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It is known that in the interaction of aqueous or alcohol solutions of sodium borohydride and a nickel salt (chloride, acetate, sulfate), a black finely divided precipitate is formed, which is an active catalyst of the hydrogenation of many organic compounds [1, 2], the hydrolysis of sodium borohydride [3], the decomposition of formic acid, the reduction of the nitrate ion to ammonia, and other processes [4, 5]. The composition of the catalyst approximately corresponds to the formula Ni₂B [3, 6]. Precipitates dried by treatment with alcohol and ether are x-ray amorphous, but after heating in an atmosphere of an inert gas, lines of the boride Ni₃B or Ni₂B and metallic nickel appear on the Debye powder pattern [7–9]. On this basis a number of researchers believe that the catalyst of the reactions indicated above is nickel boride [5]. In addition, there is an opinion that the "nickel boride" catalyst is a mixture of nickel and boron in a finely divided state [10, 11]. An investigation of the NGR-⁵⁷Fe spectra of precipitates obtained under various conditions in the reaction of iron salts with NaBH₄ has shown that the "iron boride" precipitate is a mixture of 40-70% iron, 5-10% Fe(OH)₃, and an unknown iron compound [12].

The purpose of this work was a further investigation of the chemical nature of the "nickel boride" catalyst. In the work we studied the interaction of the "nickel boride" catalyst with atmospheric oxygen, water, dilute solutions of acids, the nitrate ion, and styrene.

DISCUSSION OF RESULTS

In the precipitates obtained by the interaction of NaBH₄ with NiCl₂ at a mole ratio of 2-2.5:1 in water and ethanol, the ratio Ni:B is ~2 (Table 1); the summary content of Ni and B as a function of the conditions of preparation is 96-98% for precipitates prepared in an atmosphere of argon and decreases to 80-88% when the reaction is conducted in air. This indicates an interaction of the catalyst with water and atmospheric oxygen. The weight of the precipitate dried with alcohol and ether increases when it is stored in a desiccator over P_2O_5 . After the precipitate is heated to 400° in a closed system in air, the weight gain is ~27%, which corresponds to complete oxidation of nickel (experiment 6, Table 2). In the absence of oxygen, the "nickel boride" catalyst can be kept under water for about a year without visible changes. When samples of the catalyst are allowed to stand under a layer of water in air, after only 7-8 days greenish impregnations appear, and after 1-1.5 months all the nickel is converted to Ni(OH)₂. At the same time there is a passage of boron into solution. When the precipitates are heated in a closed system in air to 400°, a white sublimate is observed on the walls of the vessel, which, according to the data of x-ray diffraction study, is boric acid. In this case the amount of boron in the precipitate is reduced, and the ratio Ni : B = 5.8.

Medium	Atmosphere	№ + B, %	Ni : B	Medium	Atmosphere	Ni + B, %	Ni : B
${f H_{2}O \ H_{2}O$	Ar Ar Air	96 ,6 95 ,8 84 ,4 86 ,5	1,58 2,01 1,76 1,84	$\begin{vmatrix} H_2O\\ C_2H_5OH\\ C_2H_5OH \end{vmatrix}$	Air T	81 ,7 —	1 ,64 2 ,06 2 ,36

 TABLE 1. Composition of Catalyst as a Function of the Conditions

 of Production

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Experi- ment No.	Weight of catalyst sample, g		Amo	ount		Note
	before experi- ment	after experi- ment	of H_2 liberated, cm^3	trated, $\begin{cases} of H_2 per g of \\ precipitate, \\ cm^3/g \end{cases}$		
1	0.2619	0.2600	10.1	38.8	Ar	Dried with alcohol and ether
2	0.1502	0.1490	4.4	29.3	Ar	The same
3	0.5855	0.5569	24.5	42.3	Ar	*
4	0.3429	0.3219	25.4	75.0	Ar	Moist precipitate
5	0.2889	0,3332	55.0	191.0	Air	The same
6	0.1607	0.2216	-	– .	-	Complete oxidation
7	0.0670	-	60,5	905.0	**	In the presence of water
8	0.0318	-	28.9	910.0		The same

TABLE 2. Data on the Amount of Hydrogen and Change in Weight of the Precipitate during Heating to 400°

TABLE 3. Interaction of Precipitates with KNO₃

Weight of precipitate, g	Amount of NH3,g/g of catalyst	Note
0,126 0,220 0,357 0,304	0,076 0,089 0,100 0,031	Moist samples The same " Sample dry after heating at 400° for 3 h. Does not con- tain hydrogen
0,237 0,1	0,051 0,072	Raney Ni Ni – calculation according to Eq. (2)

When the precipitates are heated, there is a liberation of H_2 . The dried samples liberate ~40 cm³/g, moist samples considerably more (see Table 2). In accord with the data of [13], this is explained by the formation of hydrogen according to the reaction: Ni + $2H_2O \Rightarrow Ni(OH)_2 + H_2$. When moist samples are heated in air to $350-400^\circ$, at first an evolution of gas is observed, and then its partial absorption, evidently on account of a shift of the equilibrium of this reaction to the left. The amount of gas liberated somewhat exceeds what might have been expected. This may be explained by a decomposition of water, catalyzed by the "nickel boride" catalyst.

The "nickel boride" catalyst forms an amalgam with mercury, while it is known that only nickel containing hydrogen is capable of forming an amalgam [14]. The quantitative determination of hydrogen is difficult. The method proposed in [15] is based on the reaction

$$\mathrm{KNO}_3 + 4\mathrm{H}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{NH}_3 + \mathrm{KOH} + 3\mathrm{H}_2\mathrm{O}. \tag{1}$$

However, ammonia formation occurs not only on account of the hydrogen of the catalyst, but also as a result of the interaction of nickel with KNO_3 , which is evident from the data of Table 3. Moreover, the lines of Ni(OH)₂ are observed on the Debye powder pattern of the dry residue

$$4Ni + KNO_3 + 6H_2O = NH_3 + 4Ni(OH)_2 + KOH.$$
 (2)

It is also natural to expect the simultaneous occurrence of reactions (1) and (2) for moist catalysts.

