PHYSICAL CHEMISTRY

A. B. FASMAN, G. L. PADYUKOVA, Academician of the Academy of Sciences of the Kazakh SSR D. V. SOKOLSKY

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Abstract

Full Text

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A. B. FASMAN, G. L. PADYUKOVA, Academician of the Academy of Sciences of the Kazakh SSR D. V. SOKOLSKY

INVESTIGATION OF THE MECHANISM OF ADSORPTION AND CONVERSION OF CARBON MONOXIDE IN THE LIQUID PHASE

The catalytic conversion of carbon monoxide according to the overall equation $CO + H_2O \rightarrow CO_2 + H_2$ proceeds in the gas phase at 400-700° (1–4) and in the liquid phase at low temperatures. At present there is no single point of view on the mechanism of CO conversion in solutions. Some investigators (5–8) suppose that this reaction proceeds through the formation of formic acid or an unstable complex of the formate type. In contrast, others (9–12) consider the process of HCOOH formation to be improbable or else not the only one.

This work is devoted to the study of the mechanism of chemisorption and conversion of CO in aqueous solutions. To clarify this question, the electrochemical method of charge curves proposed by Frumkin and Shlygin (13) was used. The kinetics of the establishment of adsorption equilibrium during saturation with carbon monoxide of partially or completely degassed Pt was investigated. The experiments were carried out in an electrochemical cell on an electrode of platinized platinum with a visible surface of 6 cm^2, which was replatinized before each series of experiments.

Fig. 1. Change in the potential of a Pt electrode during adsorption of CO in a medium of 1 *N* H_2SO_4 at different temperatures:
1 –15°; 2 –50°; 3 –30°

The electrode was first saturated with hydrogen in a solution of 1 *N* H_2SO_4 to the reversible hydrogen potential and, after purging the cell with a stream of argon, was subjected to electrochemical degassing by anodic polarization to a potential of +0.5 V. At this potential, as was shown (13), electromotor-active gases are absent on platinum and the region of the double layer is reached. Subsequently, CO was introduced into the cell and the change of potential with

Fig. 2

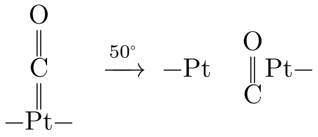
Figure 2: Fig. 2

time was determined. As is seen from Fig. 1, adsorption of CO leads to a shift of the electrode potential in the cathodic direction, and the character of this interaction depends strongly on temperature. Thus, at 15° it is possible, after prolonged saturation, to reach a potential of +0.16 V; at 30°, after 180 min, the reversible hydrogen potential (under these conditions) is reached; and at 50° the electrode potential at first shifts rapidly in the cathodic direction, reaching the reversible hydrogen potential already after 60 min, and then gradually shifts in the anodic direction up to +0.2 V after 6 hr from the beginning of saturation.

These data apparently indicate that at low temperatures (15°) physical adsorption of CO on Pt occurs; at intermediate temperatures (20–30°) the reaction of CO conversion to hydrogen takes place; and at higher temperatures (50°) conversion and chemisorption of CO occur. A similar picture was observed earlier in the study of CO adsorption on Pd (14).

To confirm the above assumption, the kinetics of the interaction of CO with Pt saturated with hydrogen up to the reversible hydrogen potential was studied. In this case, adsorption of CO at 20 and 30° does not lead to a change in the electrode potential, whereas at 50°, after 25 min, a slow shift of it in the positive direction is observed.

Obviously, at intermediate temperatures, and in the first phase of CO chemisorption at 50°, single-point, or linear, adsorption takes place, as a result of which part of the adsorbed molecules is converted to hydrogen. In the second stage at 50°, this hydrogen is displaced from the electrode surface and the first type of CO–Pt bond changes into a stronger bridge type (two-point adsorption) according to the scheme:



$$\begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{C}\\ \|\\ -\mathrm{Pt}-\end{array} \xrightarrow{50^\circ} -\mathrm{Pt}\begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{C}\end{array}\mathrm{Pt}-$$

The possibility of such a transition is also indicated by literature data on the adsorption of CO on various metals (15–19).

Fig. 2. Carbon monoxide charging curves in $1\,N$ H_2SO_4 at 30°; electrode saturation time: 1–1; 2–2; 3–3; 4–8 h.

When recording the charging curves, CO was introduced into the cell at a potential of +0.5 V, and the time of electrode saturation was varied from 1 to 8 hours. After saturation was completed, the excess gas was displaced with argon, and the charging curves were recorded at a current of 1 mA. It is seen

Fig. 3

Figure 3: Fig. 3

Fig. 4. Carbon monoxide charging curves in 1 N HCl at 20°; potential of CO introduction: 1 –0; 2 –100; 3 –200; 4 –300; 5 –500 mV

Figure 4: Fig. 4. Carbon monoxide charging curves in 1 N HCl at 20°; potential of CO introduction: 1 –0; 2 –100; 3 –200; 4 –300; 5 –500 mV

from Fig. 2 that the saturation time at 30° does not affect the course of the charging curve. This confirms the assumption made above about the nature of CO chemisorption on Pt at this temperature and once again indicates that, under certain conditions, CO is converted to hydrogen, and the electrode surface becomes covered with adsorbed hydrogen.

Fig. 3. Carbon monoxide charging curves in 1 *N* H_2SO_4 at 20°; CO introduction potential: 1–0; 2–100; 3–200; 4–300; 5–400 mV.

Analysis of the charging curves recorded at 50° showed that, at this temperature, hydrogen with a small binding energy is practically not formed. With increasing saturation time, a steeper shift of the potential in the anodic direction is observed, and the first branch of the curve is located ever closer to the ordinate axis, which indicates displacement of additional portions of weakly bound hydrogen from the Pt surface.

The study of the influence of the CO introduction potential on the course of the charging curves was carried out by an analogous method. The electrode potential was brought to +0.1, 0.2, 0.3, and 0.4 V

accordingly, the saturation time of the electrode in all cases was 1 hour. As is seen from Fig. 3, at 20° the introduction of CO at more anodic potentials increases the steepness of the charging curves, i.e., decreases the fraction of the surface occupied by adsorbed hydrogen. The same results were obtained at 30°. At 50° the angle of inclination of the initial portion of the curve to the abscissa axis is practically independent of the potential of CO introduction.

Fig. 4. Carbon monoxide charging curves in 1 N HCl at 20°; potential of CO introduction: 1 –0; 2 –100; 3 –200; 4 –300; 5 –500 mV

In a 1 N HCl solution the same regularities appear as in 1 N H_2SO_4, but the charging curves have a steeper form and are located closer to the ordinate axis (Fig. 4). On these curves a characteristic retardation is observed at +0.78 V, which is absent on the corresponding hydrogen curve. In sulfuric acid a similar segment arises at +0.45-0.50 V (depending on the temperature), but is less pronounced.

Evidently, this retardation is associated with the electrooxidation of strongly chemisorbed forms of CO. The indicated supposition requires additional verification.

Thus, it has been shown that, depending on the conditions of interaction of CO with Pt in aqueous solutions, there may occur both physical adsorption and adsorption leading to the conversion of CO to hydrogen, and, finally, strong chemisorption of CO with the formation of definite surface forms.

Kazakh State University
named after S. M. Kirov

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