



Soviet-era science, translated into English

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1958

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Abstract

Full Text

PHYSICAL CHEMISTRY

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CATALYTIC ACTIVITY OF GERMANIUM WITH RESPECT TO THE REACTION OF ISOTOPIC EXCHANGE OF HYDROGEN WITH DEUTERIUM

(Presented by Academician A. A. Balandin, 9 X 1957)

The purpose of the present work was to compare the specific catalytic activity of the semiconductor element germanium with the activity of transition metals possessing unfilled *d*-zones, with respect to the reaction of isotopic exchange of hydrogen with deuterium.

Tamaru and Budar ⁽¹⁾ studied the course of this reaction at 302° on a germanium film obtained on glass by thermal decomposition of GeH₄. Along with hydrogen-deuterium exchange, hydrogen adsorption was investigated. The authors concluded that hydrogen adsorption on germanium proceeds with dissociation into atoms. The activation energy of adsorption at low coverages is 14.6 kcal/g-mole, and the heat of adsorption is 23.5 kcal/g-mole. The authors suppose that the hydrogen atoms are bound to the germanium surface by covalent forces and that their mobility along the surface is considerably lower than in adsorption on metals.

Experimental Part

Apparatus. We investigated the catalytic activity of germanium by a static method with circulation. The content of HD in the hydrogen-deuterium mixture was determined by the thermal-conductivity method. A detailed description of the apparatus is given in work ⁽²⁾.

The reaction was carried out in a quartz reaction vessel in the temperature range from 300 to 550° at pressures from 40 to 190 mm Hg of an equimolar mixture of hydrogen with deuterium. The reaction vessel was separated from the rest of the system by two traps at the temperature of liquid nitrogen in order to protect the catalyst from poisoning by mercury vapors, vacuum grease, etc.

Catalyst. Monocrystalline germanium of the electronic type of conductivity, with a specific electrical resistance of 6 ohm · cm, was used as the catalyst. The germanium was crushed in an agate mortar to particle sizes of $\sim 10^{-1}$ mm. The surface was estimated from the particle size. Two germanium samples were

Fig. 1. Dependence of the catalytic activity of two germanium samples on reciprocal absolute temperature. *a* –sample No. 1, $S = 200 \text{ cm}^2$; *b* –sample No. 2, $S = 100 \text{ cm}^2$.

Figure 1: Fig. 1. Dependence of the catalytic activity of two germanium samples on reciprocal absolute temperature. *a* –sample No. 1, $S = 200 \text{ cm}^2$; *b* –sample No. 2, $S = 100 \text{ cm}^2$.

studied: with a surface of 200 cm^2 (weight 2.8 g) and 100 cm^2 (weight 1.8 g). Because surface roughness was not taken into account, the actual surface area may have been somewhat larger. Before investigation of the catalytic activity, the germanium was, as a rule, reduced at a temperature of 650° while circulating the hydrogen–deuterium mixture in the system for 6 hours.

Preparation of hydrogen and deuterium. The gases for the reaction were obtained electrolytically. To remove possible traces of oxygen and nitrogen, hydrogen, as well as deuterium, was passed successively through a furnace with a palladium catalyst, a silica-gel dryer, and a charcoal trap cooled with liquid nitrogen. In addition, hydrogen was passed over a nickel-chromium catalyst at a temperature of 300° to establish high-temperature equilibrium with respect to ortho-para hydrogen.

For the preparation of deuterium, heavy water containing 99.6% D_2O was used.

Results

The specific catalytic activity of germanium was calculated by the formula

$$k = \frac{n}{St} \ln \frac{C'_{\text{HD}} - C_{\text{HD}}^0}{C'_{\text{HD}} - C_{\text{HD}}},$$

where n is the number of moles of gas in the apparatus; S is the surface area of the catalyst; C'_{HD} , C_{HD}^0 , and C_{HD} are, respectively, the equilibrium, initial, and after reaction time t concentrations.

This formula is valid for any mechanism of hydrogen exchange with deuterium ⁽²⁾.

