IN SITU MONITORING OF C_{60} HYDROGENATION

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ABSTRACT

Kinetics and pathways of C_{60} reaction with hydrogen gas were studied in a broad temperature interval and over extended periods of time. Specifically, hydrogenation was monitored in situ at high temperature and high hydrogen pressure conditions using gravimetric method. The shape of gravimetric curve was found to depend on hydrogenation temperature: at 350-400ºC saturation of the sample weight was achieved, whereas at 420-440ºC the sample weight reached the maximum and decreased upon prolonged hydrogenation. The weight decrease is due to fullerene cage fragmentation with formation of light hydrocarbons evaporating from the sample. Hydrogenation products were studied by X-ray diffraction, APPI FT-ICR mass spectrometry, and elemental analysis. Hydrogenation pathways (from C60H18 up to C60H56) and possible mechanisms of hydrogenation-induced fragmentation of fulleranes are discussed.

Key words: fullerene, hydrogenation, hydrogenated fullerene, fragmentation, mass spectrometry.

INTRODUCTION

Fulleranes (hydrogenated fullerenes) are products of the reaction of fullerenes with hydrogen and were considered as promising materials for hydrogen storage application [1]. However, high temperature required for hydrogenation/dehydrogenation of fullerenes [2] and partial collapse of fullerene cage upon heat treatment required for the release of hydrogen [3] are the main obstacles for the hydrogen storage application. One of the most important methods for preparation of bulk amounts of fulleranes is a direct reaction of C_{60} with hydrogen gas at elevated temperatures and pressures [1-10]. Direct hydrogenation of C_{60} typically leads to formation of a complex mixture of fulleranes with broad distribution of hydrogen content. One of the main obstacles to the synthesis of pure highly hydrogenated fulleranes is fragmentation and collapse of the fullerene cage during prolonged reaction [9-11]. However, none of the fragmented hydrogenated fullerenes has been isolated in a pure form so far due to the complexity of the obtained mixtures. To isolate a certain isomer of ful-

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lerane or fragmented fullerane, it is important to prepare less complex samples, e.g., by variation of the P-T reaction conditions.

Fundamental understanding of the reaction pathway and kinetics is required to achieve selective synthesis of fulleranes with certain compositions. In this study we apply weight measurements of solid C_{60} powder for *in situ* monitoring of hydrogenation reaction at high temperatures (350-450^{0}C) and high hydrogen pressure (50 bar). Detailed *ex situ* characterization of hydrogenated samples was performed to evaluate the hydrogenation reaction pathways at various temperatures and to estimate conditions required for C_{60} fragmentation under hydrogenation.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Typical experiments were performed using 300mg of C_{60} powder (sublimed, >99,9% pure, purchased from MER corporation, city, USA) loaded in a stainless steel container. Rubotherm gravimetric system (Rubotherm, Germany) modified for high temperature experiments was used for the *in situ* monitoring of hydrogenation reactions. The precision of weight measurements according to specifications of the balance was ±0.02mg which gave an error less than ±0.01 Wt% considering typical weight of the sample (300mg) (more information about the experimental set up could be found in the previously published articles [12]). Hydrogenation of C_{60} was performed in the temperature range of 350-440ºC at 50 bar hydrogen pressure. Gravimetric data were used for qualitative analysis of the reaction kinetics and for evaluation of hydrogen uptake. X-ray powder diffraction data were collected using Siemens 5000 diffractometer and CuKα radiation. Elemental compositions of the samples after hydrogenation experiments were determined using a flush combustion gas chromatography (MIKRO KEMI AB, Uppsala, Sweden). High-resolution APPI FT-ICR MS was performed with a hybrid 12 T linear ion trap FT-ICR MS (LTQ FTMS, Thermo Scientific, Bremen, Germany) [13].

RESULTS AND DISCUSSION

A reaction of hydrogen gas with solid C_{60} is expected to result in a sample weight increase. As it can be seen in the *Figure 1*, hydrogenation at 50 bar H_2 pressure and temperatures up to 400ºC shows gradual weight increase.The data demonstrate that hydrogenation at 400^{0}C and below proceeds without C_{60} collapse and fragmentation. When temperature of the reaction was increased up to 420ºC-440ºC the kinetics of the process changed dramatically.

