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Catalytic carbon nanotube and fullerene synthesis under reduced pressure in a batch reactor

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Abstract

Catalytic decomposition of acetylene was studied under reduced pressure in a batch reactor over catalyst samples, which previously showed outstanding activity and selectivity in carbon nanotube formation in a fixed-bed flow reactor under atmospheric pressure. It was found that activity depends on the nature of the catalyst sample at lower acetylene pressure. Characterization of the samples was carried out by transmission electron microscopy and X-ray diffraction. Concerning the quality and the graphitization of carbon nanotubes, selectivity showed a strong dependence on the initial pressure. With decreasing pressure the formation of fullerenes was obtained. To detect the amount of fullerenes and polyaromatic hydrocarbons, Soxhlet extraction followed by high pressure liquid chromatography (HPLC) mass spectrometry (MS) analysis was carried out. Certain catalyst samples showed activity in fullerene formation independent of pressure. HPLC results support a mechanism for catalytic C_{60} formation via polyaromatic hydrocarbons as building blocks. © 2004 Published by Elsevier Ltd.

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1. Introduction

For the synthesis of carbon nanotubes several methods are successfully used. While an arc discharge technique generally works in a batch type reactor below atmospheric pressure, the chemical catalytic vapour deposition (CCVD) method operates in a quasi-continuous flow reactor under atmospheric pressure [1-5]. Using a graphite electrode, the arc discharge apparatus is suitable for both C_{60} synthesis and multiwalled carbon nanotube (MWNT) production, of course, under different conditions [6]. The optimum helium pressure for C_{60} synthesis was found to be around 100 Torr (13.3 kPa). For the formation of MWNTs 400-500 Torr helium pressure was favourable. In fullerene-forming flames, formation of carbon nanotubes was also observed using low pressure hydrocarbons [7]. Parallel formation of various carbon nanostructures, their hybrid materials and their possible conversion into each other are fascinating topics of carbon chemistry [8–11]. Moreover, fullerene traces (C_{60} and higher homologues) were extracted from CVD soot [12].

From these observations several questions arise concerning catalytic carbon nanotube formation. In this paper we investigated if there is any effect on the yield and the selectivity of carbon nanotubes if the reaction is carried out in the batch reactor instead of the flow system. We also studied how the above-mentioned parameters changed if we reduced the pressure in the reactor. The effect of varying pressure on the amount and the graphitization of MWNTs was described in this paper. We investigated whether the amount of fullerenes could be increased in the low pressure catalytic synthesis of carbon nanotubes.

2. Experimental section

2.1. Catalyst preparation

Mono- and bimetallic supported transition metal catalysts, which proved to be active, and selective in carbon nanotube formation in the atmospheric fixed bed

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flow system [13–15], were prepared for carbon nanotube synthesis. Alumina (Acros), silicagel (Aldrich, 5–25 µm) and zeolite 13X (Aldrich) were chosen as support materials. For the monometallic samples iron or cobalt was used, and for the bimetallic samples a mixture. The following chemicals were deposited on the surface of catalyst supports: Fe(CH₃COO)₂, Co(CH₃COO)₂. 4H₂O. The counter anions were assumed to meet the expectations for getting "clean" catalytic surfaces free of unknown components. For the preparation of zeoliteand alumina-supported catalysts (Co/zeolite, Fe/zeolite, Co, Fe/zeolite, Co/alumina, Fe/alumina, Co, Fe/alumina) the impregnation method was used: the calculated amount of metal salt or mixture of metal salts was dissolved in isopropanol. Upon impregnation the solvent was evaporated in a Rotovap system under continuous stirring at 70 °C. For making silicagel-supported samples (Co/silicagel, Fe/silicagel, Co, Fe/silicagel) with ionexchange precipitation, twice the quantity of metal used for impregnation was dissolved in distilled water and then, silicagel of known weight was added and the pH of the suspension was set to 7.3. After 2 h the solid material was filtered and washed. The as-prepared samples were dried at 120 °C overnight. The total cobalt and/or iron contents of the final catalyst samples were 5%.

Catalyst samples were treated at 120 °C and further weight-losses may be expected at the temperature of carbon nanotube synthesis. With this in mind thermal analysis of the samples was carried out in a nitrogen atmosphere (Derivatograph-Q, MOM) and the corrected mass values were used for calculating the carbon yield.

