Kinetics and Catalysis, Vol. 45, No. 4, 2004, pp. 558–560. Translated from Kinetika i Kataliz, Vol. 45, No. 4, 2004, pp. 592–594.

Catalytic Synthesis of Aluminum Hydride in the Presence of Palladium Black

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Received February 20, 2003

Abstract—The catalytic properties of a palladium catalyst in the formation of aluminum hydride are studied. The formation of stoichiometric aluminum hydride is determined by XRD, DTA, and spectrophotometry. Findings are rationalized in terms of the electron–chemical catalytic scheme.

INTRODUCTION

Many studies revealed high catalytic activity of platinum group metals, in particular palladium, in oxide reduction and metal hydrogenation [1–3].

There is no agreement on the role of platinum-group metals in the above processes. One of the most common and fundamental schemes that describes processes catalyzed by platinum metals is the electron–chemical scheme of catalysis [1, 2].

It is well known [4] that there are adsorbed hydrogen species of three types in addition to dissolved hydrogen: strongly bound (β^-) and weakly bound (β^+) atomic hydrogen (with the corresponding bond energies E_{des}^{I} = 100–133 kJ/mol and E_{des}^{II} = 42–100 kJ/mol), as well as molecular hydrogen. Hence, particular species of active hydrogen can be generated by external treatment of palladium with the energy $E > E_{des}^{I, II}$.

The aim of this work is to study the catalytic properties of palladium in the preparation of stoichiometric aluminum hydride.

EXPERIMENTAL

Aluminum chloride of extra purity grade was mechanically mixed with palladium black in a box purged with a dry nitrogen flow. Then the mixture (5 g) was placed on a quartz support and bombarded by a flow of partially atomized hydrogen. A high-frequency plasmochemical setup described in [5] was used in the study.

To estimate the conversion, the reaction product was dissolved in diethyl ether (200 ml). An insoluble fraction of palladium black powder precipitated on the bottom of a flask. The solution obtained was analyzed for aluminum content by trilonometry, for hydrogen in the form of hydride by the Felkin iodometry, and for chlorine by the Volgardt inverse titration. The aluminum hydride was crystallized from the ether–toluene mixture according to a standard procedure.

RESULTS AND DISCUSSION

It is obvious that the closer the contact between microcrystals of palladium black and grains of aluminum chloride, the easier the electron transfer from hydrogen, through a metallic catalyst on which hydrogen is ionized, to a reducible substance and the easier hydrogen diffuses from palladium sites to the chloride surface. Our study of the products of atomic hydrogen bombardment with the mechanical mixtures of aluminum chloride and palladium black of various dispersions confirmed this assumption. Figure 1 presents the relative yield of aluminum hydride ($\alpha/\alpha_{0.5}$, where α and $\alpha_{0.5}$ are the yields of aluminum hydride at the current size of the Pd black crystallites, and the size equal to 0.5 μm, respectively) as a function of the average size

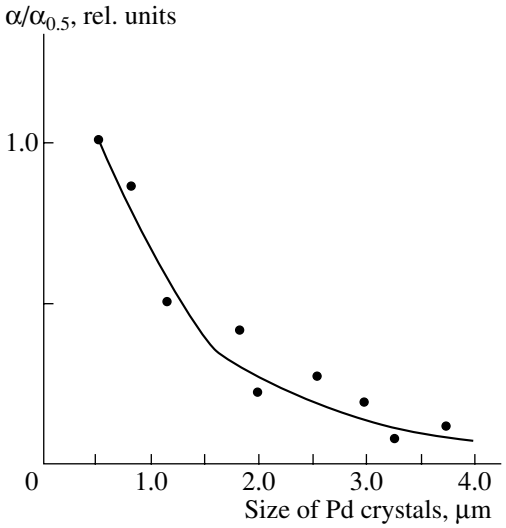

Fig. 1. Relative yield of aluminum hydride vs. average size of the catalyst crystallites.

