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B. D. POLKOVNIKOV, Academician A. A. BALANDIN, and A. M. TABER

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Abstract

Full Text

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ON THE CATALYTIC PROPERTIES OF BORIDES OF METALS OF THE PLATINUM GROUP

As catalysts for low-temperature liquid-phase hydrogenation, metals of Group VIII of the Mendeleev periodic table (Co, Ni, Pt, Pd) have found wide application in the form of "skeletal" catalysts and "blacks." It was recently shown that the borides of Ni and Co also possess considerable catalytic activity (1, 3). In studies by Paul, Buisson, and Joseph (1) it was established that a catalyst prepared by adding Na borohydride to a solution of nickel (or cobalt) chloride possesses considerable catalytic activity and stability in liquid-phase hydrogenation reactions of safrole, furfural, and *n*-benzonitrile; moreover, the activity of such a catalyst increases when it is promoted with certain metals. A catalyst promoted with 2% Cr, Mo, W, V (1), or deposited on a support (2), has an activity exceeding that of skeletal nickel. Analytical methods also established the formula of the borides obtained (1, 5). The compounds of boron with nickel and cobalt obtained corresponded to the formula Me_2B.

Fig. 1. Kinetic curves of cyclopentadiene hydrogenation in methyl alcohol; 1 —Pd black. 2 —Pd boride. 3 —Pt boride. 4 —Pt black. 5 —Rh black. 6 —Rh boride.

In later work (3) it was shown that cobalt boride, prepared by adding $NaHB_4$ borohydride to a solution of cobalt chloride, exhibits high activity and selectivity in the hydrogenation reaction of adipic acid dinitrile.

It seemed of interest to test, in liquid-phase hydrogenation reactions, borides of platinum-group metals obtained by the method described above. In obtaining borides in this way it should be borne in mind that by no means all metals form borides by this route. For example, salts of Ag, Hg, and Bi, although reduced under the action of an alkali-metal borohydride, do not give the corresponding borides (4).

In the present work the catalytic properties of borides of platinum-group metals (Pd, Pt, Rh) were studied in liquid-phase hydrogenation reactions. The activity of the catalyst samples obtained was determined in reactions of liquid-phase low-temperature hydrogenation and was simultaneously compared with the activity of palladium, platinum, and rhodium blacks.

Table 1

Hydrogenation of unsaturated compounds on Pd—B, Pt—B, Rh—B catalysts (experimental conditions: temperature 20°, pressure atmospheric, catalyst charge 0.045 g, solvent —methyl alcohol)

Experiment No.	Catalyst	Substance hydrogenated	Charge of hydrogenated substance, g	H_2 consumption, ml (theoretical)	H_2 consumption, ml (actual)	Initial hydrogenation rate, ml/min	Total hydrogenation time, min
1	Pd—B	Cyclopentadiene	0.2278	176	172	33	14
2	Pd—black	Same	0.2278	176	174	16	27
3	Pd—B	Dimethyl ester of maleic acid	1.3884	182	183	44.8	7
4	Pd—black	Same	0.8939	158	157	21.2	12
5	Pd—B	Cyclohexene	0.7748	236	232	18	22
6	Pd—black	Same	0.7748	236	234	10	34
7	Pd—B	Crotonaldehyde	0.1982	162	163	8	26
8	Pd—black	Same	0.1982	162	160	3	35
9	Pd—B	Cinnamaldehyde	0.4371	161	156	7	32
10	Pd—black	Same	0.4371	161	155	4	58
11	Pt—B	Cyclopentadiene	0.2363	181	177	8	38