2.2. Recirculatory batch reactor

The scheme of the reactor used for catalytic decomposition of acetylene can be seen in Fig. 1, its main parts are the following: reactor (I), rotary vacuum pump (II), circulatory pump (III), mercury manometer (IV) and a trap for condensates (V). The reactor part is made of quartz tube and placed in a furnace so that the temperature can be controlled. The vacuum pump provided cleaning, charging and discharging of the system. The circulatory pump with four throttle valves and a magnetic piston made of teflon was used for mixing reactant gases before reaction and forcing gases continuously above the catalyst bed during reaction. The trap was cooled in a mixture of ice and sodium nitrite with the ratio of 5:3 (-20 °C) in order to avoid contamination of other parts of the vacuum system. The exact volume of each part of the reactor was known as a function of pressure and was used for further calculations.

2.3. Carbon nanotube synthesis

Catalytic decomposition of acetylene was carried out in a recirculatory batch reactor at 700 °C. A measured



Fig. 1. The scheme of reactor used for catalytic decomposition of acetylene. Its main parts are the following: reactor (I), rotary vacuum pump (II), circulatory pump (III), mercury manometer (IV) and a trap for condensates (V).

amount (\approx 50 mg) of catalyst in a quartz boat was placed into the reactor. After evacuating the reactor part, preheating of the system was started. At the beginning of the reaction 400 or 600 Torr acetylene was allowed into the reactor. Calculated values of initial acetylene pressure were 170.1 and 258.5 Torr, respectively. Change of pressure was followed during the whole period of the reaction. After 20 min the system was evacuated again and the product was allowed to cool under vacuum.

2.4. Characterization of the carbon deposit

The amount of carbon deposit was determined by weighing the samples in the quartz boat before and after reaction. Charged quantity of acetylene can be calculated so from these data carbon yield (ratio of deposited carbon weight and corrected initial catalyst weight multiplied by 100) and carbon deposit (ratio of deposited carbon weight and total amount of carbon multiplied by 100) were calculated for quantitative characterization. Carbon deposit and carbon yield data are summarized for each catalyst sample in Table 1.

Qualitative characterization of the carbon deposit was made using transmission electron microscopy. For sample preparation, a Rh–Cu grid was dipped into a glue solution, then the catalyst sample together with the Table 1

Solid carbon, carbon deposit, carbon yield data and TEM characterization for various catalyst samples at two different initial pressures (data are averages of three parallel measurements)

Catalyst	Pressure (Torr)	Solid carbon (mg)	Carbon deposit (%)	Carbon yield (%)	TEM characterization ^a	
Co/silicagel	400	22.6	21.7	49.0	++	
-	600	26.7	16.8	60.5	+	
Fe/silicagel	400	31.5	29.1	71.9	++	
	600	40.7	25.6	91.5	+	
Co,Fe/silicagel	400	28.5	26.6	60.5	++++	
	600	36.6	23.0	78.9	+	
Co/zeolite	400	15.7	14.6	39.8	-	
	600	39.6	11.5	46.1	-	
Fe/zeolite	400	25.8	24.1	65.0	+++	
	600	33.7	21.2	91.7	++	
Co,Fe/zeolite	400	44.2	41.3	112.5	++++	
	600	43.6	27.4	109.9	++++	
Co/alumina	400	n.a.	n.a.	n.a.	+++	
	600	12.5	7.9	40.5	++	
Fe/alumina	400	n.a.	n.a.	n.a.	++	
	600	8.0	5.0	24.4	+	
Co,Fe/alumina	400	2.3	2.1	7.1	++	
	600	18.0	11.4	55.2	+	

 $a^{+}+++$ every particle covered by good quality carbon nanotubes. +++ large amount, good quality carbon nanotubes. ++ less good carbon nanotubes with some amorphous carbon. + very few carbon nanotubes. - almost bare catalyst surface.

carbon deposit as a representative portion was placed on it. In addition to taking images, a general qualitative characterization of the sample is also given in Table 1. XRD patterns of powdered samples were taken using a diffractometer (Cu K_{α} = 0.154 nm). visible detection was performed at 330 nm wavelength. The volume of the injected solution was 100 μ l.

The extracted solutions of toluene were also analyzed by mass spectrometry using a mass spectrometer (Finnigan—Mat TSQ70) equipped with a triple quadrapole in the negative ion detection mode.

