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Hydrogenation of fullerites in the presence of intermetallic compounds or metals

B. P. Tarasov,[a]* *V. N. Fokin,*[a] *A. P. Moravskii,*[b] *and Yu. M. Shul'ga*[b]

[a]*Institute of New Chemical Problems, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: 007 (096) 742 0004
[b]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: 007 (096) 515 3588

Fullerene hydrides containing 24—26 H atoms per fullerene molecule were obtained by hydrogenation of solid-phase mixtures of fullerenes with either intermetallic compounds $LaNi_5$, $LaNi_{4.65}Mn_{0.35}$, $CeCo_3$ 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 H_2. 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 storage[1—3] involving intermetallic compounds such as $LaNi_5$ and $CeCo_3$ 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 C_{60} 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 $C_{60}Pd_{4.9}$,[9] reduction of fullerenes with lithium in ammonia in the presence of Bu^tOH,[10,11] hydrogenation of fullerenes in toluene in the presence of Ru/C,[12,13] treatment of fullerenes with hydrogen at 723 K and 6.9 MPa with some EtI 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, $LaNi_5$, $LaNi_{4.65}Mn_{0.35}$, and $CeCo_3$ 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% C_{60} + 15% C_{70} + 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 m^2 g^{-1}). Vanadium was used as deuteride $VD_{1.4}$ or hydride $VH_{1.4}$ 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 $VD_{1.4}$ or $VH_{1.4}$ is removed. Vanadium deuteride and hydride were synthesized from high-purity vanadium (99.97%) 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 (the amplitude was 10 mm; the ball load was 50 : 1; duration of the treatment was 0.5 h, vibration frequency was 28 Hz, and argon was used as the medium).

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.[19] The temperature was controlled with an accuracy of ±10 °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-1 diffractometer (Cu-Kα-radiation) in the $6° < 2\theta < 90°$ 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 maxima on the DTA curve.

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 $C_{60}D_x$ exhibits[9] 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 $C_{60}H_{36}$ are due to[9,11,20] the stretching vibrations of the C—H bonds. The C—H-frequency region of the fullerene hydride (2830—2910 cm^{-1})[20] 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 D_2 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 C_{60} (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 $C_{60}H_{36}$ in toluene has a typical light-yellow color; however the estimated contribution of fullerene hydrides to the overall extinction is also 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 "D_2 sorption $\rightleftharpoons$ desorption" cycles. In our experiments, the highest content of deuterium corresponding to 24—26 deuterium atoms per C_{60} 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) $\rightleftharpoons$ 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

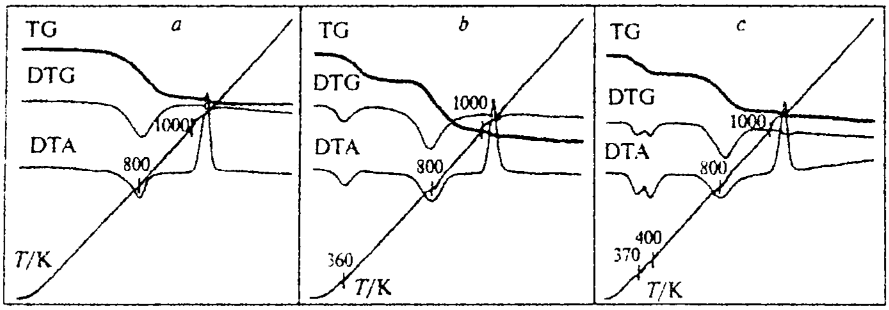

Fig. 1. Typical TG, DTG, and DTA curves for deuterated (hydrogenated) mixture compositions (50 : 50% (w/w)) of fullerite with intermetallic compounds: $LaNi_5$ (*a*); $LaNi_{4.65}Mn_{0.35}$ (*b*); $CeCo_3$ (*c*). Heating rate — 10 deg min^{-1}; 50-mg samples, argon as the medium.

effects not accompanied by a change in the mass of the sample are observed at 950—1000 K. In some cases, endothermal effects in the 350—600 K range, accompanied by hydrogen (deuterium) evolution from the hydrides $PdH(D)_{0.8}$ (360 K), $VH(D)_{1.4}$ (450 and 550 K) and hydride phases of intermetallics $LaNi_{4.65}Mn_{0.35}H(D)_6$ and $CeCo_3H(D)_4$ (350—400 K), are quite discernible. The magnitudes of these low-temperature endo-effects and the amounts of the gas evolved correlate with the content of metal or intermetallic compound in the composition and correspond to 70—90% of the hydrogen amount present in completely saturated stoichiometric hydrides.

