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Abstract

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STUDY OF CATALYSTS OBTAINED BY THE REACTION OF SODIUM BOROHYDRIDE WITH SALTS OF HEAVY METALS

It has recently been established that catalysts prepared by treating solutions of salts of platinum, palladium, and rhodium with sodium borohydride possess high activity and stability in reactions of liquid-phase low-temperature hydrogenation of various organic compounds (1,2). According to preliminary qualitative analysis, the catalyst samples obtained contain about 9% boron in the case of the reaction of cobalt and nickel salts and 2–3% boron in the case of platinum, palladium, and rhodium (1). It is known that, during the reduction of metal salts with sodium borohydride, in a number of cases "borides" of metals are formed (Co(II), Ni(II), Fe(II)); exchange reactions may also occur with the formation of new borohydrides (Be, Al, Li, K, Ca); and, finally, the reduction reaction may lead to the formation of free metals (Ag, Bi, As) (3,4). In addition, the reaction may be complicated by side reactions involving the formation of products of partial hydrolysis of sodium borohydride.

Table 1

Salt	Taken, g	Taken, g	Analysis of products, wt.%	Analysis of products, wt.%	Analysis of products, wt.%	Analysis of products, atomic fractions	Analysis of products, atomic fractions	Analysis of products, atomic fractions
Salt	salt	$NaBH_4$	Me	B	H	Me	B	H
$PdCl_2$	0.25	1.0	96.3	3.1	0.37	0.88	0.28	0.37
$RhCl_3$	0.25	1.0	92.8	2.9	0.40	0.90	0.29	0.40
H_2PtCl_6	0.25	1.0	95.7	2.28	0.42	0.48	0.21	0.42

In view of the foregoing, it seemed of interest to clarify the chemical nature and to study the properties of Pd, Pt, Rh– "boride" –catalysts. The catalysts were prepared by reducing aqueous solutions of the chlorides of platinum, palladium, and rhodium with sodium borohydride. It is desirable to maintain the order of

Fig. 1

Figure 1: Fig. 1

mixing of the reagents in which the aqueous solution of sodium borohydride is added to the salt solution. Otherwise the precipitate of the "boride" that is formed accelerates the decomposition of sodium borohydride, and the reaction proceeds very vigorously and with considerable overheating ([1]).

The resulting voluminous black precipitates are not pyrophoric and have reducing properties; they dissolve readily in aqua regia and much less readily in hydrochloric and sulfuric acids.

Table 1 presents the results of quantitative analysis of the precipitates obtained. The metal content was determined gravimetrically. Platinum and rhodium were precipitated as the metals, palladium as dimethylglyoxime. Boron was determined by titration with alkali in the presence of mannitol using phenolphthalein. In addition, the boron content was determined spectrally. The catalysts under study contain considerable amounts of hydrogen, which is evolved even upon slight heating. The amount of hydrogen evolved was measured volumetrically.

Heating curves of the catalysts were obtained on an N. S. Kurnakov pyrometer using a Stepanov vessel filled with argon. Simultaneously, the volume of hydrogen evolved was measured. In all cases hydrogen evolution occurs in the interval 70–120° and is characterized by

endothermic effect (Fig. 1). The amount of hydrogen released per 1 g of substance is ~ 40 ml/g.

The curves of the dependence of the amount of hydrogen released on temperature have an S-shaped form and obey the equation $V = V_0 e^{-E/RT}$, where V_0 is the total volume of hydrogen, V is the volume of hydrogen released at a given temperature, and E is the energy of the bond of hydrogen with the catalyst. On the basis of the calculation, E proved to be approximately equal to 3 kcal/mole. The low value of the energy of the bond of hydrogen with the catalyst, the small amount of hydrogen per 1 g of substance, and the reversibility of the effect on the thermogram indicate that the hydrogen is adsorbed, and not chemically bound.

Fig. 1. Thermogram of the Pd– "boride" catalyst

IR absorption spectra were obtained on a double-beam IKS-14 infrared spectrophotometer using KBr, NaCl, and LiF prisms. In the work, a substance pressed with potassium bromide was used. For comparison, spectra were obtained of Pd–B and Pt–B skeletal catalysts prepared from Pd–B–Al and Pt –B–Al alloys. The spectra of the alloys and samples of the catalysts studied have a similar appearance (Fig. 2), which possibly indicates the closeness of their structure. There is reason to believe[5] that the broad, rather weak band near 2000 cm^{-1} belongs to the vibration of the metal–hydrogen bond and ap-

Fig. 2

Figure 2: Fig. 2

pears more distinctly in the spectra of boride catalysts owing to their greater hydrogen content.

Fig. 2. IR absorption spectrum of a Pd–B alloy (1), Pd- "boride" catalyst (2), hydrogen (5) adsorbed on platinum (3). A –35° 40 cm, B –after evacuation at 35°, C –350° 40 cm

Since the preparation of the catalysts was carried out in an aqueous medium, it was possible

one might expect partial oxidation of BH_4^- to BO_2^- and $B_4O_7^{--}$. However, the characteristic frequencies of these ions are not observed in the spectra. The specific surface areas of the catalyst samples obtained were measured by the BET method and are, for the "boride" catalysts of palladium, platinum, and rhodium, respectively 32, 27, and 42 m^2/g.

Thus, as a result of the present study of the boride catalysts of platinum, palladium, and rhodium, it has been established that, in addition to metal and boron, they contain hydrogen. The bonding of the hydrogen to the catalyst is weak and, apparently, is of an adsorption nature.

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