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Hydrogenation of fullerenes C_{60} and C_{70} in the presence of hydride-forming metals and intermetallic compounds

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Abstract

Hydrogen-absorbing intermetallics generate very pure and chemically active hydrogen. In this communication we report on the use of this property for hydrogenation of fullerenes (C_{60}, C_{70}) in solvent-free solid-phase systems. Fullerene hydrides with high contents of hydrogen (24–26 H atoms per fullerene molecule) have been obtained by hydrogenation of solid-phase mixtures of fullerite with either intermetallic compounds $LaNi_5$, $LaNi_{4.65}Mn_{0.35}$, $CeCo_3$ or V and Pd metals in relatively mild conditions, a hydrogen gas pressure of 1.0–2.5 MPa and 573–673 K. The mechanochemical treatment of initial solid compositions and repeated 'hydrogenation–dehydrogenation' cycling are both essential to ensure the highest performance of the systems studied, thus emphasizing the importance of a highly developed contact surface between two solid phases and indicating a probable formation of metal–carbon bonds. The fullerene hydrides thus obtained decompose in all cases at 800 K, liberating hydrogen gas. After further heating up to 1000 K vanadium reacts with fullerenes yielding a cubic phase of vanadium carbide. Intermetallics under the same conditions react with fullerenes by disintegrating their cage and producing a metallic phase of the corresponding 3d metal. In the case of palladium that reaction is not observed and the fullerene remains intact. The nature of the transformations in the mechanical mixtures of fullerite with metals or intermetallics is discussed.

Keywords: Hydrogen; Fullerenes; Hydrides; Intermetallic compounds; Rare earth metals

1. Introduction

Recent interest in fullerene hydrides is connected to their possible use for hydrogen storage with more than 7 wt.% of reversibly added hydrogen [1–3]. A direct non-catalytic hydrogenation of the fullerene C_{60} proceeds at fairly high hydrogen pressures (50–85 MPa) and temperatures (573–623 K) [4], thus substantially restricting possible applications.

Hydrogen evolving from metal hydrides exhibits enhanced chemical activity [5,6]. Thus, hydrogen-absorbing intermetallic compounds (IMC) are possible catalysts for the processes involving molecular hydrogen.

This work was aimed at studying the formation of hydrides (deuterides) of fullerenes obtained by interaction of solid fullerites with gaseous hydrogen (deuterium) in the presence of various IMC including $LaNi_5$, $LaNi_{4.65}Mn_{0.35}$ and $CeCo_3$, as well as palladium and vanadium and their hydrides.

2. Experimental details

The polycrystalline powdered material used in the experiments was a mixture of fullerenes (fullerite) containing 83% C_{60}+15% C_{70}+2% of higher fullerenes. This material was prepared by drying a toluene extract of arc-generated fullerene black. The extract was washed with ether and heat-treated in vacuo at 550 K in order to remove the crystallization solvents. A uniform mixture of metal (or IMC) and fullerite having equal masses (0.5+0.5 g) was formed in a vibromill (time of treatment 30 min; Ar atmosphere; vibration amplitude 10 mm; ball loading 50:1; frequency of vibration 28 Hz). The hydrogenation (deuteration) of this composite mixture was performed at hydrogen pressures of 1.0, 2.0 and 2.5 MPa and tempera-

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tures of 473, 573 and 673 K in an experimental set-up described in [7]. Before each run the sample was degassed at 500 K in 1 Pa vacuum, which generally lead to a uniform initial state of the sample independent of whether a hydride or a pure metal powder was initially mixed with fullerite.

Thermal analyses of the hydrogenated (deuterated) samples of composite mixtures were performed in an argon atmosphere with a temperature sweep up to 1500 K. The temperature of endothermic effects was determined at the minimum of the DTA peak, while that of the exothermic effects was determined at the onset of the peak.

Chemical analyses of the hydrogen content were made by conventional burning of the sample in oxygen flow by microanalysis.

IR spectra were taken on 2 mg deuterated powder pellets mixed with 300 mg of KBr in dry argon. CuKα radiation was used to obtain X-ray powder diffraction patterns before and after each run, with a peak position accuracy of 0.02°. Magnetization curves of initial and final composite mixtures were taken with a vibrational magnetometer M 4500 EG&G PARC.

