ADSORPTION OF CARBON MONOXIDE ON COPPER AND THE STRUCTURE OF ITS SURFACE COMPOUNDS ACCORDING TO INFRARED SPECTRA

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Abstract

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ADSORPTION OF CARBON MONOXIDE ON COPPER AND THE STRUCTURE OF ITS SURFACE COMPOUNDS ACCORDING TO INFRARED SPECTRA

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The adsorption of hydrogen, ethylene, oxygen, carbon monoxide, and other gases on many metals, as established earlier ($^{1-5}$), even at temperatures $\leq 195^\circ$ and pressures $\leq 1 \cdot 10^{-7}$ mm Hg, is completely or to a considerable extent due to chemical interaction of the adsorbate molecules with the surface atoms of the adsorbent, proceeding extremely rapidly. This interaction is a complex process involving the formation and subsequent transformations of various kinds of surface compounds ($^{6-8}$). It has been found that the nature of adsorption phenomena and the forms of surface compounds in the case of adsorption of hydrogen and ethylene depend on the position of the metal in D. I. Mendeleev' s periodic system (^{8,9}), and the boundary of their sharp change lies between nickel, palladium, platinum, and the metals of the copper subgroup (^{9}). In the case of carbon monoxide, according to our preliminary data, this boundary shifts to the right and passes between the metals of the copper and zinc subgroups (^{8}). The importance of this fact for elucidating the nature of the chemisorption and catalytic activity of metal surfaces prompted us, using copper as an example, to study in detail the adsorption of carbon monoxide, which is characteristic of it and its analogues, and, with the aid of infrared spectroscopy, to determine the surface compounds that are formed.

The adsorption of CO was studied at temperatures from -195 to 100° and pressures from 10^{-7} to $2—4 \cdot 10^{-2}$ mm Hg on condensed copper layers and on copper deposited on aluminum oxide or on aerosil. The copper layers were obtained by thermal evaporation from a tungsten evaporator (Cu purity 99.99%) in a vacuum of $\sim 0.8 \cdot 10^{-7}$ mm Hg on the walls of a round-bottom flask with an inner surface area equal to 200 cm^2. The adsorption of CO was measured by the method of gas flow through a capillary (^{12}) and by portionwise introduction of gas into the reactor. The procedure of the experiments and the method for measuring pressures and calculating adsorption were analogous to those described earlier (^{10}).

Copper samples for the study of infrared spectra were obtained by impregnating high-purity aluminum oxide or aerosil with an aqueous solution of cupric nitrate

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

(chemically pure). Portions of powders of the dried and ground suspension of 100 mg were pressed into disks 28 mm in diameter under a pressure of $\sim 7 \cdot 10^3$ kg/cm^2. The disks were placed in a vacuum cell described earlier (11), but used in the present study for recording infrared spectra also at low temperatures: −195 and −78°. The samples were reduced with hydrogen at 300—350° at pressures up to 100 mm Hg, and then degassed to a vacuum $\leq 1 \cdot 10^{-6}$ mm Hg and cooled to the required temperature.

The transmittance of disks of composition 12% Cu and 88% SiO_2 in the region of 2000 cm^{-1} reached 10%. The average size of the copper crystallites distributed in aluminum oxide, according to X-ray structural analysis, was ~ 300 Å. The spectrum was recorded on an IKS-12 infrared spectrometer with an NaCl prism. The methods of preparation and purification of the gases we used have been described earlier (11).

The study showed that the qualitative features of the adsorption of carbon monoxide on copper are similar to those found in the study of its adsorption on palladium (10): at all temperatures studied, CO is adsorbed extremely rapidly, and even at −195° its rate is difficult to measure. The total adsorption is made up of strong (irreversible) and weak (reversible) adsorption (Fig. 1); the former proceeds extremely rapidly, while the latter practically

instantaneously. Strong adsorption of CO decreases with increasing temperature, while weak adsorption increases with increasing temperature and pressure. In general, as shown by the study of CO adsorption at its constant amount in the reaction system (Fig. 2), in the region of low pressures the total adsorption decreases very sharply as the temperature is increased from −195° to 100°. Figure 2 also shows that the total adsorption does not depend on the sequence in which the temperature is changed. The adsorption curves measured upon increasing (2 and 3) and decreasing (2′ and 3′) the temperature are well reproduced, i.e., practically coincide. This circumstance indicates the equilibrium character of the adsorption.

