Hydrogen Storage on Fullerenes

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Initial enthusiasm regarding the use of nanotubes as hydrogen storage devices has been greatly reduced by several investigations revealing that the storage capacity of nantubes is disappointingly low. While interaction of hydrogen with the nanotube is based on sorption, thus involving only relatively weak forces, hydrogen can easily be stored on fullerenes, such as C_{60}, through much stronger chemical bonding. The resulting hydrofullerenes, such as $C_{60}H_{36}$, possess long-term stability and release hydrogen already at relatively moderate temperatures, so that the notion of chemical hydrogen storage on C_{60} has attracted recent interest.

The paper reports the evaluation of several essential features that are connected with the idea of hydrogen storage on fullerenes.

Applying matrix-assisted laser desorption/ionisation (MALDI) and direct laser desorption/ ionisation (LDI) mass spectrometry, the release of hydrogen from hydrofullerene samples has been studied. It has been found that hydrofullerenes undergo distinctly different decompositions depending on their charge state. While activation of the neutral hydrofullerenes can be controlled in such a way that partial or complete loss of hydrogen can be achieved, thus regenerating the pure fullerene core, ionised hydrofullerenes decompose upon excitation through cage rupture, leading to the evaporation of alkyl moieties.

A further important achievement would be connected with higher hydrogen attainment to C_{60} than achieved by the common $C_{60}H_{36}$. Therefore, C_{60} hydrogenation has been performed applying high pressures and high temperatures. Interestingly it is found that under these conditions $C_{60}H_{36}$ forms very efficiently oligomers of the type $(C_{60}H_{36})_n$, where up to n=5 was readily observed. Since coalescence and aggregation phenomena are common for laser desorption-based experiments, as applied in this case for analysis, it was necessary to establish that these polymerised species are not the result of a gas-phase reaction during analysis. Labelling experiments revealed that these compounds were in fact present in the sample material. Dissociation experiments indicate that both $C_{60}H_{36}$ units retain their structural identity in the $(C_{60}H_{36})_2$ dimer. This in turn excludes that a giant C_{120} fullerene core has been formed. However, it is also evident that a [2+2] cycloaddition cannot account for these observations. It is therefore concluded that the two units are partly fused with each other in such a manner that upon excitation dissociation into separate monomer units is feasible.

Finally, the hydrogen initially stored on C_{60} has been used for the reduction of the aza-fullerene dimer $(C_{59}N)_2$. Using $C_{60}H_{36}$ as the source of hydrogen, it has been possible to hydrogenate $(C_{59}N)_2$, whereby $C_{59}NH$ and $C_{59}NH_5$ were obtained as the major products.

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