After the initial increase the weight of the sample started to decrease. The downturn in the gravimetric curve can be explained only by suggestion that some light hydrocarbons are formed in the process of the hydrogenation reaction and evaporate from the sample. Content of hydrogen deduced from gravimetrical curves was in good agreement with data obtained by elemental analysis for samples hydrogenated at 350ºC and 375ºC (see *Table 1*).

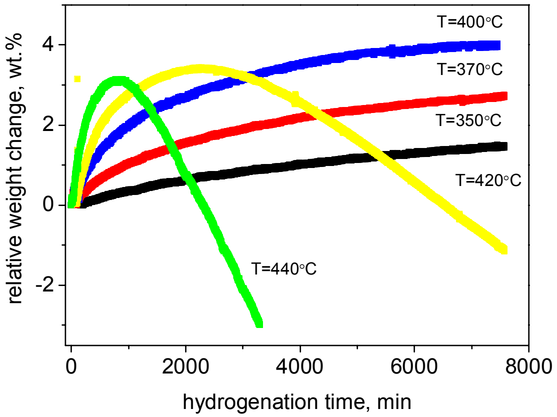

Fig. 1 - Weight change recorded *in situ* in process of C_{60} hydrogenation performed at 50 Bar H_2 pressure and various temperatures

Table 1 – Summary of the elemental analysis and its comparison with results deduced from gravimetrical data

Synthesis T, °C	C content, elem. analysis, wt.%	H content, elem. analysis, wt.%	H content, gravim. analysis, wt.%	Number of H per C_{60}, elem. analysis
350	97,4	1,7	1,67	10
375	96,4	2,9	2,73	20
400	94,9	4,4	3,96	31
420,max.weight	95,0	4,0	3,40	28
440,max.weight	94,9	3,8	3,11	27
420, long	94,3	4,9	N/A	35
440,long	94,0	4,7	N/A	33

However, for higher reaction temperatures (e.g., 400ºC, 420ºC, and 440ºC) elemental analysis showed higher content of hydrogen compared to the expected. Samples hydrogenated at 420ºC and 440ºC had the highest hydrogen content despite the negative total weight change. The negative total weight change could be due to the partial collapse of C_{60} fullerene cage and release of some light hydrocarbons while higher hydrogen content can be expected if some solid hydrocarbons are formed due to C_{60} fragmentation or collapse [7, 9-10]. Hydrogenated samples prepared were studied *ex situ* by X-ray diffraction. All samples had *fcc* cubic lattice as pristine fullerene C_{60} but with the increased cell parameter (see *Figure 2*). All samples were also studied by high resolution APPI FT-ICR MS in order to get detailed information about products of hydrogenation reactions. MS analysis indicated that sample synthesized at 350ºC mostly consisted of $C_{60}H_{18}$ (data not shown).

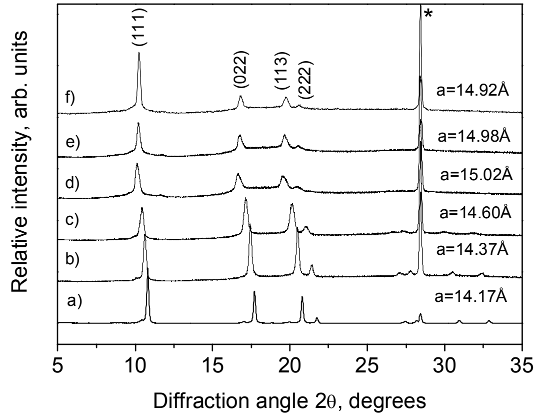

Fig. 2 - X-ray diffraction patterns of fullerenes hydrogenated at different temperatures: a) pristine C_{60}, b) T=350°C, c) T=375°C, d) T=400°C, e) T=420°C (max. hydrogenation), f) T=440°C (max. hydrogenation). A (111) reflex from Si was used for the calibration (marked with an asterisk)