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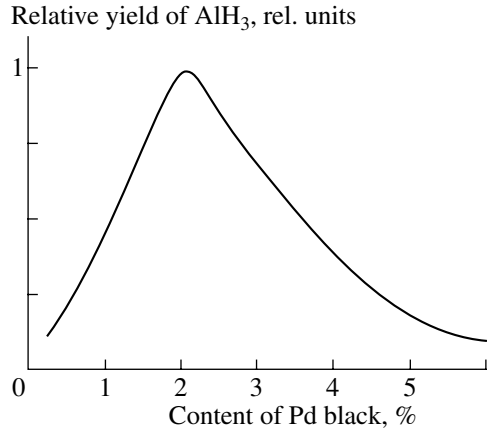

Fig. 2. Relative yield of aluminum hydride vs. Pd black concentration in the mechanical mixture.

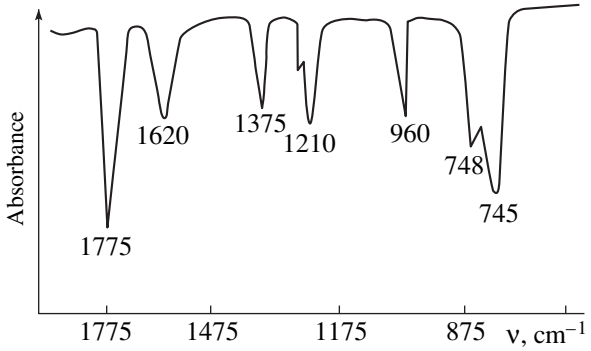

Fig. 3. The IR absorption spectrum of aluminum hydride.

of the palladium black microcrystals in the mechanical mixture. As can be seen from Fig. 1, the relative yield of the target product decreases with increasing size of catalyst microcrystals. An increase in dispersion, that is, an increase in the palladium surface, results in an increase in the amount of adsorbed hydrogen. At the same time, an increase in dispersion leads to a more uniform distribution of the catalyst over the sample bulk and consequently, closer contact with the grains of aluminum chloride. During bombardment of the mechanical mixture with hydrogen atoms, which supply a noticeable portion of energy, the close contact and uniformity of the catalyst distribution stimulate the formation of aluminum hydride.

Note that when the catalyst is distributed over the bulk of the material treated, its high dispersion prevents the formation and enlargement of the nuclei of aluminum crystallization and hence, the formation of the metal layer.

Since palladium black is an initiator of the reduction and formation of aluminum hydride, one can suggest that the higher the catalyst concentration, the higher the relative yield of the target product should be. To verify this suggestion, we bombarded the mechanical mixtures of aluminum chloride with concentrations of palladium black ranging from 1.0 to 6.0%. The runs were carried out under the same pressure in a reactor; contact time, and other parameters of the electric charge were kept the same.

The results of our experiments (see Fig. 2) showed that the relative yield of aluminum hydride (the ratio of the AlH_3 yield to its maximal value obtained at the 2% concentration of Pd black in the mixture) increases with an increase in the catalyst concentration in the mechanical mixture and reaches a maximal value at the catalyst concentration of ~2%. When the catalyst concentration increases further, the relative yield of the target product monotonically decreases.

These findings can be rationalized in terms of the electron–chemical catalytic scheme. According to this scheme, the donor stage is accelerated to such an extent that it ceases to be rate-determining when the catalyst concentration reaches a certain value. Another process, probably solid-phase diffusion, becomes a slow stage. The catalyst does not affect the diffusion rate, and a further increase in the catalyst concentration does not provide additional acceleration of the reaction [6]. We believe that an external action on the mechanical mixture with a high concentration of the catalyst causes the desorption of inactive hydrogen species (namely, molecular species) to prevail.

Figure 3 presents the results of the spectroscopic studies of the product of bombardment of the mechanical mixture of aluminum chloride and palladium black (2%) with hydrogen atoms for 200 min at a hydrogen pressure of 6 Pa. As can be seen from Fig. 3, the absorption bands at 1375 and 1210 cm^{-1} and the bands from bending vibrations with maxima at 960, 748, and 745 cm^{-1} are observed along with the absorption bands with maxima at 1775 and 1620 cm^{-1} typical of the bridging vibrations of the Al–H bond in the hexagonal modification of aluminum hydride.

