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On the role of catalyst, catalyst support and their interaction in synthesis of carbon nanotubes by CCVD

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Abstract

The catalytic growth of carbon nanotubes was investigated from the point of view of reaction mechanism. A great variety of catalyst supports (silica gel, zeotype materials, alumina, etc.) with different pore diameter was tested in acetylene decomposition at 1000 K. Quality and existence of carbon deposit was followed by transmission electron microscopy and the state of catalyst was investigated by in situ X-ray photoelectron spectroscopy measurements. It was proved that only catalyst particles deposited on the external surfaces of porous support could take part in the catalytic carbon nanotube formation.

Keywords: Carbon nanotubes; CCVD; Porous support

1. Introduction

The chemical vapour deposition (CVD) method for production of carbon nanotubes is of great interest since it gives large quantity, good quality single wall carbon nanotubes (SWNTs) and/or multi-wall carbon nanotubes (MWNTs). The product can easily be varied by changing the catalyst and the carbon source.

A particular case of the CVD method is when gas phase hydrocarbon or hydrocarbon derivatives are the carbon sources, and they decompose on the metal component of the catalysts at rather high temperature, generally above 800 K [1]. This preparation technique is frequently called as catalytic chemical vapour deposition (CCVD) [2]. In this procedure simple hydrocarbons such as methane, ethylene, acetylene or benzene and toluene were dominantly used [3]. Transition metals, most frequently Fe, Ni or Co, supported on oxides or zeolites are the catalyst precursors [4]. When a bimetallic catalyst is used, the alloy phase forms, which is supposed to be the active component of the catalyst. The relatively high yield and excellent quality of carbon nanotubes have been explained by the peculiar behaviour of this alloy phase [5].

Recently, several papers dealt with the mechanism of the formation of nanotubes [6]. Particularly, the role of the catalyst support and the particle size of the metal have been discussed [7]. The most frequently used catalyst supports are silica, zeolites and alumina. Well-crystallised carbon nanotubes were formed on catalysts supported by these materials [8]. A part of these supports are molecular sieves having a sharp pore diameter distribution in molecular dimensions (0.4–1 nm), the others' pore diameter is much larger. The role of pore structure of the support in the formation of nanotubes is one of the most intriguing problems to be answered. Structural and textural properties of pyrolitic carbon formed in the inner pores of zeolitic structures have been studied [9]. Taking into consideration that the metal component, which is the catalytic active centre, may situate in the pores and on the external surface, the chance to find the correct answer to the former question is rather challenging. As the state of the metal component is concerned, the most discussed problem is the influence of the size of metal clusters generated. Does it determine the pore diameter of the carbon nanotubes formed on them? If yes, how?

In this paper, we present results in connection with the role of the catalyst support and the state of the metal in the CCVD production of MWNT.

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2. Experimental

2.1. Preparation and characterisation of catalysts

The metal component (Co or Fe) was introduced to the silica support by ion adsorption and precipitation. The metal was deposited from a slightly basic aqueous solution ($\mathrm{pH} = 8$) of its acetate. After 24 h the catalyst was filtered, washed and dried at 400 K overnight.

Zeolite NaY and a mesoporous zeolite-like material (MCM-41), were loaded with metal ions using ion exchange and impregnation. After evaporation of the solvent, the catalyst sample was dried at 400 K overnight. The final catalyst contained 5 wt.% of Co or Fe, respectively.

Since these materials have a high ion exchange capacity, and when they are in contact with cobalt or iron ion containing solution, the ion exchange immediately starts. Upon drying the solution onto the zeolite the ion concentration in the solution increases and consequently the ion exchange of zeolite gets complete. After this point, extra ion incorporation takes place if the initial Co or Fe content of the solution used for the preparation of a given amount of zeolite was larger than the ion exchange capacity of zeolite. This is the source of Co or Fe ions on the outer surface of zeolite catalysts.

Ion exchange of MCM-41 in aqueous solution of Co acetate ($0.1\,\mathrm{mol\,dm^{-3}}$) was the preparation procedure for Co-MCM-41(ex) catalyst. Ion exchange was performed twice at 343 K for 12 h each time ($0.5\,\mathrm{mmol}$ metal ion $\mathrm{g^{-1}}$ silicate). Co-MCM-41(iso) sample was prepared by isomorphous substitution of Si for Co following the description in [10]. Co/MCM-41 was prepared by impregnation. The calculated amount of Co salt (2.5%) was dissolved in distilled water, which was evaporated slowly under gentle heating.

Alumina supported iron catalyst was also prepared by the impregnation technique. To the alcoholic solution of Co acetate, the calculated amount of alumina (Acros) was added, and the solvent was evaporated slowly. The final catalyst sample contained 5 wt.% of metal.

The composition of catalyst was checked by X-ray fluorescence (XRF) analysis. The transition metal content was determined by classical analytical methods. The zeolite sample and the MCM-41 material showed the characteristic X-ray diffraction (XRD) pattern.

The BET surface areas of the samples were determined by N_2 adsorption isotherms measured at 77 K using a volumetric apparatus. For the MCM-41 sample, the pore size distribution was calculated by the Barrett–Joyner–Halenda method [11] from the adsorption data. The nominal composition, the BET areas (and pore size) of supports and the Co or Fe ion content of the catalysts are given in Table 1.

