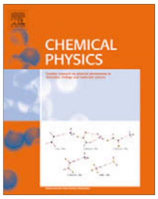
Chemical Physics 368 (2010) 49–57

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys



High-temperature reactions of C_{60} with polycyclic aromatic hydrocarbons

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ARTICLE INFO

Article history:
Received 16 October 2009
In final form 4 December 2009
Available online 21 December 2009

Keywords:
Fullerene
Polycyclic aromatic hydrocarbons
Hydrogen adsorption
Raman spectroscopy
IR spectroscopy
X-ray diffraction

ABSTRACT

Fullerenes are proposed as a precursor for preparation of nanocarbon materials using controlled collapse of cage structure by high temperature reaction with polycyclic aromatic hydrocarbons. The chemical modification of C_{60} by reaction with anthracene and coronene was studied over a broad temperature interval. The products of the reaction were characterized by X-ray diffraction, and Raman and IR spectroscopy. Mono- and multi-adducts of C_{60} with anthracene were obtained in the temperature interval 290–400 °C. Above 400 °C the C_{60} adducts are not stable and decompose back to C_{60} and anthracene. No chemical adducts of C_{60} with coronene were found below 500 °C. Above this temperature fullerite structure was found to expand reflecting interaction with coronene melt and vapor. The reactions of C_{60} with anthracene and C_{60} with coronene at temperatures above 650 °C resulted in fullerene cage collapse and formation of nanocarbons. These nanocarbons were found to store up to 0.45 wt% of hydrogen at ambient temperatures despite negligible surface area.

1. Introduction

Studies of hydrogen storage in various carbon nanomaterials (e.g. carbon nanotubes [1] and activated carbons [2]) have been rapidly expanding research field during last decade. So far, the best hydrogen adsorption properties among carbon materials were observed for high surface area activated carbons [2]. In many cases, this kind of materials is produced starting from graphite by very strong chemical or mechanical treatment. Since the graphite has an extremely stable structure, it is rather difficult to break it into nanoparticles. Alternative method is carbonization of various hydrocarbons at high temperature, see e.g. [3].

In this study it is proposed to use fullerenes as a precursor for preparation of nanocarbon materials. Fullerene molecules are, in fact, carbon nanoclusters. However, fullerite as a solid is not nanoporous material and surface of fullerene molecules is not accessible for hydrogen adsorption. The idea of this study is to modify or collapse fullerenes in controlled way in order to make porous carbon materials. For this purpose collapse of fullerene molecules should be performed in a controlled way that would allow avoiding formation of bulk graphite structure. Fullerene C_{60} cage collapse is known to occur under high temperature treatment at ambient or high pressure conditions [4,5], by laser irradiation or by high energy ball milling [6] or by extensive chemical addition reactions [7].

C_{60}-fullerene can be easily functionalized using many different methods and a large variety of derivatives have been obtained to date including some derivatives with polycyclic aromatic hydrocarbons (PAH's). The Diels–Alder cycloaddition reaction is one most studied fullerene reaction [8]. C_{60} reacts as a dienophile with number of dienes by [4 + 2] mechanism, including reaction with anthracene. Anthracene is the simplest PAH consisting of three benzene rings, it has melting point 218 °C and boiling point 340 °C. A number of studies related to the cycloaddition of C_{60} with anthracene have been carried out during last decade, e.g. reaction occurs easy in moderately heated solution with addition of one (mono-adduct) or several (multi-adducts) anthracene molecules. Naphthalene was used as a solvent in early experiments made by Komatsu et al. [9] at 200 °C. Schlueter et al. [10] obtained 13% yield of mono-adduct using reaction in toluene at 115 °C. Reaction yielded also some multi-adducts, which were not identified. Other organic solvents common for C_{60} and anthracene also have being used [11] as well as various activation methods, e.g. microwave irradiation of a solution [12].

It should be noted that precise hydrogen adsorption measurements require relatively large amount of material (about 0.5 g in our experiments). However, solution methods of fullerene functionalziation are difficult to scale up due to relatively low solubility of C_{60} (typically few mg/ml) which makes solid-state reactions more attractive for bulk production of fullerene–anthracene adducts. Reaction products obtained by solution method also appeared to be unstable over longer periods of time. Solid-state reaction provides higher yields and more stable products as it was shown by Murata et al. [3] who applied the high-speed vibration

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doi:10.1016/j.chemphys.2009.12.008

milling (HSVM) technique to the cycloaddition reaction of fullerene with anthracene. Using the solid-state mechanochemical reaction of fullerene, Komatsu et al. [14] increased the mono-adduct yield to 60%. It is interesting also to note that heat treatment of mono-adducts at 180 °C yields antipodal bis-adducts ("trans-1") C_{60}-anthracene [15].

Compared to C_{60}-anthracene mono-adducts, there have been far fewer examples of the investigation of bis- or multiple adducts, mainly due to the difficulties in their isolation and characterization [16,17]. One of the most detail characterization of the bis-adducts was performed by Duarte-Ruiz et al. [16]. Five (out of eight) possible constitutional isomers (in which the two anthracene adducts do not occupy the same hemisphere of the fullerene core) were identified in this study.

Very few studies have been carried out for functionalization of C_{60} with anthracene using direct high temperature reaction. Duarte-Ruiz et al. [18] performed "one-pot" reaction by heating mixture of C_{60}/anthracene powders which resulted in high yield of adducts, however only one specific reaction temperature 240 °C was tested in this study.