The IR spectra of the rhombic modification of aluminum hydride differ from that of the hexagonal modification in the presence of intense bands at 1376 and 1208 cm^{-1} and a band from bridging vibrations with a maximum at 1620 cm^{-1}. The transformation of the rhombic modification to hexagonal modification is accompanied by an exothermal effect at 110–120°C on the thermal pattern.

The thermal analysis data (Fig. 4) for the product of bombardment of the mechanical mixture of $AlCl_3$ and Pd black with hydrogen atoms exhibit an exothermal effect at the temperature of 110°C on the DTA pattern. This finding suggests that the rhombic modification of aluminum hydride is formed upon the plasmochemical treatment of aluminum chloride with hydrogen atoms over the palladium catalyst. This conclusion is confirmed by the result of X-ray diffraction study performed on a DRON-1.5 diffractometer with CuK_α radiation in an inert atmosphere (see table). The following

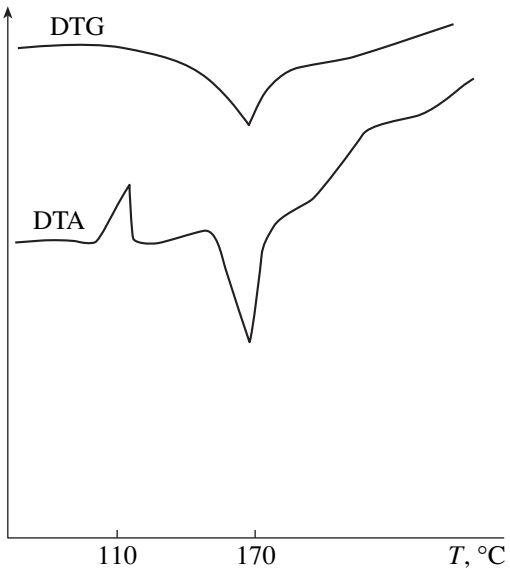

Fig. 4. DTG and DTA patterns of aluminum hydride.

lattice parameters (Å): $a = 5.34$, $b = 7.44$, and $c = 5.75$ were found by processing the X-ray data.

When the mechanical mixture of $AlCl_3$ and Pd black is bombarded, a heat flow supplied by the hydrogen atoms stimulates migration of the adsorbed particles to the grains of aluminum chloride. The energy of recombination of hydrogen atoms on the surface of the mechanical mixture (434 kJ/mol) is absorbed by the mixture and is consumed for the activation of the starting component and the acceleration of hydrogen atom migration. The recombination energy absorbed by the starting component increases the vibration amplitude of terminal chlorine atoms in the $AlCl_3$ molecule and hence, results in some elongation of the bond. When adsorbed hydrogen atoms come close to each other, the electron density is shifted to the hydrogen atoms. Such intermediate bonds between hydrogen and chlorine, which have been found earlier in [7], disturb the equilibrium state of the $AlCl_3$ molecule. The continuous supply of energy to the sample during bombardment favors HCl removal, and hydrogen fills the place of the eliminated chlorine atom in the $AlCl_3$ molecule.

Data of X-ray diffraction analysis of the product of bombardment of $AlCl_3$ + 2% Pd black with hydrogen atoms

θ, deg	I_{rel}, %	d, Å	hkl
11.31	85	3.85	101
12.42	80	3.65	020
17.57	40	2.55	102
19.62	100	2.29	211
20.68	30	2.18	220
22.22	50	2.05	221
26.19	30	1.75	222

Hence, the contact points of microcrystals with the grains of aluminum chloride become the sites of fast appearance and growth of the nuclei of a new phase, aluminum hydride. It seems that the deeper the process of formation, the stronger the isolation of palladium black crystallites from aluminum chloride with a layer of the reaction product. This might affect the yield of the final product. However, our findings give no evidence for this effect. As the crystallization nuclei are formed and the layer of reaction product becomes thicker, the reaction product, aluminum hydride, begins to play the role of catalyst at this stage.

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