2.5. Analysis of fullerenes

Soluble components were extracted with toluene from each carbon soot sample prepared over different catalysts and at various initial pressures. Before Soxhlet extraction, each sample was suspended in 20 cm³ toluene and treated in an ultrasonic bath for 30 min, which helps liberation of encapsulated components. After that an additional 80 cm³ portion of toluene was added to the suspension and Soxhlet extraction was carried out for 24 h. During this procedure refluxing toluene dissolves soluble compounds from the solid sample. The toluene solution was used for further analysis.

The Soxhlet extracted solution of toluene was concentrated, filtered through a 0.45 μ m Acrodisc-3 syringe filter and analyzed by a high performance liquid chromatography (HPLC) in a Millipore Waters^M 600E controller instrument equipped with a diode-array detector. An analytical Cosmosil packed Buckyprep column (4.6 i.d. × 250 mm), was used with toluene as the mobile phase in gradient elution mode for the quantitative analysis of polyaromatic hydrocarbon (PAH) and fullerene compounds. The qualitative results of C₆₀ and C₇₀ present in different samples were determined after a calibration of the column using standard samples of C₆₀ and C₇₀. The flow rate was 1.0 ml/min and the UV–

3. Results and discussion

3.1. Carbon deposit over silicagel supported catalyst

Using Co/silicagel, catalyst particles are mostly covered with carbon nanotubes at 400 Torr initial pressure. In some regions a slight alignment of the tubes can be observed. In spite of the higher carbon yield at 600 Torr, the quality of the carbon deposit is quite poor. If we compare TEM images of samples deposited at different initial pressures (Fig. 2a and b), beside amorphous carbon one can see a few poor quality carbon nanotubes in the latter sample and selectively formed carbon nanotubes in the other. It is interesting to remark that spiral carbon nanotubes characteristic of silicagel supported samples [16] were also observed.

Although carbon yields were found to be higher for the Fe/silicagel catalyst, the quality and the quantity of carbon nanotubes were lower than those obtained on Co/silicagel. In the carbon deposit obtained at higher pressure the ratio of less graphitized carbon nanotubes and carbon fibers having a cone-like structure increased. In addition, the amount of amorphous carbon deposited



Fig. 2. TEM images of carbon deposit obtained in the decomposition of acetylene over Co/silicagel catalyst at 400 Torr (a) and at 600 Torr initial pressure. Amorphous carbon and a few bad quality carbon nanotubes can be seen in (b) and selectively formed carbon nanotubes in (a).

on the outer surface of the carbon nanotubes was also higher.

At 400 Torr initial pressure bimetallic Fe,Co/silicagel catalyst produced carbon nanotubes of the highest selectivity. Every catalyst particle was densely covered with well-graphitized carbon nanotubes. Their diameter dispersion was quite homogeneous, the outer diameter was typically between 15 and 25 nm (Fig. 3). As over monometallic catalysts, the quality of carbon deposit became worse with increasing initial pressure. Although less amorphous carbon and more carbon nanotubes formed than over Co/silicagel and Fe/silicagel samples, the graphitization of the latter product was quite poor.

3.2. Carbon deposit over zeolite supported catalysts

Although Co/zeolite was found to be suitable for large scale synthesis of carbon nanotubes in the flow reactor [13], the recirculatory batch reactor at lower pressure showed no selectivity at all. Concerning carbon



Fig. 3. Carbon nanotubes at 400 Torr initial pressure over bimetallic Fe,Co/silicagel catalyst.

yield data the above-mentioned catalyst proved to be active but TEM observations revealed mostly amorphous carbon and very few carbon nanotubes on the surface both at 400 and 600 Torr initial pressure (Fig. 4a).

The quality of carbon deposited on Fe/zeolite was much better. Low magnification TEM showed carbon nanotubes on almost every catalyst particle. A slight difference was also observed between samples prepared at various initial pressures. In Fig. 4b carbon nanotubes free of amorphous carbon can be seen on the surface of Fe/silicagel catalyst.