The dependence of the catalytic activity kS of both germanium samples on the reciprocal temperature, determined at a mixture pressure of 40 mm Hg, is shown in Fig. 1. The activation energy of the reaction is 17 kcal/g-mole. The specific catalytic activity of both germanium samples at 330° was about $3 \cdot 10^{-10} \text{ g-mole/cm}^2 \text{ sec}$. The catalytic activity determined before reduction of the samples at 650° was somewhat higher.

Fig. 1. Dependence of the catalytic activity of two germanium samples on reciprocal absolute temperature. *a* –sample No. 1, $S = 200 \text{ cm}^2$; *b* –sample No. 2, $S = 100 \text{ cm}^2$.

Table 1

Pressure, mm Hg	Degree of conversion	Amount of HD in moles ($\times 10^3$)
189	0.49	2.8
130	0.50	1.9
40	0.50	0.5

The order of the reaction was investigated on the first germanium sample at a temperature of 480°. Table 1 gives the number of moles of hydrogen deuteride formed in 24 min and the corresponding degree of conversion at different pressures. The identical degree of conversion at different pressures shows that the reaction proceeds as first order.

Discussion of results

Table 2 gives the specific catalytic activities of germanium and of several metals with respect to the hydrogen-deuterium exchange reaction at a temperature of 300° and a mixture pressure of 40 mm Hg.

Table 2

Catalyst	Ge (film on glass)	Ge (single crystal)	Fe	Co	Ni	Cu	Au
Specific catalytic activity, g-mole/cm ² sec	$1 \cdot 10^{-10}$	$1.5 \cdot 10^{-10}$	$1.5 \cdot 10^{-10}$	$2.4 \cdot 10^{-9}$	$3.5 \cdot 10^{-7}$	$0.65 \cdot 10^{-11}$	$5.9 \cdot 10^{-9}$
Activation energy of exchange, kcal/g-mole	—	17	8.1	7.9	8.0	16	7.0

The specific catalytic activity of a germanium film obtained by thermal decomposition of GeH₄ was estimated from the data of work ⁽¹⁾. It is evident from Table 2 that this activity is of the same order of magnitude as the specific

activity of single-crystal germanium in our experiments. The fact that the reaction is first order and that its activation energy (17 kcal/g-mole) is close to the activation energy of adsorption of hydrogen on germa-

...value (14.6 kcal/g-mole), obtained in work ⁽¹⁾, indicates that under the conditions of our experiments the exchange proceeds by an adsorption-desorption mechanism at low degrees of filling of the germanium surface by gas atoms, and the limiting stage of the reaction is adsorption. On going to higher degrees of surface filling, the activation energy of the reaction apparently must increase, approaching the activation energy for hydrogen desorption (about 41 kcal/g-mole) at degrees of filling close to unity.

The values of the specific catalytic activities of the metals Fe, Co, Ni, Cu, and Au in Table 2 were calculated from the data of work ⁽²⁾, assuming a first-order reaction. As is seen from Table 2, the catalytic activity of the metals of Period IV increases with increasing atomic number and reaches a maximum for nickel.

On going from nickel to copper—an element with a filled *d*-zone—the catalytic activity decreases sharply. It is seen from Table 2 that at 300° the activity of germanium is 3 orders of magnitude lower than that of nickel and is close to the activity of iron. On going to lower temperatures, the catalytic activity of germanium should apparently become several orders of magnitude lower than that of the transition metals, because of the larger value of the activation energy of the reaction.

The catalytic activity of copper is an order of magnitude lower than that of germanium. This is apparently due to the fact that, in germanium, there is a different type of interaction with hydrogen than in metals, one not associated with the electrons of the *d*-zone.

Scientific Research Physico-Chemical Institute
named after L. Ya. Karpov

Received
1 X 1957

CITED LITERATURE

¹ K. Tamaru, M. Boudart, *Adv. in Catal.*, **9** (1957). ² M. A. Avdeenko, T. K. Boreskov, M. G. Slin'ko, *Problems of Kinetics and Catalysis*, **9**, *Isotopes in Catalysis*, 1957, p. 61.

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