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Abstract

Full Text

PHYSICAL CHEMISTRY

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CATALYSIS AND ADSORPTION OF HYDROGEN ON GERMANIUM FILMS

The catalytic activity of the elements of the 4th period with respect to the isotopic exchange reaction of molecular hydrogen decreases sharply on going from nickel to copper ([1]), which is apparently associated with the filling of vacant states in the *d*-zone. Low catalytic activity was also observed for the next element—germanium, which was studied both in the form of films obtained by decomposition of germane ([2]), and by pulverizing germanium single crystals in air ([3], [4]) and in vacuum ([5]). In contrast to this, Sandler and Gajewski ([6]) found a very high catalytic activity of a germanium film obtained by cathodic sputtering of germanium onto the surface of glass cooled with liquid nitrogen. According to the data of Sandler and Gajewski, the specific catalytic activity of such a film is more than 5 orders of magnitude higher than the activity obtained in the works cited above, and approaches the activity of transition metals. The possibility of so sharp a change in the specific catalytic activity of catalysts of one and the same composition merely by varying the conditions of preparation is of considerable interest for the theory of heterogeneous catalysis.

We therefore considered it useful to investigate additionally the catalytic and adsorption properties of a germanium film obtained by evaporation in vacuum with condensation at the temperature of liquid nitrogen.

Fig. 1. **A** —reaction vessel for studying the rate of adsorption of hydrogen on germanium films; **B** —device for immersing a tungsten spiral in liquid gallium.

Method of investigation

Apparatus

For the investigation of the catalytic activity and the rate of adsorption of hydrogen, the present work used the apparatus described in (5), except that the quartz-glass reaction vessel was replaced by one of the devices in which the films were deposited.

The device for investigating the rate of adsorption of hydrogen is shown schematically in Fig. 1A. Into a bulb of molybdenum glass **1** are sealed two molybdenum leads **2**, 3.5 mm in diameter, which serve to supply current to a spiral **3** made of tungsten wire 0.5 mm in diameter. A graphite crucible **4** is placed in the spiral. A glass [[unclear: continuation cut off on this page]]

tube 5, in which there is a germanium bead 6, weighing about 0.1 g. An iron wire with a glass capillary 7 placed on it is inserted into the openings in the walls of tube 5 and holds the germanium bead 6 in the latter. If wire 7 is removed with the aid of a magnet, the germanium bead falls into the spiral. Such a device makes it possible to degas the spiral with the graphite crucible without germanium at a temperature higher than that at which deposition is carried out. The position of the germanium drop in the spiral during deposition is shown in Fig. 1 A, at right. The drop lies on the graphite and does not touch the spiral. Otherwise an alloy of germanium with tungsten would be formed, which would lead to destruction of the spiral and, possibly, to partial evaporation of the tungsten. To study the catalytic activity of the film, a reaction vessel was used which differed from that described above in that in the lower part of the glass ampoule 1 it had a device allowing the spiral to be immersed in liquid gallium after deposition of germanium, in order to eliminate the catalytic action of tungsten (Fig. 1 B). An iron rod 2, sealed into a glass tube, makes it possible, with the aid of a solenoid, to raise the test tube 3 with liquid gallium 4 in vacuum, while a copper wire 5 fixes the device in the upper position. A glass rod 6 with an iron rod 7 sealed into the glass serves to remove air bubbles from the inner walls of test tube 3 with gallium.

Deposition of films. Before deposition of germanium, the reaction vessel was heated at 450°C with pumping down to a vacuum of $3 \cdot 10^{-7}$ mm Hg. The spiral with the graphite crucible was then heated by current to a temperature higher than that at which deposition is carried out, with pumping down to a vacuum of $3 \cdot 10^{-7}$ mm Hg. The current was switched off, the germanium was dropped into the spiral, and the iron wire in the glass capillary was removed from the reaction vessel by a magnet. The temperature of the germanium was raised to somewhat above its melting point (current 9 A), with pumping down to a vacuum of $2 \cdot 10^{-7}$ mm Hg. (At this temperature deposition of germanium is negligible.) After this the current was switched off, the walls of the ampoule were brought into contact with liquid nitrogen, and the current was brought up to 13.5 A. At this current, deposition of germanium was carried out for 20–40 min. The amount of deposited germanium was 30–50 mg. During deposition the vacuum remained 1–2 $\cdot 10^{-7}$ mm Hg. High-purity germanium was used for evaporation ($\rho = 50\ \Omega \cdot$ cm).

Measurement of the surface of the deposited film in the study of the rate of hydrogen adsorption was carried out by krypton adsorption at the temperature of liquid nitrogen directly in the reaction vessel. In studying catalytic activity, the surface was calculated from the weight of deposited germanium and from the specific surface determined for a film obtained under analogous conditions.

Measurement of catalytic activity and the rate of hydrogen adsorption was carried out in the same way as in work ([5]).