The endo-effect at 800 K is accompanied by gas evolution; the amount of the gas evolved (1—3% (w/w)) coincides in all cases with the proportion of deuterium in fullerene deuteride found by chemical analysis. This stage, which is common to all the mixtures, corresponds to decomposition of fullerene deuteride to evolve gaseous deuterium; this is in agreement with the published data on the temperature range of decomposition of fullerene hydrides.[3,13] The fact that the peak temperature (800 K) is identical for all samples implies that dehydrogenation of fullerene hydrides is not affected by metals or intermetallic compounds, unlike their hydrogenation, which is substantially facilitated in the presence of these components of the mechanical mixtures. These facts point to the possibility of irreversible spillover of metal-activated hydrogen to the C=C double bonds of the fullerene component of the mixture. This assumption is supported by the fact that to achieve effective operation of a composition, in addition to the fine mechanical grinding of the mixture in a vibrational mill which ensures a large contact surface area of the components, it is necessary to conduct several "hydrogenation—dehydrogenation" cycles; apparently, during these cycles, the molecular structure of the contact changes, the surface oxygen is removed, and M—C bonds probably arise. The fact that hydrogen moves along these M—C bridges "in one direction" can be understood, for example, by considering the difference between the hydrogenation and dehydrogenation temperatures: at higher temperatures when dehydrogenation can occur efficiently, the M—C bonds largely dissociate, thus preventing the back transfer of hydrogen, and the organic subsystem is thus forced to evolve excess hydrogen independently. Another explanation is also possible: if the hydrogen in the interfacial layer is bound less firmly, it is evolved first, thus ensuring the formation of an interlayer separating the two subsystems.

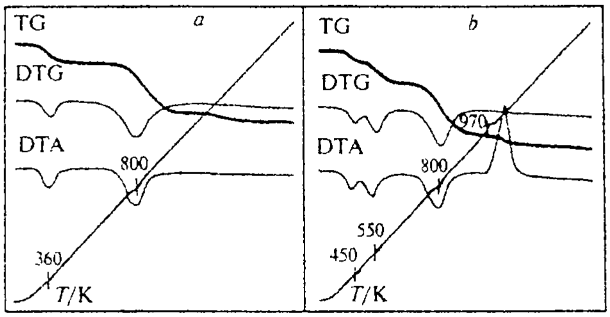

Fig. 2. Typical TG, DTG, and DTA curves for deuterated (hydrogenated) mixture compositions (50 : 50% (w/w)) of fullerite with metals: palladium (*a*); vanadium (*b*). Heating rate — 10 deg min^{-1}; 50-mg samples; argon as the medium.

The exo-effects at 950—1000 K are accompanied by only a slight decrease in the weight of the sample and are due to the chemical interaction of fullerenes with intermetallic compounds or metals. The nature of this interaction depends on the type of the inorganic component; it yields various final reaction products as indicated by the data of X-ray diffraction analysis and IR spectroscopy and also by magnetic measurements.

In the case of vanadium, the exo-effect at 950 K is associated with decomposition of fullerene and formation of vanadium carbide (see Fig. 2). In fact, the IR spectra of samples heated to 1200 K under the conditions of derivatography exhibit no bands typical of fullerenes, and the X-ray diffraction patterns contain clear-cut peaks for the vanadium carbide VC_x with a NaCl-type lattice. The lattice period *a* for VC_x in the samples under consideration ranges from 0.4143 to 0.4151 nm. An estimation of x from the $x = ka + b$ linear dependence with calibration based on the published data[21] affords in our case a fairly precise value: $0.78 < x < 0.82$. The formation of the carbide indicates that the fullerene structure has decomposed, because fullerene is the only source of carbon in the system. It can be assumed that the carbide results from decomposition of fullerene deuterides.

In the case of palladium, no high-temperature exoeffect is observed, and the initial phase state of the metal does not change. The samples heated to 1200 K exhibit somewhat different IR spectra, but they are partially soluble in toluene, which may attest to a relatively small extent of C—C bonding between fullerene molecules.

In the mixtures containing intermetallic compounds, high-temperature treatment of deuterated samples yields rare earth metal carbides and metal phases of the corresponding transition metals. In fact, the IR spectra of samples heated to 1200 K contain no absorption bands due to fullerene, and X-ray diffraction patterns exhibit peaks corresponding to the Ni, Mn, or Co metal phases. The magnetic measurements for the products of heat treatment (1200 K) showed that the contents of ferromagnetic Ni and Co are approximately equal to the amounts of Ni and Co in the initial intermetallic compounds, which indicates that the latter have almost completely decomposed. This fact, together with the destruction of the fullerene structure, makes it possible to assume that the rare earth metal remains in the sample as a carbide amorphous to X-rays. The chemical interaction of intermetallic compounds and fullerenes occurs after completion of the decomposition of the fullerene hydrides; the latter process probably facilitates formation of carbides due to the removal of the oxygen impurity and also due to the possibility of preliminary formation of a small number of metal—carbon bonds.

In the mixture compositions of fullerite with a number of intermetallic compounds and metals, the conditions of hydrogenation of the C=C double bonds of fullerene molecules become markedly milder, and repeated "hydrogenation—dehydrogenation" cycles are readily accomplished. Due to the presence of carbide-forming metals in the systems, including those incorporated in intermetallic compounds, the fullerene structures are destroyed, when the temperature is only slightly higher than the temperature of hydrogen evolution from the hydrogenated composites. The observed formation of metal carbides and metal phases decreases the capacity of these systems with respect to hydrogen and the reversibility of the sorption—desorption process. Elimination of this effect, which is undesirable for hydrogen storage systems, could involve determination of the upper admissible limit for heating the composite material as well as the search for materials for which the formation of carbides is either hampered or impossible.

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