3. Results and discussion

At room temperature and hydrogen pressures up to 2.5 MPa the fullerene does not react with hydrogen under the experimental conditions employed in the present work. However, when the temperature was increased up to 573–673 K at hydrogen pressures of 1.0–2.5 MPa a strong band at 2120 cm^{-1} appeared in the IR spectrum of the deuterated samples indicating the formation of C–D bonds in the fullerene deuteride $C_{60}D_x$. IR spectroscopy was used in all cases as a very sensitive technique which allowed us to define the contribution from C–D bonds in the presence of Me–D, C–C and Me–Me bonds. As shown previously [8], the range 2100–2190 cm^{-1}, where IR absorption takes place in the case of $C_{60}D_x$, is free from any contribution in the spectra of the initial fullerite and deuterated metals and IMC.

The deuterium contents in the deuterated samples were determined by chemical analysis. As a general trend a gradual increase of the extent of saturation of a solid mixture by D/H was observed as the temperature increased to a certain limit of about 673 K. The higher the deuterium pressure and number of 'absorption–desorption' cycles, the stronger the attained saturation. In this work the highest content of deuterium, corresponding to 24–26 D atoms per C_{60} molecule, was obtained at a deuteration pressure of 2.5 MPa after 7 cycles of 'heating up to 673 K for 1 h-cooling down to 293 K for 1 h'. Nearly the same content was obtained in case of hydrogen.

We believe that the hydrogenation of fullerenes is promoted by the fine mechanical dispersion of the mixture in the vibromill which ensures a sufficient contact between the components and the probable formation of Me–C bonds. The prolonged 'absorption–desorption' cycling where active hydrogen is repeatedly generated in the cycle also promotes a higher saturation of the sample with hydrogen. These observations suggest a possible transfer of hydrogen activated by the metal to the double bonds of the fullerene molecules.

DTA and TG studies of the hydrogenated (deuterated) mixtures of fullerenes+IMC or metal hydrides indicated the presence of three temperature regions where decomposition is observed (Fig. 1 and Fig. 2). The first decomposition takes place at relatively low temperatures, 350–600 K depending on the behaviour of a particular metal of the IMC. This feature is associated with hydrogen desorption from the metal hydrides. Endothermic effects of H desorption are observed at 360 K (Pd), 450 K and 550 K (V), 350–450 K ($LaNi_{4.65}Mn_{0.35}$ and $CeCo_3$) and include one (Pd, $LaNi_{4.65}Mn_{0.35}$) or two (V and $CeCo_3$) desorption peaks. As expected, no effects of such a type are observed for $LaNi_5$ where a fast decomposition proceeds at room temperature when the hydrogen pressure is reduced below 0.1 MPa.

The second feature in the DTA curves—a well defined endothermic effect at 800 K—is similar for all hydrogenated composite mixtures studied and is connected with a decomposition of the fullerene hydride. This conclusion

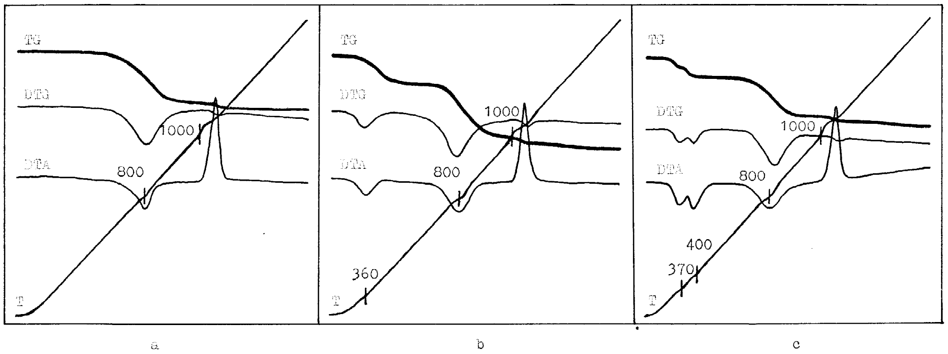

Fig. 1. Typical TG, DTG and DTA curves for the hydrogenated (deuterated) composite mixtures (50:50 mass%) of fullerite with intermetallics: (a) $LaNi_5$; (b) $LaNi_{4.65}Mn_{0.35}$, and (c) $CeCo_3$. Obtained in Ar atmosphere at 10 °min^{-1} sweeping rate with 50 mg samples.