The mass spectrum of the sample synthesized at higher temperature, 375°C, is more complex. Besides the main peak assigned to $C_{60}H_{18}$, a set of low intensity peaks was present in the higher mass range with local maxima at $C_{60}H_{36}$ and $C_{60}H_{44}$ compositions (see Figure 3). After hydrogenation at 400°C most of the material was converted into highly hydrogenated species with rather broad mass distribution with the most abundant atoms at $C_{60}H_{36}$, $C_{60}H_{44}$, $C_{60}H_{52}$, and $C_{60}H_{18}$. Moreover, the spectrum showed minor fraction of fragmented fullerenes with a loss of 1-2 carbon atoms of the C_{60} cage, the most abundant ion corresponding to $C_{59}H_{44}$. Mass spectrum of the sample hydrogenated at 420°C showed peaks mostly from fragmented fullerenes, e.g., $C_{59}H_{44}$, $C_{59}H_{42}$, $C_{58}H_{44}$, and $C_{58}H_{42}$.

The sample hydrogenated at 440°C had a similar mass spectrum but the material showed higher degree of fragmentation. Analysis of the MS data shows that some hydrogenated fullerenes prevailed at certain synthesis conditions while others were not observed. For example, $C_{60}H_{18}$ was synthesized at 350°C while higher temperature of 375°C was needed in order to start the synthesis of $C_{60}H_{36}$ or $C_{60}H_{44}$ (*Figure 3*). All other hydrogenated fullerenes had substantially lower abundance. Therefore, we consider $C_{60}H_{18}$ as the first step of hydrogenation. Upon increase of the synthesis temperature up to 375°C additional peaks assigned to $C_{60}H_{36}$ and $C_{60}H_{44}$ appeared in the mass spectrum while other peaks were significantly less pronounced. We assume that $C_{60}H_{36}$ is the second major step in the hydrogenation of fullerenes and formation of

$C_{60}H_{44}$ is the third main step. As it could be seen in Figure 3 $C_{60}H_{18}$ was almost completely transformed into $C_{60}H_{36}$ and $C_{60}H_{44}$ upon hydrogenation at 400ºC. Moreover, a new strong peak due to $C_{60}H_{52}$ was found in the mass spectrum which we consider as forth main step in hydrogenation. Hydrogenated fullerenes with number of hydrogen atoms up to 56 were observed in mass spectra but with rather low abundance.

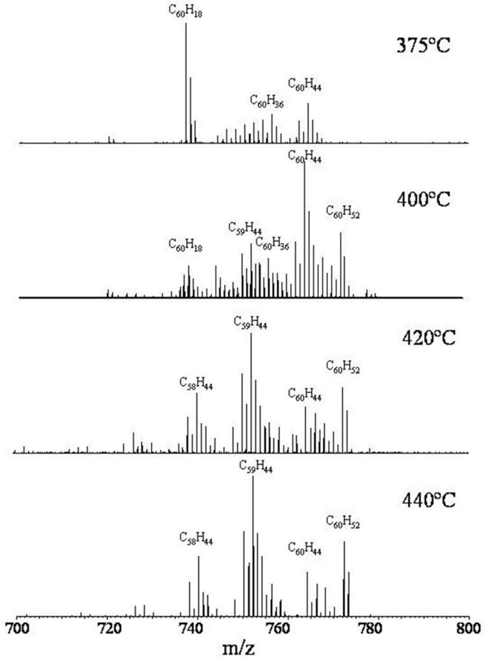

Fig. 3 - APPI FT-ICR mass spectra of C_{60} samples hydrogenated at different temperatures for prolonged periods of time (correspond to experiments shown in the Figure 1)

Therefore, we assume that synthesis of $C_{60}H_{52}$ is critical step in the hydrogenation of fullerenes, and further hydrogenation is either not possible or (most likely) results in a collapse of the fullerene cage. The main steps of the hydrogenation reaction of C_{60} can be summarized as following: $C_{60} \rightarrow C_{60}H_{18} \rightarrow C_{60}H_{36} \rightarrow C_{60}H_{44} \rightarrow C_{60}H_{52}$. In principle, synthesis of reasonably pure $C_{60}H_{52}$ could be expected after sufficiently long duration of hydrogenation reaction following chain of reaction suggested above. However, synthesis of final products of the chain is complicated by a “side reaction” of fullerene cage fragmentation which starts for $C_{60}H_x$ with X over 36. Using the mass spectrum of the sample hydrogenated at 440ºC we propose two fragmentations models. Those models suggest reforming some dangling bonds (formed when carbon atom is taken off the cage) into new C-C bonds (models are summarized in *Figure 4*).