Experiment No.	Catalyst	Substance hydrogenated	Charge of hydrogenated substance, g	H_2 consumption, ml (theoretical)	H_2 consumption, ml (actual)	Initial hydrogenation rate, ml/min	Total hydrogenation time, min
12	Pt—black	Same	0.2363	181	175	4.6	96
13	Pt—B	Dimethyl ester of maleic acid	0.3891	192	192	7	52
14	Pt—black	Same	1.0881	192	192	2	120
15	Pt—B	Cyclohexene	0.3134	110	107	4.2	14
16	Pt—black	Same	0.3134	110	105	1.5	27
17	Pt—B	Crotonaldehyde	0.1982	162	157	4	42
18	Pd—black	Same	0.1982	162	155	2.4	76
19	Pt—B	Cinnamaldehyde	0.4371	161	152	4.4	34
20	Pt—black	Same	0.4371	161	157	2	74
21	Rh—B	Cyclopentadiene	0.2342	180	174	4.2	44
22	Rh—black	Same	0.2342	180	172	2.4	97
23	Rh—B	Dimethyl ester of maleic acid	1.0632	176	174	5	42
24	Rh—black	Same	1.0632	176	167	3	78
25	Rh—B	Cyclohexene	0.6348	217	215	3.6	32
26	Rh—black	Same	0.6348	217	212	2.2	40
27	Rh—B	Crotonaldehyde	0.1892	170	163	3	72
28	Rh—black	Same	0.1892	170	163	1.8	96

Experiment No.	Catalyst	Substance hydrogenated	Charge of hydrogenated substance, g	H_2 consumption, ml (theoretical)	H_2 consumption, ml (actual)	Initial hydrogenation rate, ml/min	Total hydrogenation time, min
29	Rh—B	Cinnamaldehyde	0.4374	164	156	2.8	78
30	Rh—black	Same	0.8802	164	162	1.4	102

Experimental Part

The preparation of Pd—B, Pt—B, and Rh—B catalysts was carried out as follows: to 20 ml of a 5% aqueous solution of platinum chloride (palladium or rhodium), a 25% aqueous solution of sodium borohydride (or potassium borohydride) was gradually added over 20-30 minutes at room temperature and with constant stirring; stirring was then continued for another 10-15 minutes. The resulting voluminous black precipitate was washed with distilled water until a negative reaction to phenolphthalein was obtained and was stored under ethyl alcohol. The catalysts are not pyrophoric.

A preliminary analysis of the catalyst samples obtained indicates the presence in them of boron in the form of a chemical compound. However, determination of the formula of the compounds obtained will be the subject of further investigations.

The preparation of platinum, palladium, and rhodium "blacks" was carried out by reducing the metal chlorides with formalin in an alkaline medium at a temperature of 0° ± 5°. Hydrogenation was carried out in a glass duck-shaped vessel at atmospheric pressure. The reaction products were analyzed by chemical and chromatographic methods. The hydrogenation substrates used were: cyclopentadiene, cyclohexene, dimethyl ester of maleic

acids, crotonic and cinnamic aldehydes. For a qualitative comparison of the hydrogenation rates under analogous conditions, experiments were carried out on hydrogenation over "blacks." The results of the experiments presented in Table 1 and the kinetic curves (Fig. 1) make it possible to judge that Pd—B, Pt—B, and Rh—B exhibit high catalytic activity in liquid-phase catalytic hydrogenation reactions. The rate of catalytic reactions on boride catalysts considerably exceeds the rate of analogous catalytic hydrogenation reactions on "blacks."

Fig. 2. Change in the initial rate of hydrogenation of cyclopentadiene in methyl alcohol upon repeated use of the catalysts. Designations as in Fig. 1.

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Figure 2: Fig. 2. Change in the initial rate of hydrogenation of cyclopentadiene in methyl alcohol upon repeated use of the catalysts. Designations as in Fig. 1

A decrease in catalytic activity is observed in the series of catalysts Pd—B → Pt—B → Rh—B. In addition to revealing the catalytic activity of this new type of catalyst, it was important to establish their stability in catalytic hydrogenation reactions. Therefore, under the previously established conditions, a series of experiments was carried out with repeated use of one portion of catalyst. In parallel, a series of analogous experiments was carried out with the “blacks” of the corresponding metals.

The results presented in Fig. 2 show that the boride catalysts (Pt—B, Pd—B, Rh—B) exhibit greater resistance to fatigue than the “blacks” of the corresponding metals.

The work carried out on the study of the catalytic properties of borides of platinum-group metals (Pt—B, Pd—B, Rh—B) indicates that, because of their considerable activity and rather high stability, boride catalysts may find broad application in the hydrogenation of various organic compounds.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

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