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Mechanism of the catalytic synthesis of water on silver

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A mechanism of the macroscopic step of water synthesis in the oxidation of hydrogen on silver has been revealed.

The oxidation of hydrogen on silver is of interest for the theory of chemical kinetics and catalysis, and it can be used as a model redox catalytic reaction. This reaction makes it possible to study surface intermediates in order to understand the mechanisms of many important catalytic hydrogenation and oxidation reactions. This reaction is also of practical importance for the development of fuel cells.

Early studies[1–3] have demonstrated that the test reaction proceeds by the mechanism consisting of two consecutive steps: the chemisorption of oxygen and the interaction of gaseous hydrogen with adsorbed oxygen. However, further studies have revealed that the reaction has a more complicated mechanism and occurs *via* the intermediate formation of surface hydroxyl groups[4,5] by the three-step mechanism:

$$O_2 = 2\,O_{ads}, \qquad (1)$$

$$H_2 + 2\,O_{ads} = 2\,OH_{ads}, \qquad (2)$$

$$H_2 + 2\,OH_{ads} = 2\,H_2O. \qquad (3)$$

The kinetics and mechanism of steps (2) and (3) are unknown. The adsorption of oxygen (1) and step (2) proceed more rapidly, as compared to step (3).[6] In the steady state, the preponderant fraction of adsorbed oxygen will reside most likely on the silver surface as the OH_{ads} groups. In this case, the rate of hydrogen interaction with the silver surface, which has a stationary composition, will be the rate of step (3) in the test reaction mechanism. The aim of this work was to elucidate the regularities of this step.

Step (3) is highly unlikely to be considered elementary, as it was emphasized by Hillary and Stoukides.[7] Involving two adjacent hydroxyls in the collision with the hydrogen molecule should require the reaction being second-order with respect to surface hydroxyl groups. If step (3) is a macroscopic one and consists of elementary steps, it may contain the elementary rate-determining step whose activated complex has only one hydroxyl group; in this case, step (3) will be a first-order reaction with respect to surface hydroxyl groups. The reaction scheme by Hillary and Stoukides considered the dissociation of dihydrogen and the consecutive reactions of adsorbed oxygen and the resulting OH group with adsorbed hydrogen atoms; the latter stage was concluded being rate-determining. The weak point of the proposed scheme is that molecular hydrogen is not dissociatively adsorbed on a metallic silver surface.[8–10]

This study was carried out with polycrystalline silver obtained *via* the reduction of silver oxide by hydrogen. Silver oxide was prepared by precipitation from an aqueous solution of silver nitrate [chemically pure, GOST (State Standard) 1277-75] with potassium hydroxide (high purity). After the precipitation, silver oxide was carefully washed with distilled water and dried. The sample had a weight of 5.00 g, a silver grain size of 0.25–0.50 mm, and a specific surface area of 0.75 m^2 g^{-1}.

The study was performed using a volumetric static method in a glass vacuum setup equipped with McLeod gauges for pressure measurements. Hydrogen was purified by diffusion through a heated palladium capillary. Oxygen was produced by the vacuum decomposition of potassium permanganate (chemically pure). The setup made it possible to prepare hydrogen–oxygen mixtures with specified pressure and composition.

A stationary adsorbed layer was obtained by consecutive transformations of three portions of a stoichiometric hydrogen–oxygen mixture (a 30% conversion in each portion). The unreacted mixture was promptly removed by evacuation, and the reaction was carried out with a new portion of the mixture. The initial pressure of the reaction mixture was 22.8 Pa, and the reaction temperature was 298 K. The temperature was controlled by water circulating through a reactor jacket and measured by a thermocouple at the center of the catalyst layer. The resulting stationary adsorbed layer interacted with hydrogen at the same temperature and an initial pressure of 15.7 Pa, which was close to the hydrogen pressure in the stoichiometric mixture portions (15.2 Pa constitutes 2/3 of 22.8 Pa). Although the reaction is highly exothermal, the probable adiabatic rise in temperature is less than 0.2 K since polycrystalline silver had low dispersion and only 1 μmol of the reaction mixture interacted over 5 g of the catalyst during the experiment. Therefore, we considered that the collected data correspond to a constant temperature of 298 K.

Kinetic curves of the stoichiometric mixture flow rate are shown in Figure 1. Equal initial rates of the reaction during the transformation of second and third portions indicate the steady-state occurrence of the process. It can be concluded that the stationary adsorbed layer formed at 298 K and 22.8 Pa; the steady-state reaction rate was 1.18×10^{-9} mol m^{-2} s^{-1} at an average pressure of 21.4 Pa.

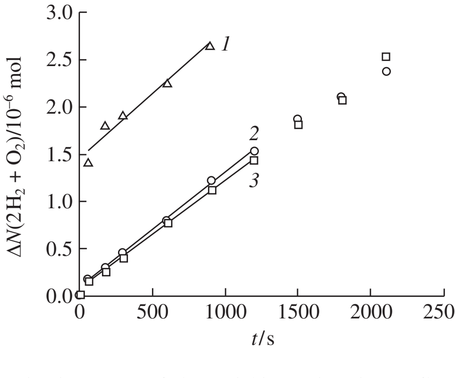

Figure 1 Kinetic curves of the stoichiometric mixture flow rate in the oxidation of hydrogen on silver at 298 K and 18.0–22.8 Pa. The conversion reached 30% in each portion. (*1*), (*2*) and (*3*) are the first, second and third portions of the mixture, respectively.