Freshly prepared precipitates are entirely dissolved by HNO_3 and slowly dissolved by dilute HCl, H_2SO_4 , and CH_3COOH . The method of determining hydrogen according to dissolution of the catalyst in HCl [16] does not give positive results (Table 4), since in this case the oxidation of nickel and the amount of sorbed hydrogen liberated are not considered

$$Ni + 2HCl = NiCl_2 + H_2,$$
(3)

$$B + 3HCl = BCl_3 + \frac{3}{2} H_2.$$
 (4)

Acid	Determined, g		Volume of H ₂	Volume of H_2 , cm ³ , according to Eqs.	
	Ni	В	Inderated, Chi	(3)	(4)
H ₂ SO ₄	0.2290	0.0167	141.8	87.4	58,1
HC1	0.2141	0.0214	149.2	81.7	67.2
HC1	0.0646	0.0068	45.3	24.7	21.3
HC1	0.1644	0.0162	115.3	62.6	50.2
HC1	0.1760	0.0176	113,5	67.3	54,8
HC1	0.2647	0.0244	190.2	102.4	75.4

TABLE 4. Interaction of a "Nickel Boride" Catalyst with Acids

TABLE 5. Interaction of a "Nickel Boride" Catalyst with Styrene

		Amount		
Catalyst	Weight of pre- cipitate, g	of ethylbenzene formed, g	of H ₂ per g of precipitate, cm ³ /g	
Ni-B produced in water	1.0	0.606	126.8	
Ni-B produced in ethanol	1.0	0,965	204.0	
Raney Ni	1.0	0.354	74.8	

It seems more advisable to determine the amount of H_2 with the aid of hydrogenating agents, conducting the experiment in a medium of anhydrous solvent, where there can be no interaction with nickel. Determination of the absorbed H_2 according to the amount of ethylbenzene formed from styrene (Table 5) shows that a "nickel boride" catalyst absorbs a substantial volume of hydrogen.

However, here too it is difficult to say whether the value obtained corresponds to the true content of hydrogen.

Thus, our investigations showed that a "nickel boride" catalyst is oxidized by atmospheric oxygen, interacts with water, reduces KNO_3 to ammonia, i.e., behaves like Raney nickel in these reactions. The passage of boron into solution when the precipitate is allowed to stand, as well as the formation of boric acid during heating, indicate the presence of boron in the elementary state. The use of $NaBH_4$, a foam former and hydrogen source, as the reducing agent leads to the fact that the deposited nickel has a highly developed surface and absorbs hydrogen.

When the precipitates are heated in an inert atmosphere to $250-500^{\circ}$, the borides Ni₂B and Ni₃B are formed [8, 10]. The question of the formation of a boride phase during the production of the catalyst at room temperature still remains somewhat obscure. Considering the hypothesis of the formation of a solid solution of boron and hydrogen in nickel during the production of a Ni-B coating (~90°), which is converted to borides upon heating [17], it can be assumed that first a mixture of nickel or its hydride with boron is formed, and it then is converted to nickel boride by heating.

EXPERIMENTAL

 $NaBH_4$ (purity 99%) was produced by recrystallization of the technical product from water. Grade cp nickel chloride and acetate were recrystallized from water. The precipitates were obtained by pouring together aqueous solutions of the nickel salt and $NaBH_4$ (mole ratio 2.2-2.5:1), followed by filtration and washing in a stream of argon.

The analyses were conducted by a volumetric method. Boron was determined by titration with alkali in the presence of mannitol according to naphtholphthalein, whereupon nickel was bonded by Trilon. Ni was determined by titration with a solution of Trilon according to murexide.

The Debye powder patterns of the precipitates were obtained on a URS-55 apparatus in an RKD camera in copper radiation with a nickel filter, time of exposure 16 h.

Heating of moist or dried samples in an atmosphere of argon or air was conducted in a test tube placed in a thermostatically controlled furnace $(\pm 2-3^{\circ})$. The test tube was connected to a gas burette through a trap cooled to -78° .

Decomposition with Hydrochloric Acid. A sample of the moist catalyst was placed in a vessel for decomposition, to which 20 ml of 6 N HCl was added, then the vessel was heated to $80-90^{\circ}$. Water vapors, boric and hydrochloric acids were removed in a trap with alkali and frozen out at -78° . H₂ was collected in a gas burette. After complete dissolution the content of boron and nickel was determined.

Interaction with KNO₃. A sample of the moist catalyst was placed in a flask, and 3 ml of a 1 M solution of KNO_3 was added. The mixture was gradually heated to 140°. The KNO₃ liberated was absorbed by titration with a solution of acid. The content of nickel and boron was determined in the dry residue.

Interaction with Styrene. A weighed sample of the catalyst in abs. THF was placed in a long-necked hydrogenation flask, and 1.82 g of styrene was introduced in an atmosphere of argon. Samples were collected for gas-liquid chromatographic analysis after definite time intervals (1, 3, 30 min). The hydrogen content was calculated according to the amount of ethylbenzene.

CONCLUSIONS

1. The dependence of the composition of a "nickel boride" catalyst on the temperature at which it was produced was established.

2. The interaction of "nickel boride" precipitates with atmospheric oxygen, water, acids, the nitrate ion, and styrene was investigated.

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