CHEMISTRY

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1960

SovietRxiv

Abstract

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ADSORPTION OF HYDROGEN ON LOW-PERCENTAGE Pt/Al_2O_3 AND Pd/Al_2O_3 CATALYSTS IN THE LIQUID PHASE

In studying hydrogenation catalysts it is very important to have information on the amount and state of the hydrogen sorbed by them. An extensive literature is devoted to this question; however, most investigations concern pure metals, partly mixed catalysts, or individual samples of supported catalysts with a relatively high content of active metal.

We prepared a series of Pt/Al_2O_3 and Pd/Al_2O_3 catalysts with platinum and palladium contents from 0.05 to 3.47 wt. %.

The alumina gel used as the support was prepared by precipitating aluminum hydroxide with ammonia from an $Al_2(SO_4)_3$ solution by the method of ([1]). Samples for platinum and palladium were prepared separately; therefore their specific surface area may differ somewhat. Platinum and palladium were deposited on Al_2O_3 powder from dilute solutions of $PtCl_4$ and $PdCl_2 \cdot 2NaCl$ of various concentrations at room temperature and with vigorous stirring for two hours for platinum and three hours in the case of palladium. Adsorption of platinum on Al_2O_3 was complete at all concentrations. Palladium was already detected in the filtrate at a content of 0.6% on the support. However, the palladium deposited on Al_2O_3 was adsorbed irreversibly and was not detected in the wash waters. Analyses of the filtrates for Pd•• were carried out on a photocolorimeter. The catalysts, washed free of Cl^- and dried, were reduced in a stream of electrolytic hydrogen under the following conditions: two hours at 220–230°, a brief rise in temperature to 355°, and further reduction at 355–360° for two hours. After cooling to room temperature, the catalysts were brought into contact with air and subsequently stored in bottles with ground-glass stoppers.

A convenient method for determining the amount of hydrogen sorbed by catalysts is the method of chemical dehydrogenation. It was shown that benzoquinone is quantitatively hydrogenated to hydroquinone by hydrogen sorbed by nickel, platinum, and palladium catalysts ([2]). In the presence of an excess of quinone, all the hydroquinone formed can be detected in solution.

Experimental procedure. A weighed portion of catalyst (0.5–1.0 g), brought to constant weight (at 115–120°), was placed in a known volume of solvent and

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

shaken in an atmosphere of hydrogen. After saturation of the catalyst with hydrogen, the reaction vessel—a duck—was stopped, and the hydrogen from the gas phase was displaced with purified nitrogen. In the nitrogen atmosphere a quinone solution was introduced and shaking was resumed. At the end of the experiment the catalyst was rapidly filtered off, and the filtrate was immediately analyzed for hydroquinone.

Aqueous-alcoholic suspensions of the support and of the finished catalysts differed somewhat in pH; therefore the reaction was carried out in a buffer solution CH_3COOH + NaOH (0.14 N with respect to acid), pH 5.2. The volume of solution was 20–25 ml. The time for saturation of the catalysts with hydrogen was 30–40 min. For

Pt/Al_2O_3 and from 40 to 150 minutes for Pd/Al_2O_3, depending on the palladium concentration. The reversible hydrogen potential was $E_0(Pt)$ = 540–550 mV, $E_0(Pd)$ = 550–580 mV relative to the normal calomel electrode. Quinone (0.05 g) was introduced in the form of an alcoholic solution (4–5 ml). In this case the catalyst potential fell into the oxygen region by 720–730 mV. During shaking with quinone (20–30 min in the case of Pt/Al_2O_3 and 40–60 min in the case of Pd/Al_2O_3) the potential

Fig. 1

Fig. 2

increased by several mV, after which it remained constant. The temperature of the experiments was 25°. Blank experiments without catalyst were carried out periodically. In this case a small amount of hydroquinone was found in the solution, and this was subsequently taken into account.