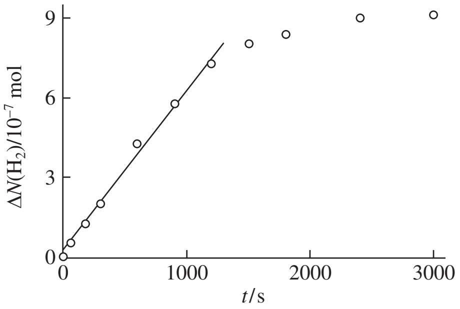

Figure 2 Interaction of hydrogen with the stationary adsorbed layer produced by the transformation of three successive portions of the stoichiometric mixture ($2H_2 + O_2$). Initial hydrogen pressure, 15.7 Pa; temperature, 298 K.

The following assumptions can be made:

(1) The initial rate of the interaction of hydrogen with the stationary adsorbed layer equals one-half of the rate of the catalytic oxidation of hydrogen because equal amounts of hydrogen are consumed in two steps: the formation of hydroxyl groups and the hydrogenation of surface hydroxyl groups.

(2) The hydrogenation of surface hydroxyl groups follows the first-order law with respect to surface hydroxyl groups, and it can be expressed as

$$H_2 + OH_{ads} = H_2O + H_{ads}. \quad (4)$$

To verify these assumptions, the interaction of hydrogen with the stationary adsorbed layer, which was produced during the transformation of the stoichiometric mixture, was investigated (Figure 2).

The initial rate of hydrogen interaction with the stationary adsorbed layer is $W = 6.00\times10^{-10}$ mol m^{-2} s^{-1}, and the steady-state rate of hydrogen oxidation in the reaction of stoichiometric mixture oxidation is 1.18×10^{-9} mol m^{-2} s^{-1}. It means that the initial rate of hydrogen interaction with the stationary adsorbed layer is two times lower than the rate of the steady-state catalytic oxidation of hydrogen under identical reaction conditions. Figure 3 shows that the reaction obeys a first-order equation with respect to surface hydroxyl groups at a constant hydrogen pressure: $\ln[1/(1 - x)] = kt$. Here, k is the rate constant (s^{-1}), and x is the conversion of surface hydroxide. These data were acquired at relatively small changes in the hydrogen partial pressure (average value of ~15.7 Pa). Nevertheless, these changes provided the accurate determination of the conversion of the adsorbed layer during its reaction with hydrogen.

The results support the hypothesis that the interaction of hydrogen with the stationary adsorbed layer obeys a first-order equation with respect to surface hydroxyl groups; thus, step (3) is macroscopic and the interaction of hydrogen with the stationary adsorbed layer is an elementary step of the catalytic reaction, which can be expressed as reaction (4). The rate constant of this step is $k = 7.60\times10^{-4}$ s^{-1} at a hydrogen pressure of 15.7 Pa. The results were reproduced in the repeated series of experiments. The apparent activation energy of the reaction at 273–473 K was 36.8 kJ mol^{-1}. Then, the rate constant at 298 K is 4.83×10^{-5} s^{-1} Pa^{-1}, which differs from the value obtained earlier[11] for the hydrogenation of surface hydroxyl groups, 4.25×10^{-5} s^{-1} Pa^{-1}, only by a factor of 1.14. This reliably confirms the accuracy of the obtained result.

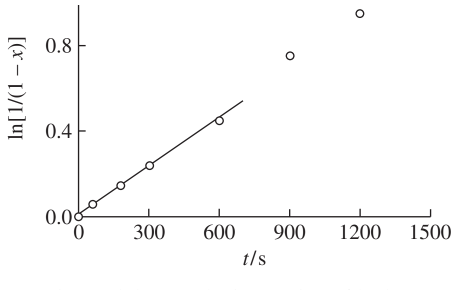

Figure 3 Experimental data on the interaction of hydrogen with the stationary adsorbed layer plotted in the coordinates of equation $\ln[1/(1 - x)] = kt$.

In the mechanistic scheme (1)–(3), step (3) is really a macroscopic one, which can be presented as the sum of two elementary steps, (4) and

$$H_{ads} + OH_{ads} = H_2O. \quad (5)$$

Each elementary act of step (4) is immediately accompanied by the interaction of the adsorbed hydrogen atom with the second hydroxyl group, which results in the formation of a second water molecule by reaction (5). Thus, step (4) is the key step of hydrogen oxidation on silver, and the surface hydroxyl group is a key intermediate directly involved in the formation of water. A hydrogen molecule and a surface hydroxyl group interact with each other to produce directly a water molecule without any intermediate species. Thus, it has been shown for the first time that the hydrogenation of surface hydroxyl groups during the oxidation of hydrogen on silver follows a first-order kinetic law with respect to hydroxyl groups. Chemical equation (4) was earlier unknown in catalysis. Some processes resembling those examined in this work were proposed when a model of hydrogen interaction with oxygen adsorbed on silver was analyzed using the density functional theory.[12,13] The results obtained in this study are novel and essential; in particular, a mechanistic similarity between the catalytic oxidation of hydrogen on silver and the branched chain reaction of hydrogen combustion including the similar step:[14]

$$^{\bullet}OH + H_2 = H_2O + {}^{\bullet}H, \quad (6)$$

where a hydroxyl group is the key species directly involved in the formation of water, is of interest.

Thus, the rate-determining step of the oxidation of hydrogen on silver is the interaction of a hydrogen molecule with a surface hydroxyl group giving a water molecule and an adsorbed hydrogen atom, which is described by equation (4). The adsorbed hydrogen atom rapidly interacts with the second surface hydroxyl group according to equation (5).

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