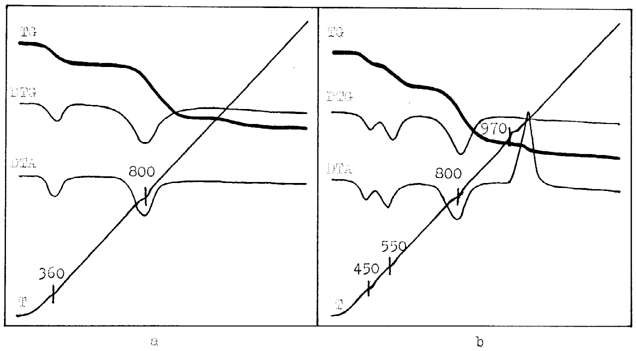

Fig. 2. Typical TG, DTG and DTA curves for the hydrogenated (deuterated) composite mixtures (50:50 mass%) of fullerite with metals: (a) palladium; (b) vanadium. Obtained in Ar atmosphere at 10 °$\min^{-1}$ sweeping rate with 50 mg samples.

is based on: (a) the good agreement of this temperature effect with published data [3,9], and (b) the exact correspondence of the measured weight drop of 1–3 wt.% on desorption, which is equal to the deuterium content determined by chemical analysis.

The constancy of the peak position at 800 K for all materials means that the presence of metals, IMC and their hydrides does not influence the process of decomposition of the fullerene hydrides, in contrast to the process of hydrogenation, which is appreciably facilitated in the presence of these compounds.

For Pd-containing mixtures only these two features exist and on further heating from 800 K up to 1200 K fullerene and palladium do not interact with each other.

However, for V and all the IMC under investigation the third feature, now exothermic, was observed on the DTA curves at 950–1000 K with no weight change of the samples. As indicated by XRD, IR spectroscopy and magnetization measurements this feature is a result of a chemical interaction between fullerenes and the metallic matrices.

In the case of vanadium the exothermic reaction at 950 K results in a decomposition of the fullerenes and the formation of vanadium carbide. In the IR spectra of the samples heated to 1200 K the characteristic bands of the fullerenes disappear, and on the XRD patterns the peaks of vanadium carbide VC_x with the cubic lattice of rock salt-type appear. The cell parameter *a* for the samples studied varies from 0.4143 to 0.4151 nm. Thus, the composition of this carbide is estimated to be $VC_{0.78-0.82}$.

For the IMC studied the products of the high-temperature treatment of the hydrogenated mixtures were tentatively attributed to the corresponding 3d-transition metals and rare earth carbides. The IR spectra of the samples heated to 1200 K show the absence of the absorption bands of the fullerenes, while the XRD spectra clearly indicate the presence of the metallic phases of nickel, manganese and cobalt. The magnetization measurements of the decomposition products show that they contain ferromagnetic nickel and cobalt in quantities almost equal to their contents in the initial IMC suggesting a complete disproportionation of the latter. The occurrence of these metals in the products and the decomposition of the fullerene structure suggests the formation of a carbide of the rare earth metal as the second product of interaction. Evidently, the chemical interaction of the IMC and fullerenes proceeds mainly after termination of the decomposition of fullerene hydrides. The latter process removes the oxygen from the metal surface and promotes metal–carbon bond formation, thus facilitating the occurrence of metal carbide phases in samples heated to only 950–1000 K.

4. Conclusions

The composite mixtures of the fullerite with IMC or metals display attractive hydrogen absorption properties. The conditions for the hydrogenation of double bonds in the fullerene molecules are much milder compared with direct interaction of fullerenes with gaseous H_2. It becomes easily possible to perform repeated 'hydrogenation–dehydrogenation' cycles which is important from the point of view of hydrogen storage. Moreover, the cycling is a necessary prerequisite for fast and complete saturation of the samples by hydrogen. However, carbide formation in the metals and IMC may cause the decomposition of the fullerenes even at temperatures slightly above the temperature of hydrogen release (800 K). The low-temperature formation of carbides is of possible interest for different applications, but for the materials under investigation it results in a substantial decrease of both capacity and reversibility of hydrogen absorption. The elimination of this undesired effect in hydrogen storage systems requires the determination of the maximum temperature limit for heating the composite material to release hydrogen and the search for materials, where the formation of carbides is hindered or eliminated.

Acknowledgments

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