Fig. 1. Adsorption of CO at −78° on a Cu layer 2643 Å thick: 1 −leakage into the evacuated reactor, 2 −total, 3 −reversible, 4 −strong adsorption

Fig. 2. Adsorption of CO (at a constant amount of CO in the system) on a Cu layer 1930 Å thick. 1 −calibration curve of the change in CO pressure in the evacuated reactor; 2 and 2′ −change in CO pressure in the presence of the Cu layer; 3 and 3′ −adsorption of CO on Cu

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Calculations show that the initial part of the isotherm of reversible adsorption of carbon monoxide on copper follows a logarithmic dependence (^{14}), while its subsequent part follows the Langmuir equation; the latter circumstance, as in the previously described cases (^{12}), made it possible to calculate (by the method of rectilinear anamorphoses) the limiting value of weak, reversible adsorption, and then the fractions of strong and weak adsorption in the maximum total adsorption. At -78° they amount, respectively, to ~ 45 and $\sim 55\%$.

Our observations of the adsorption of carbon monoxide on pressed samples of copper deposited on aluminum oxide give grounds for believing that it does not differ qualitatively from CO adsorption on condensed metal layers, although its rate is not so high, evidently because of diffusion retardation in the pores of the sample. This phenomenon has been studied in detail on palladium deposited on aerosil (^{11}). Finally, we note that at -195 and -78° and a pressure of 1 mm Hg no appreciable adsorption of CO on aluminum oxide is observed.

The existence of strong adsorption of carbon monoxide on copper and the considerable magnitude of the total adsorption at temperatures above the critical point of the gas testify to its chemical nature. The very existence of two types of chemisorption may be due to at least two forms of surface compounds of carbon monoxide with surface copper atoms. However, strong chemisorption may be due to several forms of surface compounds ($^{10-12}$). In studying this question

By methods of infrared spectroscopy at low and moderate temperatures we found that, in the spectrum of surface compounds of carbon monoxide on copper at -195, -78, and 20° and a gas pressure of 1.3 mm Hg, an absorption band is observed in the region of 2120 cm^{-1}. The intensity of the band increases on going from room temperature to -78° and reaches its greatest value at -195°. This phenomenon is observed on copper samples deposited both on aerosil and on aluminum oxide, i.e., it does not depend on the nature of the support. When carbon monoxide is pumped out of the reactor to a pressure $\ll 1 \cdot 10^{-5}$ mm Hg, i.e., when the reversibly adsorbed gas is removed,

Fig. 3. Spectrum of a carbon monoxide compound on the surface of copper.
$1 - P_{\mathrm{CO}} = 1.3$ mm Hg,
$2 - P_{\mathrm{CO}} = 10^{-5}$ mm Hg.

Fig. 4. Spectrum of a carbon monoxide compound on the surface of copper deposited on different supports. CO pressure 1.3 mm Hg. 1 –on copper deposited on aluminum oxide, 2 –on copper deposited on aerosil.

the intensity of the absorption band decreases, but, as is seen from Fig. 3, the band itself does not disappear. No appreciable shift of the indicated absorption band, which in this case is due to strongly chemisorbed carbon monoxide, is observed.

Comparison of the spectra of surface compounds of carbon monoxide on copper with the spectra of carbonyls of known structure makes it possible to conclude that the 2120 cm^{-1} band belongs to the valence vibrations of a CO molecule bound to only one surface copper atom, i.e., to the so-called linear structure. Taking into account that this band is observed both in the case of strong and in the case of reversible chemisorption, it may be assumed that for both these types of chemisorption the positions of the absorption bands coincide and that both forms of surface compounds of carbon monoxide with copper have a linear structure. Thus, the adsorption data make it possible to distinguish the existence of two types of adsorption: weak reversible and strong irreversible. Infrared spectra measured over a wide range of pressures and temperatures indicate that strongly adsorbed molecules exist only in one form, namely, a linear structure.

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