Outstanding activity and selectivity were found using Fe,Co/zeolite catalyst. All particles were densely covered selectively with carbon nanotubes. In many regions growing tubes aligned into bundle-like structure at 400 Torr initial pressure as is illustrated in Fig. 5a. From normal resolution TEM results it can be concluded that using higher pressure resulted in somewhat crooked carbon nanotubes (Fig. 5b). Although catalyst particles were covered mainly with carbon nanotubes, their structure was not well-graphitized as became clear after HRTEM analysis discussed later.

3.3. Carbon deposit over alumina supported catalysts

A large amount of carbon nanotubes was found on the surface of Co/alumina catalyst in the decomposition of acetylene at 400 Torr. Almost every particle was covered and not only bundles but also spirals, unusual on this catalyst, were observed as can be seen in Fig. 6. At higher pressure the amount of carbon nanotubes is significantly lower.

Compared to Co/alumina or even to other catalyst samples supported on silicagel or zeolite, Fe/alumina produced very few carbon nanotubes at both initial pressures. Other carbon nanostructures such as spheres or graphite flakse can often be observed on the surface.

Fig. 4. Co/zeolite 600 Torr (a): mostly amorphous carbon and very few carbon nanotubes have grown on the surface of the catalyst. Fe/zeolite 400 Torr (b): almost each catalyst particle is covered by carbon nanotubes.

Fig. 5. TEM images of carbon deposit obtained over Fe,Co/zeolite catalyst. All particles were densely covered selectively with carbon nanotubes. In many regions growing tubes aligned into bundle-like structure at 400 Torr initial pressure (a). Using higher pressure resulted in somewhat crooked carbon nanotubes (b).

Fe,Co/alumina at 400 Torr initial pressure was found to be the most effective in the synthesis of carbon nanotubes among alumina supported catalysts. The amount of carbon nanotubes observed on the surface of the catalyst particles is, however, much lower than that over zeolite supported samples. At higher pressure mainly amorphous carbon and only a very few carbon nanotubes formed.



Fig. 6. Carbon nanotubes of quite large amount was found on the surface of Co/alumina catalyst in the decomposition of acetylene at 400 Torr. Almost every particle was covered and not only bundles but also spirals unusual on this catalyst were observed.

3.4. Structure of carbon deposit: HRTEM and XRD studies

Carbon deposits obtained at both initial pressures over Fe,Co/silicagel and Fe,Co/zeolite samples, which provided the best quality by normal resolution TEM, was also analyzed by HRTEM. The following general observations can be made. The density of nanotubes is higher for zeolite-supported samples (Fig. 7a and c) than for silicagel-supported ones (Fig. 7b and d). Graphitization is better for 400 Torr (Fig. 7a and b), the 600 Torr samples are very sensitive to electron irradiation (Fig. 7c and d). It can be assumed that the structure contains a lot of defects. Nanotubes obtained using a zeolite support at 400 Torr initial pressure seem to be the ones which are narrow and have limited number of sheets (<10) (Fig. 7a). The worst nanotubes are present in the



Fig. 7. High resolution TEM images of carbon structures prepared: (a) at 400 Torr initial pressure over Fe,Co/zeolite catalyst; (b) at 400 Torr initial pressure over Fe,Co/zeolite catalyst; (c) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; and (d) at 600 Torr initial pressure over Fe,Co/zeolite catalyst; at 200 Torr initial pressure over Fe,Co/zeol

silicagel sample at 600 Torr as can be seen in Fig. 7d. Here, it is almost impossible to find nicely graphitized nanotubes, rather the structure seems to be between graphite sheets and an amorphous structure.

In order to compare the quality of carbon deposits on a macroscopic scale, X-ray diffraction measurements were carried out. Limited amounts of various samples did not allow us to study purified, i.e. catalyst support free materials, so in the spectra of zeolite supported samples other also peaks appeared. XRD investigations confirmed HRTEM results. Graphitization of samples prepared at lower initial pressure was definitely higher. As an illustration XRD patterns of silicagel-supported samples are shown in Fig. 8b and c compared to pure graphite powder (Fig. 8a).

3.5. Fullerenes from CVD samples

Extracts obtained after Soxhlet extraction are multicomponent, thus analysis without preliminary separation was prevented both by mass spectrometry and by infrared spectroscopy. HPLC equipped with a special column developed for fullerene detection proved to be the proper technique for this purpose. Since we had to condense our toluene solutions by evaporation, HPLC analysis provided only qualitative results. Fig. 9 shows the HPLC chromatogram obtained for a sample produced on Fe,Co/zeolite at 400 Torr initial pressure. For all the samples analyzed we observe a large distribution of PAH compounds in the region with from 3 to 7 min retention time. The PAH compounds were more abundant than fullerenes in a sample produced by the CVD technique.



