Hydrogenation of fullerites in the presence of intermetallic compounds or metals

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Fullerene hydrides containing 24–26 H atoms per fullerene molecule were obtained by hydrogenation of solid-phase mixtures of fullerenes with either intermetallic compounds LaNi5, LaNi4.65Mn0.35, CeCo3 or V and Pd metals with gaseous hydrogen at 1.0–2.5 MPa and 573–673 K. These fullerene hydrides decompose at 800 K with evolution of H2. Upon subsequent heating to 1000 K, vanadium reacts with fullerene to yield a cubic phase of vanadium carbide. The intermetallic compounds react with fullerene with the formation of a metallic phase of the 3d-metal and destruction of fullerene. Palladium does not react with fullerene.

Key words: fullerite, hydrogenation, intermetallic compounds, mechanism.

Studies of the mechanism of hydrogenation and dehydrogenation of fullerenes are associated with the development of systems for hydrogen accumulation and storage1–3 involving intermetallic compounds such as LaNi5 and CeCo3 or metals such as V and Pd, capable of absorbing selectively and reversibly substantial quantities of hydrogen under mild conditions.4–6 The hydrogen evolved from hydrides of these compounds is highly pure and highly reactive at the instance of evolution.7 These properties of hydrogen-sorbing intermetallic compounds and metals make it possible to regard them not only as reversible nonconsumable accumulators of high-purity hydrogen but also as catalysts of processes involving molecular hydrogen. However, the too low contents of hydrogen and the high densities of these materials restrict the applications of the known hydrogen-sorbing materials based on intermetallics and metals.

Of special interest in this respect are fullerene hydrides, which have low densities and are theoretically able to bind reversibly more than 7% (w/w) of hydrogen.1–3 The direct noncatalytic hydrogenation of C60 fullerene occurs at fairly high pressures (50–85 MPa) and temperatures (573–623 K).8 Other known chemical methods for the synthesis of fullerene hydrides also do not seem very attractive for the reversible accumulation of hydrogen due to the difficulties in accomplishing repeated "hydrogenation–dehydrogenation" cycles. These methods include the reaction of gaseous hydrogen with palladium fulleride C60Pd4.9,9 reduction of fullerenes with lithium in ammonia in the presence of Bu'OH10,11 hydrogenation of fullerenes in toluene in the presence of Ru/C12,13 treatment of fullerenes with hydrogen at 723 K and 6.9 MPa with some Et3 added as a promoter of radical hydrogenation,14 the transfer of hydrogen from dihydroanthracene to fullerene at 623 K,15 and hydrogenation of fullerenes in a toluene solution with nascent hydrogen resulting from the reaction of zinc with concentrated hydrochloric acid.16

In this study, we report on the preparation of the fullerene hydride (and deuteride) by the reaction of fullerene with gaseous hydrogen (or deuterium) in the presence of intermetallic compounds, LaNi5, LaNi4.65Mn0.35, and CeCo3 and V and Pd metals, which efficiently sorb hydrogen, and hydrides of these compounds. Preliminary data concerning the palladium–fullerite–hydrogen system have been published previously.17 Our results open more real prospects for the development of fullerene-based systems for reversible storage of hydrogen than the methods listed above.

Experimental

A polycrystalline mixture of fullerenes (fullerite) of the approximate composition 83% C60 + 15% C70 + 2% higher fullerenes was used. This material was obtained as a powder of the toluene extract from the electric-arc fullerene carbon black washed with ether and dried in vacuo at 550 K to remove the solvent molecules of crystallization.

The intermetallic compounds were used as powders prepared by the hydride dispersing of alloys.18 Palladium was used as a metallic powder with a particle size of 1–10 μm and as palladium clusters deposited on the surface of activated carbon (catalyst 10% Pd/C, the specific surface of the support was


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350 m² g⁻¹. Vanadium was used as deuteride VD₁₄ or hydride VH₁₄ powder, which have some advantages over the metallic vanadium powder: first, they are more brittle and, second, they can be divided more finely (to 1–10 μm particles) by treatment in a vibrational mill. During the preliminary degassing in vacuo at 500 K, all the deuterium or hydrogen present in VD₁₄ or VH₁₄ is removed. Vanadium deuteride and hydride were synthesized from high-purity vanadium (99.9%97) and gaseous deuterium or hydrogen.

Homogeneous mixtures of equal amounts (0.5 g each) of a powder of a metal or intermetallic compound and fullerite were prepared by mixing the components in a vibrational mill. During the preliminary treatment in a flow of oxygen in a setup for organic synthesis on the appearance of fullerene deuteride in the system metal–intermetallic(metal)–hydrogen, since the IR spectrum of Cr0D₁₄ exhibits a fairly intense band in the region of the C–D bonds.