Results

Rate of hydrogen adsorption. Table 1 gives the specific rates of hydrogen adsorption, divided by the pressure,

$$v = \frac{1}{PS}\frac{dn}{dt}$$

at $\theta = 0$ and room temperature for three germanium films and for a powder obtained by grinding, in vacuum, germanium with a resistance close to its intrinsic resistance, from work ([5]).

From the data of Table 1 it is evident that at $\theta = 0$ the rate of hydrogen adsorption at room temperature on films is an order of magnitude higher than on the powder. On the films, as on the powder, no areas on which rapid adsorption of hydrogen takes place were detected, to an accuracy of 0.2% of the surface.

Figure 2 shows the dependence of the adsorption rate at 100° on the degree of surface coverage for two germanium films and for the powder from work ([5]). The dashed line shows portions of the curves for the films, calculated from data on adsorption at room temperature and from the adsorption activation energy ($\varepsilon_{ads} \simeq 3$ kcal/mol at $\theta = 0$). As is seen from the graphs, for the films there is a sharper decrease in the adsorption rate with surface coverage than for the powder.

Catalytic activity. The study of catalytic activity with respect to the reaction of isotopic exchange of hydrogen with deuterium was carried out on two germanium films. On the first film ($S = 2.5$ m^2, $m = 0.05$ g) the catalytic activity was studied at 100°. It proved to be less than $1 \cdot 10^{-15}$ mol/cm$^2 \cdot$ sec. On the second film ($S = 0.6$ m^2, $m = 0.035$ g) the activity was studied in the temperature interval 228-192° C. Figure 3 gives the values of the specific activity of the germanium film and of the powder from work ([5]) as a function of temperature at

Table 1

Specific adsorption rates of H_2 on Ge films and powder

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Catalyst	v, mol/cm^2 · sec · mm Hg	Weight, g	Surface, m^2
Germanium films	$35 \cdot 10^{-14}$	0.05	2.5
Germanium films	$56 \cdot 10^{-14}$	0.029	1.4
Germanium films	$29 \cdot 10^{-14}$	0.046	2.1
Germanium powder	$4 \cdot 10^{-14}$	17	2.3

Fig. 2. Dependence of the hydrogen adsorption rate at 100° on the degree of surface coverage of germanium.
1 —crushed in vacuum; 2, 3 —films

Fig. 3. Dependence of the specific catalytic activity of a germanium film and powder on temperature at pressures of 0.7 (a, v) and 0.1 (b, g) mm Hg. a, b — germanium film; v, g —powder

pressures of 0.7 and 0.1 mm Hg. From the graphs it is seen that the activity of the film exceeds the activity of the powder by no more than a factor of 3-5.

Discussion of the results

The specific catalytic activity of the germanium film studied in the present work proved to be of the same order as that of the film obtained by decomposition of germanium, according to the data of Tamaru and Budar (^{2}), and of germanium powder, according to the data of our previous investigations ($^{3-5}$), and more than 5 orders of magnitude lower in comparison with the data given in the work of Sandler and Gazish (^{6}). There are no grounds to expect differences in the structure of films obtained in the present work by evaporation of germanium in vacuum onto glass at 77 °K and the film-

films obtained by Sandler and Gazith by cathodic deposition of germanium on glass at the same temperature.

It seems to us that the high rate of isotopic exchange observed in the experiments of Sandler and Gazith is associated with the catalytic action of tungsten leads.

We found very high activity with respect to the indicated reaction in a tungsten spiral heated at temperatures of 1500-2000° C under pumping. The activity of the spiral was sometimes so high that already at room temperature it could be limited by diffusion of the gas into the reaction vessel. The high background activity of the spiral also compelled us to use the device described above for immersing the spiral in gallium after deposition of germanium. Sandler and Gazith used tungsten leads in their apparatus and allow for the possibility of partial sputtering of tungsten during cathodic deposition of germanium. The high rate of reaction in their experiments may have been connected with a very strong catalytic action of the tungsten leads cleaned during cathodic sputtering. Their paper contains no mention of measurements of the background activity of the tungsten leads.

The absence of a large difference in the specific activity of germanium in the form of a powder and in the form of films (crystal sizes ∼ 200 Å) indicates that the method of preparing the catalyst (germanium) plays a subordinate role.

The kinetics of hydrogen adsorption on germanium films is qualitatively the same as on powders: the adsorption is activated and its rate falls rapidly as the surface is filled. However, at $\theta = 0$ the adsorption rate on films proves to be somewhat higher than on powders and decreases more sharply with surface filling. This indicates a certain difference in the heterogeneity of the surface of germanium obtained by the two indicated methods. The smaller difference in catalytic activity indicates that isotopic exchange of hydrogen takes place on the principal part of the surface, whose properties differ little in the case of films and powders.

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Note: Figure translations are in progress. See original paper for figures.