Analysis of synthesis methods described above allows to conclude that simple heat treatment of C_{60}/anthracene powders seem to be most suitable method for bulk production of fullerene adducts which could possibly be used later for conversion into various nanocarbons. It should be noted that similar reactions with larger PAH's (e.g. perylene or coronene) have not yet being tested to our knowledge.

In this study we performed heat treatment experiments with mixed powders of C_{60} and PAH's (anthracene and coronene) in broad temperature interval (290–800 °C), and analyzed reaction products using X-ray diffraction and IR spectroscopy. Anthracene was selected as smallest PAH and most studied for reaction with C_{60}. Coronene is a PAH consisting of seven fused benzene rings and therefore could be considered as the smallest piece of graphene sheet terminated by hydrogen atoms. It was anticipated that some new derivatives of C_{60} with coronene could be synthesized at moderate temperatures and coronene could contribute to formation of complex nanocarbons at temperatures above C_{60} collapse point.

2. Experimental

The samples were synthesized using thermal treatment of C_{60}/PAH powders under argon at temperatures 290–800 °C for 20–24 h. The powder of fullerene (99.5%, provided by SES Research, Huston, USA) was mixed with coronene (97% provided by Aldrich, Germany) or anthracene (96.9% provided by Fluka, Sigma–Aldrich, Germany) using agate mortar, loaded into a stainless steel reactor (inner volume $\sim$0.6 cm^3) and closed under argon. According to control tests performed previously in our laboratory, that kind of stainless steel containers remain to be sealed keeping inert gas even during prolonged heat treatment at temperatures up to 900 °C. Experiments were performed for powders mixed in proportion 1 molecule of C_{60} per one molecule of anthracene. Several additional experiments were performed with proportion anthracene to C_{60} 2:1 as well, however the difference appeared to be insignificant. Final products were analyzed by Renishaw 1000 Raman spectrometer with a 514 nm excitation laser and a resolution of 2 cm^{-1}. X-ray diffraction patterns were recorded using Siemens D5000 diffractometer with Cu K_α radiation. IR spectra were collected using Perkin–Elmer Spectrum BX FT-IR system. Hydrogen adsorption was measured by gravimetric method using magnetic suspension balance from Rubotherm. Details of Rubotherm hydrogen adsorption system employed for our measurements can be found elsewhere [6].

3. Results and discussion

3.1. C_{60}-anthracene

X-ray diffraction patterns recorded from samples heated at various temperatures are shown in Fig. 1. Analysis of this figure shows that reaction of C_{60} with anthracene does occur in process of annealing and is temperature dependent. Some additional reflections compared to pure C_{60} and anthracene are observed already for the sample synthesized at 290 °C which indicates the formation of C_{60}-anthracene adducts. These new peaks are especially strong for the sample synthesized at 330 °C, become weaker at higher temperature and completely disappeared for samples prepared at 400 °C and higher. It is not surprising since C_{60}-anthracene adducts formed using Diels–Alder reaction are known to decompose back to pristine C_{60} and anthracene upon heat treatment. The temperature interval 400–500 °C is above stability limit of Diels–Alder adducts and only reflections from unmodified C_{60} are observed for samples treated at these temperatures, see Fig. 1. However, starting from 650 °C reflections of C_{60} are not observed anymore indicating some chemical reaction which is different from Diels–Alder addition. Below discuss separately two temperature intervals: moderate temperature interval (below 400 °C) and high-temperature interval (400 °C and higher).

3.1.1. Moderate temperatures (below 400 °C)

This temperature interval is interesting due to formation of various Diels–Alder adducts of C_{60} with anthracene. However, it is obvious from our experiments that even multiple addition of anthracene to C_{60} do not induce collapse of cage structure unlike to e.g. hydrogenation reaction [7]. Evidence for formation of fullerene–anthracene adducts was obtained by powder XRD, IR and Raman spectroscopy.

3.1.1.1. X-ray diffraction. All patterns recorded for samples annealed in the temperature interval 290–350 °C exhibited reflections from un-reacted C_{60} and anthracene but also many additional reflections. Since the anthracene melting point is 218 °C, boiling point at ambient conditions is 340 °C and it is stable approximately up to 600 °C [19], we can conclude that the anthracene was in a molten state in process of reaction for samples prepared in the temperature range 290–330 °C. Analysis of Fig. 1 shows certain difference for samples prepared at 350 °C and

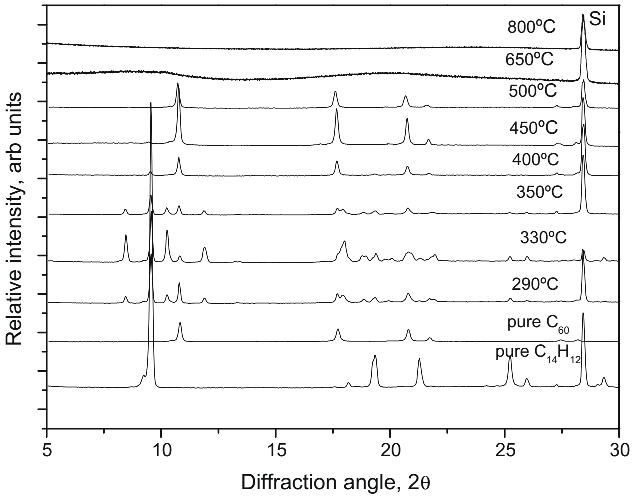

Fig. 1. X-ray diffraction patterns recorded from C_{60}-anthracene samples synthesized at different temperatures. Some silicon powder was added for calibration of patterns. Diffraction patterns of pure C_{60} and anthracene are shown as reference.