Table 1

Dehydrogenation by quinone of Pt/Al_2O_3 catalysts

Platinum content in the catalyst, wt. %	Catalyst charge, g	Hydroquinone obtained, mg	Hydrogen removed, ml: total	Hydrogen removed, ml: per 1 g catalyst	Hydrogen removed, ml: per 1 g Pt
0.171	0.498	2.51	0.511	1.03	600
0.171	0.756	3.21	0.650	0.86	505

Platinum content in the catalyst, wt. %	Catalyst charge, g	Hydroquinone obtained, mg	Hydrogen removed, ml: total	Hydrogen removed, ml: per 1 g catalyst	Hydrogen removed, ml: per 1 g Pt
0.893	0.472	7.34	1.49	3.16	354
1.334	0.449	6.59	1.34	2.98	224
1.331	0.504	6.43	1.31	2.59	195
1.766	0.490	6.04	1.26	2.51	142
1.766	0.452	6.48	1.32	2.56	145

Experiments with pure Al_2O_3, as well as with its mixture with the catalyst, showed that under these conditions hydrogen is not adsorbed on it.

Hydroquinone was determined by amperometric titration with $Ce(SO_4)_2$ in $2N$ H_2SO_4 [3]. At the same time the filtrate was analyzed for quinone (iodometrically). Adsorption of quinone on the catalysts under the experimental conditions is very small; its magnitude lay within the error of the analysis. An experiment with increased charges of Al_2O_3 and quinone showed that, under the adopted conditions, less than 1 mg of quinone is adsorbed on one gram of alumina.

For each catalyst 2-3 parallel experiments were carried out. The reproducibility of the experiments on Pt/Al_2O_3 is satisfactory. Palladium catalysts are more capricious; the deviation from the mean value in some cases reaches $\pm 20\%$. After appropriate purification, nitrogen was additionally passed through a series of wash bottles with hydroquinone and pyrogallol absorbents; however, complete removal of traces of oxygen was not achieved (control by the potential drop in a standard experiment on Ni skeletal catalyst), and therefore the results may be somewhat underestimated.

The experimental data are given in Tables 1 and 2. In Figs. 1 and 2 the mean values from parallel experiments are plotted. Curves 1 in Figs. 1 and 2 show the dependence of the amount of H_2, in ml (right ordinate), removed from 1 g of catalyst, on its composition. This amount at first increases with increasing metal content, then begins to decrease somewhat. For Pt/Al_2O_3 this transition lies in the region of 0.8-1.0% Pt; for Pd/Al_2O_3, in the region of 0.5-0.6% Pd. With a further increase in the palladium content, hydrogen adsorption on the catalysts, after a small minimum, again increas-

decreases. The absolute amount of hydrogen adsorbed on Pd/Al_2O_3 is smaller than on analogous platinum catalysts. The greatest amount of hydrogen—about 3 ml per 1 g of catalyst—occurs for the catalysts with the highest of the concentrations studied: 1.766% Pt and 3.47% Pd (the latter lies beyond the limits of Fig. 2).

If the amount of hydrogen removed is recalculated per 1 g of metal, it turns out that its capacity to retain hydrogen is the greater, the smaller the filling of the surface by metal (curves 2 in Figs. 1 and 2). At a Pt content of 0.171%, one gram of it accounts for 550 ml H_2, i.e., about ten H atoms per Pt atom; while at a content of 1.766% the ratio Pt : H < 3. Palladium behaves analogously: for the catalyst with the lowest concentration (0.05%), the greatest amount of hydrogen was found—510 ml per 1 g Pd, or about five H atoms per Pd atom. A palladium atom is approximately half the size of a platinum atom; correspondingly, its adsorption capacity for hydrogen is smaller.