First proposed fragmentation pathway (see *Figure 4*, top) suggests to explain the loss of a single carbon atoms while keeping the same number of hydrogen atoms (e.g., from $C_{60}H_{44}$ to $C_{59}H_{44}$). This reaction can be performed either in one step (1) or in two steps (2, 3) with the same final product. Second possible fragmentation pathway suggests slightly different consequence of dangling bond reformation (see *Figure 4*).

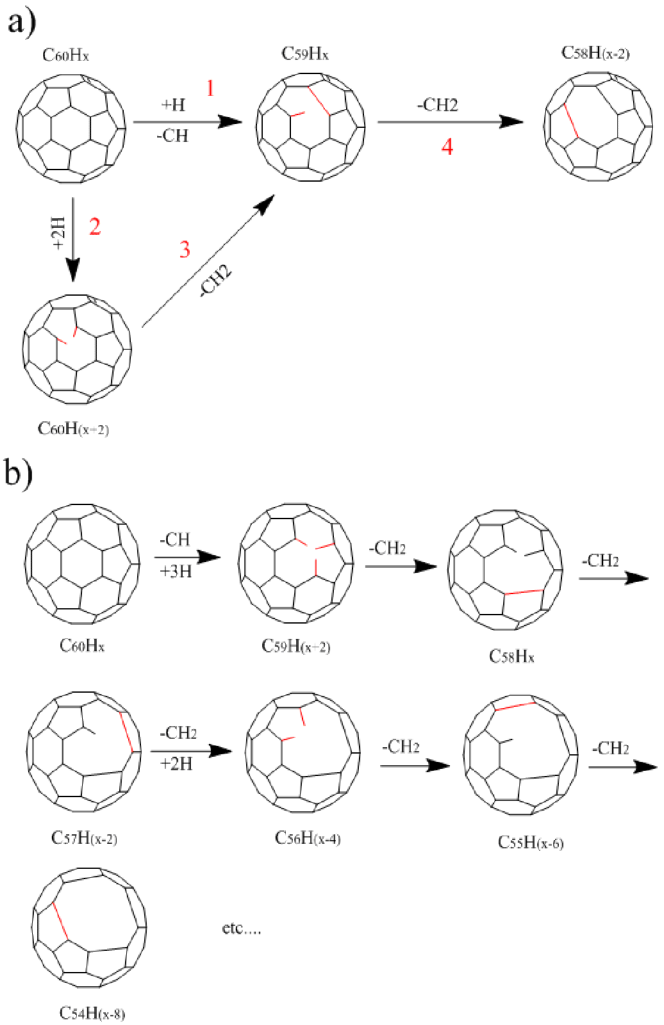

Fig. 4 - Suggested C_{60} fragmentation pathways induced by hydrogenation: a) first fragmentation pathway, b) second fragmentation pathway

As it was observed in our previous experiments the fragmentation of fullerenes always could be described by the total loss of either –C or –CH_2 [10]. Both pathways 1 and 2 proposed in this study would satisfy observed results. Additional experiments are required to establish which fragmentation mechanism (or may be both of them) is valid for a certain hydrogenation reaction of C_{60}.

CONCLUSIONS

The reaction of solid C_{60} with hydrogen gas was studied *in situ* and *ex situ* in the temperature interval of 350ºC-440ºC and at 50 bar of hydrogen pressure. Advantages of *in situ* monitoring of hydrogenation reactions using gravimetric method are demonstrated. A set of hydrogenated fullerenes with different content of hydrogen was prepared and main products of reaction analyzed. Despite rather broad distribution of hydrofullerene compositions, some of the products had significantly higher abundance which allowed suggesting the following reaction pathway: $C_{60} \rightarrow C_{60}H_{18} \rightarrow C_{60}H_{36} \rightarrow C_{60}H_{44} \rightarrow C_{60}H_{52}$. Prolonged hydrogenation at 400ºC-440ºC resulted in the fullerene cage fragmentation and formation of hydrogenated fragmented fullerenes. Several mechanisms of fragmentation with the loss of up to 7 carbon atoms were discussed.

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