extremely rapidly, and its rate is difficult to measure (Fig. 1). During the first minute after the gas is admitted, more than 90% of the total amount of gas adsorbed in the experiment is taken up. Adsorption is completely finished after 15–20 min. At elevated temperatures the adsorption rate is still higher.

The total adsorption at the temperatures investigated consists of strong, irreversible adsorption and weak, reversible adsorption. Strong adsorption proceeds rapidly, and reversible adsorption practically instantaneously. The strong adsorption of CO decreases with increasing temperature, whereas reversible adsorption increases as the temperature and pressure are raised. The instantaneous occurrence and complete reversibility of weak adsorption at all

temperatures makes it possible to regard it as a function of pressure. The initial part of the isotherms of weak adsorption follows the logarithmic dependence found by A. N. Frumkin and A. N. Shlygin ([4]), while its final part follows the Langmuir equation. On the whole (Fig. 2), the total uptake is practically independent of the sequence of temperature changes, since the adsorption curves, starting from low (−195°) to high temperatures (100°) and back to low ones, are well reproduced. These facts indicate the equilibrium character of the adsorption.

An estimate was made of the fractions of strong and weak adsorption (its saturation limit was calculated by the method of rectilinear anamorphoses of the Langmuir equation). The fractions of strong and weak adsorption (by the saturation limit) in the total uptake are, respectively: at −78°, 92 and 8%; at 0°, 84 and 16%; at 50°, 75 and 25%. In work ([5]) it was found that weak adsorption at 0° and a pressure of 10^{-2} mm Hg amounts to 5%.

Fig. 2. Adsorption of CO (at a constant amount of CO in the system) by a Pd layer 510 Å thick: **1** –calibration curve of the change in CO pressure in the reactor; **2** –changes in CO pressure in the presence of a Pd layer; **3** –adsorption of CO on Pd

Adsorption of CO on palladium deposited on aerosil retains all the features of gas adsorption on condensed layers of the metal. In this case there is also an equilibrium coexistence of strong and weak reversible adsorption, an increase in reversible adsorption and a decrease in strong adsorption with increasing temperature. Reversible adsorption at 25° and a pressure of $2 \cdot 10^{-2}$ mm Hg is about 10%. The presence of adsorption of carbon monoxide on palladium above the critical temperature of the gas (−140.2°), and the existence of a strong and reversible part throughout the entire investigated temperature range, indicate

Figure 3

Figure 3: Figure 3

the chemical nature of the uptake. The existence of two kinds of chemisorption —strong and weak—makes it possible to suppose that chemisorbed molecules may be present in at least two forms. To investigate these forms, the method of infrared spectroscopy was used; it was first applied to the study of surface compounds on metals by Terenin ([6]), and recently has been used in the works of Eischens ([7], [9]) and Gryaznov ([8]).

Fig. 3. Spectrum of carbon monoxide compounds on the surface of palladium: **1** —at CO pressure 1.5 mm Hg; **2** —after evacuation to a pressure of 10^{-4} mm Hg; **3** —in the presence of O_2 at a pressure of 8 mm Hg; **4** —after treatment with O_2 at a pressure of 8 mm Hg at 200° for 5 min.

In the spectrum of carbon monoxide compounds on the surface of palladium, at large values (Fig. 3, 1), bands at 2085 and 1990 cm^{-1} are observed. Evacuation of the sample to a pressure of 10^{-4} mm Hg decreases the intensity of the bands, and bands with maxima at 2085 and 1960 cm^{-1} are observed in the spectrum (Fig. 3, 2). Absorption bands in this region, belonging to strongly chemisorbed CO molecules, were observed by Eischens ([7], [9]), and on

on the basis of a comparison of the spectrum of the surface compounds of CO with the spectra of carbonyls of known structure, were assigned to two different forms of bonding of CO molecules with surface Pd atoms. It may be considered that the band at 2085 cm^{-1} belongs to the valence vibrations of a CO group bonded to one surface Pd atom, the so-called linear structure, whereas the band at 1960 cm^{-1} belongs to vibrations of a CO group bonded to two surface Pd atoms, the so-called bridge structure. The ratio of the band intensities in the spectrograms (Figs. 3, 4, 1) indicates that the surface compounds on the palladium surface exist predominantly in the form of bridge structures. The change in the spectrum (Fig. 3, 1, 2) upon evacuation of the sample in vacuum to 10^{-4} mm Hg indicates the removal mainly of the linear forms (a decrease in the intensity of the 2085 cm^{-1} band) and of part of the molecules of the bridge form more weakly bound to the surface (a decrease in intensity and a shift of the 1960 cm^{-1} band). It is not possible to observe a separate absorption band of reversibly sorbed molecules, apparently because of the small values of reversible adsorption under the temperatures and pressures studied, and possibly also because of the weak localization of reversibly adsorbed molecules on the surface Pd atoms.

Fig. 4. Spectrum of carbon monoxide compounds on the surface of palladium: 1 —after evacuation to 10^{-4} mm Hg; 2 —after treatment with H_2 at a pressure of 1 mm Hg at 200° for 15 min.; 3 —after treatment for 30 min.

The admission of oxygen at a pressure of 8 mm Hg and 25° practically does not change the spectrum of the surface compounds of CO. This indicates the

Fig. 4. Spectrum of carbon monoxide compounds on the surface of palladium: 1—after evacuation to 10^{-4} mm Hg; 2—after treatment with H_2 at a pressure of 1 mm Hg at 200° for 15 min.; 3—after treatment for 30 min.

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existence in the oxidation reaction of an induction period ([5]). Treatment of the surface compounds of CO with oxygen at 200° accelerates this process (Fig. 3, 4). In the spectrum there remain, in this case, absorption bands of low intensity at 1995 and 2120 cm^{-1}, which may be assigned to CO compounds remaining on the surface and perturbed by chemisorbed O_2.

The reaction of surface CO groups with hydrogen proceeds more slowly (Fig. 4). As a result of the reaction, the intensity of the absorption bands of the linear and bridge structures decreases and their shift toward longer wavelengths is observed: the band of the bridge forms shifts to 1940 cm^{-1} (Fig. 4, 3). Shifts in opposite directions of the absorption bands of surface CO compounds in reactions with oxygen and hydrogen are observed on other metals ([7]) and are explained by a change in the electronic state of the metal surface as a result of the difference in the electron-acceptor properties of O_2 and H_2, adsorbing on the surface in the course of the reaction.

Thus, the adsorption data make it possible to distinguish the existence on the surface of two types of adsorption: weak reversible and strong irreversible. The infrared spectra indicate that strongly adsorbed carbon monoxide molecules exist mainly in the form of bridge structures.

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