Table 2

Dehydrogenation of Pd/Al_2O_3 catalysts with quinone

Pd content in catalyst, wt.%	Catalyst sample weight, g	Quinone received, mg	Hydrogen removed, ml: total	Hydrogen removed, ml: per 1 g catalyst	Hydrogen removed, ml: per 1 g palladium	Pd content in catalyst, wt.%	Catalyst sample weight, g	Quinone received, mg	Hydrogen removed, ml: total	Hydrogen removed, ml: per 1 g catalyst	Hydrogen removed, ml: per 1 g palladium
0.050	1.4360	1.64	0.33	0.23	460	0.58	0.5177	2.49	0.51	0.98	168
0.050	1.0629	1.48	0.30	0.28	560	0.58	0.5575	1.87	0.38	0.68	117
0.10	1.1652	1.57	0.33	0.27	274	0.69	0.5445	1.84	0.37	0.68	99.4
0.10	1.0135	1.88	0.40	0.38	377	0.69	0.7327	2.28	0.46	0.63	91.5
0.20	0.8554	1.87	0.39	0.44	223	0.79	0.4990	1.54	0.31	0.63	79.5
0.20	0.7000	2.28	0.46	0.66	330	0.79	0.5142	1.90	0.39	0.75	95.0
0.40	0.8556	2.52	0.51	0.60	149	0.97	0.5310	1.97	0.40	0.76	77.8
0.40	0.5427	1.75	0.36	0.66	164	0.97	0.5214	2.03	0.41	0.79	81.6
0.50	0.9848	4.54	0.92	0.94	186	3.47	0.1982	3.00	0.61	3.09	89.1
0.50	0.6881	2.14	0.43	0.63	126	3.47	0.1970	2.56	0.52	2.67	76.7

As the concentration of Pt and Pd in the catalyst increases, their adsorption capacity with respect to hydrogen at first falls rapidly and then more slowly. On Pt/Al_2O_3, the decrease in adsorption capacity slows after the addition of 1.3–1.5% Pt. On palladium catalysts, in the range 0.7–3.47% Pd, the ratio Pd : H remains close to unity. Thus, hydrogen dissolved in Pd, which is characteristic of Pd, does not appear even at a palladium content in the catalyst of 3.47%, which indicates its strong dispersion on the surface. In general, under the conditions studied, the properties of Pt/Al_2O_3 and Pd/Al_2O_3 in the region of small coverages proved to be very similar.

The special properties of catalysts in highly diluted layers on supports have already been noted by other authors. Thus A. N. Mal' tsev and N. M. Kobozev

([4]), in the hydrogenation of olefins on Pt/SiO_2 and Pt/Al_2O_3, found that at a very small content of platinum on the support its specific activity increases with dilution of the layer. It turned out that, at these coverages, the specific magnetic susceptibility of platinum also increases manyfold. The phenomenon of superparamagnetism was found for a large number of platinum, palladium, and other catalysts in highly dispersed layers ([4]). The manifestation of special properties by platinum and palladium atoms when deposited in very small amounts on supports of the Al_2O_3 type may be regarded as an established fact.

The explanation for this phenomenon should evidently be sought in the electronic interaction of the deposited atoms with the support (a semiconductor). A single metal atom, upon reaching the surface of the support, creates around itself a field on which hydrogen (obviously molecular hydrogen) is also adsorbed. Thus, the adsorbed catalyst atoms exhibit a certain long-range effect. This picture is consistent with Patterson' s view^6 of the active center as an extended region with surface diffusion. If it is assumed that the deposited platinum and palladium are present in the form of crystals, then each surface atom of the metal must account for even more hydrogen atoms than was calculated.

As for the similarity of dilute layers of platinum and palladium with respect to hydrogen adsorption in the liquid phase, it confirms existing observations that the catalytic properties of palladium on a support are closer to those of platinum than to those of pure palladium, for example, in the hydrogenation of compounds with a triple bond.

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Received
21 III 1960

CITED LITERATURE

1. V. I. Shekhobalova, I. V. Krylova, and N. I. Kobozev, *ZhFKh*, **26**, 703 (1952).

2. N. I. Popova, D. V. Sokol' skii, *Tr. Inst. Khim. AN KazSSR*, **2**, 70 (1958).

3. S. P. Bogdanov, N. S. Sukhobokova, *ZhA* , **6**, 344 (1951).

4. A. N. Mal' tsev, N. I. Kobozev, *ZhFKh*, **29**, 142, 290 (1955).

5. N. I. Kobozev, V. B. Evdokimov, I. A. Zubovich, and others, *ZhFKh*, **33**, 2811 (1959).

6. D. Patterson, *Trans. Farad. Soc.*, **49**, No. 367, 802 (1953).

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