Fig. 9. HPLC chromatogram obtained from the toluene extracted solution (sample 1). Experimental conditions: injection volume of 100 μ l, toluene as eluant; flow rate 1ml/min; UV detection at 330 nm.



Fig. 8. A region of X-ray diffractograms of pure graphite powder (a), carbon deposit formed at 600 Torr initial pressure over Fe,Co/silicagel catalyst (b), carbon deposit formed at 400 Torr initial pressure over Fe,Co/silicagel catalyst (c).

Table 2Results of HPLC and MS analysis after Soxhlet extraction

Sample	Initial pres- sure (Torr)	Mass spectrometry			HPLC	
		C ₆₀	C ₇₀	PAH	C ₆₀	C ₇₀
Co,Fe/zeolite	400			+++	+	
Fe/silicagel	400	+		+++	+	
Co/silicagel	400			+++	+	
Co,Fe/silicagel	400	+		+++	+	++
Fe/silicagel	600	+		+++	+	++
Co/silicagel	600	+		+++		
Co,Fe/silicagel	600	+		+++	+	++
Co/alumina	600	+		+++	+	+

(+++): very large abundance of PAH compared to fullerene compounds.

(++) and (+): are used to compare the relative abundance of C_{60} and C_{70} fullerenes in the same sample.



Fig. 10. HPLC chromatogram obtained from the toluene extracted solution of sample 13, where C_{70} is more abundant than C_{60} . Experimental conditions: Injection volume of 100 µl, eluant, toluene; flow rate 1 ml/min; UV detection at 330 nm.

However, the formation of C_{60} and C_{70} were observed mainly at lower initial pressures independent of catalyst sample. Table 2 summarizes the results obtained by HPLC and MS analysis after Soxhlet extraction. The presence of C_{60} and C_{70} fullerenes was confirmed by comparing their UV spectra with those obtained from standard samples of C_{60} and C_{70} at 330 nm. In samples produced on Fe,Co/silicagel at 400 Torr, produced on Fe/silicagel at 600 Torr, and produced on Fe,Co/silicagel at 600 Torr, respectively, the amount of C_{70} is much higher than that of C_{60} (Fig. 10). The catalytic carbon nanotube synthesis technique can produce samples with a higher concentration of C_{70} fullerene.

The mass spectra were obtained after chemical ionization of different samples through the use of a mixture of CH_4/N_2O as chemical ionization reagent gas. The negative ions mass spectrum of the toluene solutions readily showed that the samples are composed primarily of PAH compounds with molecular ions mass m/e ratio ranges from 126 to 660 (Fig. 11) clearly detected with HPLC. The spectra obtained show the presence of more than 18 different PAH compounds, while the presence of fullerene compound, as C_{60} remains very weak in most of the samples. PAH compounds may play an important role in the fullerenes such as C_{60} , C_{70} and in nanotube formation in the catalytic decomposition of acetylene.

4. Conclusions

Carbon deposit and carbon yield values increase with higher initial pressure, but the carbon deposit, ratio of deposited carbon weight and total amount of carbon becomes lower with increasing pressure, and the amount of trapped by-products is also increased. Complete



material balance and analysis will be given in a following paper. Here we have focused on nanotube formation and carbon deposit data. In spite of considerable inner pore volume, which tends to accumulate large amount of amorphous carbon [17], silicagel supported samples showed no higher carbon yield data.

In this system the difference between the activities of mono- and bimetallic catalysts is not as great as was observed previously in the flow reactor, although a zeolite-supported bimetallic catalyst produced carbon nanotubes of the best quality independently of initial pressure.

From TEM observations and XRD patterns it can be concluded that lower pressure is definitely favourable for the selective formation of carbon nanotubes. At higher initial pressure worse selectivity and too many other kinds of carbon nanostructure were observed.

The formation of C_{60} was observed mainly at lower initial pressure independent of catalyst sample. Polyaromatic hydrocarbons were detected in all samples in a significant amount. They probably play a significant role as an intermediate in the formation of both fullerenes and carbon nanotubes.

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