The composite mixture was hydrogenated (deuterated) at pressures of 1.0, 2.0, and 2.5 MPa and temperatures of 473, 573, and 673 K using the setup described previously.18 The temperature was controlled with an accuracy of ±0.15°C, and the pressure was maintained within ±0.02 MPa. The samples were preliminarily degassed by heating to 500 K in vacuo (-1 Pa). High-purity hydrogen was introduced into an autoclave serving as the reactor at room temperature from a low-pressure absorption accumulator packed with an intermetallic compound. The autoclave was discharged in an inert atmosphere after cooling to 300 K.

IR absorption spectra were recorded using a Specord 75 IR spectrophotometer. The samples were prepared in an atmosphere of dry argon as pellets with KBr (2 mg of the compound under study and 300 mg of KBr).

X-ray diffraction patterns were recorded using an ADP-I diffractometer (Cu-Kα-radiation) in the 6° < 2θ < 90° range; the positions of peak maxima were determined with an accuracy of ±0.02°.

The curves of magnetization of the initial and final samples of the composite powders were studied using an M 4500 vibrational magnetometer (EG and G PARC).

The thermal analysis of the mixture composites were carried out using Q-1000 and C-1500 derivatographs in an argon atmosphere. The temperatures of endo-effects were determined from the minima on the DTA curves, while the temperatures of exo-effects were found as the onsets of the endo-effects.

The chemical analysis for the content of hydrogen (deuterium) was carried out by the standard method involving combustion of the sample in a flow of oxygen in a setup for organic semimicroanalysis.

Results and Discussion

In this study, we used IR spectroscopy of deuterated samples as a method providing reliable rapid information on the appearance of fullerene deuteride in the fullerene–intermetallic(metal)–hydrogen system, since the IR spectrum of C₀₀Dₓ exhibits a fairly intense absorption band in the region of 2100–2190 cm⁻¹ corresponding to stretching vibrations of the C–D bonds. The IR spectra of the initial fullerite and deuterides of intermetallic compounds and metals contain no absorption bands in this region. The most intense absorption bands in the IR spectrum of C₀₀H₁₆ are due to the stretching vibrations of the C–H bonds. The C–H frequency region of the fullerene hydride (2830–2910 cm⁻¹) is unsuitable for the analysis, because vibrations of many aliphatic hydrocarbons including the molecules adsorbed on the KBr surface from the atmosphere and vibrations of the residual solvent of crystallization also fall in this region. Therefore, the vibrations of the C–D bonds provide much more information.

Neither of the IR spectra of samples prepared by treating the mixtures of fullerene and an intermetallic compound or metal powder with gaseous D₂ at a pressure of 0.1–2.5 MPa and room temperature exhibit absorption bands in the region of the C–D bonds. When these mixtures are treated with deuterium at a pressure of 1.0–2.5 MPa and at a temperature raised only to 573–673 K, a fairly strong band with a maximum at 2120 cm⁻¹ appears in the IR spectra, which indicates that fullerenes are deuterated under these conditions.

Some other characteristic features are also manifested in the IR spectra. In fact, in the case of the mixture composition with vanadium, the absorption bands (AB) that correspond to the vibrational modes of C₀₀H₁₆ (1425, 1175, 565, and 525 cm⁻¹) undergo substantial changes: (1) the relative intensity of the AB at 1175 and 525 cm⁻¹ sharply decreases; (2) the AB at 1425 and 565 cm⁻¹ are broadened; (3) two new fairly intense AB appear at 1380 and 670 cm⁻¹.

An attempt to isolate unreacted fullerene from the composition with vanadium by dissolving the sample in toluene was not successful: the solution above the sample remained slightly colored for two weeks, which indicated that no more than 1% of the initial fullerite had dissolved. A solution of fullerene hydride C₀₀H₁₆ in toluene has a typical light-yellow color, however the estimated contribution of fullerene hydrides to the overall absorption is very low. Taken altogether these data imply that virtually all the fullerene has reacted and has become chemically bound in the sample.

The content of deuterium in the samples, in which the presence of C–D bonds was shown by IR spectroscopy, was determined by chemical analysis. It was found that in all cases, it increases monotonically with an increase in the temperature, the deuterium pressure, and the number of "D₂ sorption = desorption" cycles. In our experiments, the highest content of deuterium corresponding to 24–26 deuterium atoms per C₀₀ fullerene molecule was achieved when deuterium reacted with mixtures of fullerite with intermetallic compounds or metals under a pressure of 2.5 MPa and with the "heating to 673 K (1 h) = cooling to 293 K (1 h)" cycle repeated seven times. Samples containing similar proportions of hydrogen were also obtained when light hydrogen was used under the same conditions.

Figures 1 and 2 show typical thermogravigrams of hydrogenated (deuterated) mixtures of fullerite with intermetallic compounds or metals. It can be seen that clear-cut endothermal effects accompanied by gas evolution are manifested in all cases at 800 K; besides (except for the reaction with palladium), exothermal...