Table 1
Characteristics of catalysts

Sample	Metal content (wt.%)	Surface area ($\mathrm{m^2\,g^{-1}}$)	Pore diameter (nm)
Co/silica	5	497	6.0
Fe/Y	5	608	0.7
Co/Y	5	632	0.7
Co/MCM-41	2.5	978	3.4
Co-MCM-41(ex)	0.29	1169	3.3
Co-MCM-41(iso)	0.01	1077	3.8
Co/alumina	5	<10	–
Fe/alumina (in situ)	5	<10	–

2.2. Synthesis of carbon nanotubes

The catalytic reaction was carried out in two ways. Generally, a fix bed flow reactor was used in the temperature range 900–1100 K. The catalyst samples were placed in a silica boat that was placed into a horizontal tube reactor. Before introducing the reactant mixture (10% acetylene, 90% N_2, with a flow rate of $300\,\mathrm{ml\,min^{-1}}$) the catalysts were purged in a nitrogen stream ($300\,\mathrm{ml\,min^{-1}}$) in order to remove water and pre-treat the catalyst at 999 K. The reactions were carried out for different reaction times (1–60 min) to get some approximate information on the rate of nanotube formation.

When in situ X-ray photoelectron spectroscopy (XPS) measurements were carried out to clarify the state of Fe catalyst supported on alumina, the reaction was conducted in the sample preparation chamber of XPS instrument. The XPS experiments were performed in an ultra-high vacuum system with a background pressure of 10^{-7} Pa, produced by an ion getter pump. The photoelectrons generated by Al Kα primary radiation (15 kV, 15 mA) were analysed with a hemispherical electron energy analyser (Kratos XSAM 800). The pass energy was set to 40 eV. An energy step width of 50 meV and a dwell time of 300 ms were used. Typically, 10 scans were accumulated for each spectrum. Fitting and deconvolution of the spectra were performed with the help of VISION software. All binding energies were referenced to Al(2p) at 74.7 eV.

Before measurements, the sample was evacuated at 300 K and calcined at 1000 K for 20 min in the sample preparation chamber, which was connected directly to the analysing chamber by a sample transfer system. In the sample preparation chamber the catalyst can be heated up to 1100 K in various gas atmospheres (in the present case in an acetylene–nitrogen mixture).

2.3. Characterisation of the product MWNTs

As the initial weight of catalysts introduced into the reactor was known, we measured the weight increase after the reaction. From this the total carbon produced was determined. This value was used as first, approximate measure of the synthesis, keeping in mind that the MWNT content of this carbon product may vary in very wide range. This raw product was tested by transmission electron microscopy (TEM).

The purification of the raw products was as follows. The catalyst was dissolved from the product either by HF (for zeolites and silica) or NaOH solution (in the case of alumina support). From the resulted carbon the traces of catalyst was removed by further acidic/basic treatment followed by oxidation of the amorphous part of the product. The nanotubes thus purified were the subject of further investigations.

For TEM and high-resolution transmission electron microscopy (HRTEM) Philips CM20 and JEOL 200CX were used. For the preparation of sample holder grids, the glue technique was used described elsewhere in detail [8].

3. Results and discussion

3.1. MWNT production

Fig. 1 shows the TEM images of MWNT synthesised in the flow reactor on Co/silica, Co/alumina, Co/NaY and Fe/NaY. It is clearly seen that MWNT was formed on each catalyst; however, both their quality and quantity were different.

TEM images taken on MWNT grown on Co-containing MCM-41 samples are shown in Fig. 2. There are obvious differences between these catalysts concerning both the quantity and the quality of MWNT formed. No nanotube could be detected on Co-MCM-41(iso) (Fig. 2b) and only a tiny indication of nanotube formation is seen on Co-MCM-41(ex) (Fig. 2c). Numerous, well-graphitised nanotubes formed on Co/MCM-41 (Fig. 2a). It is worth to note here that the samples proved to be inactive in the production of MWNT were prepared by isomorphous substitution and ion exchange, not by impregnation.

As HRTEM images revealed the tubes generated on the following catalysts: Co/silica, Co/alumina, Co/NaY, Fe/NaY and Co/MCM-41 were well-graphitised, crystalline products. They are bent or curved and their diameter varies as well.

As far as the formation rate of carbon nanotubes is concerned, we should conclude that after several seconds of the introduction of an acetylene/nitrogen mixture the catalyst samples become black indicating the fast carbon deposition, that reflects to a probable immediate MWNT formation. In these experiments, in which both Fe/Y and Co/silica catalysts were used, MWNT formation was experimentally proved even after 1 min reaction time. (Using shorter reaction times seemed to be meaningless since some sort of thermal equilibrium should be reached or at least approached that takes some time!) From this follows that the MWNT formation should be a very fast process under the conditions we applied and which was similar to that reported by Jiang et al. [12]. However, these authors claimed a low carbonisation rate.

3.2. Active sites on the catalysts

As it is known from the zeolite chemistry the ion exchange positions of zeolites are situated in their pore system, which has molecular dimensions. In our case, zeolite NaY has a pore opening, i.e., an entrance for the ions and/or molecules, around 0.7 nm. Its ion exchange capacity depending on the

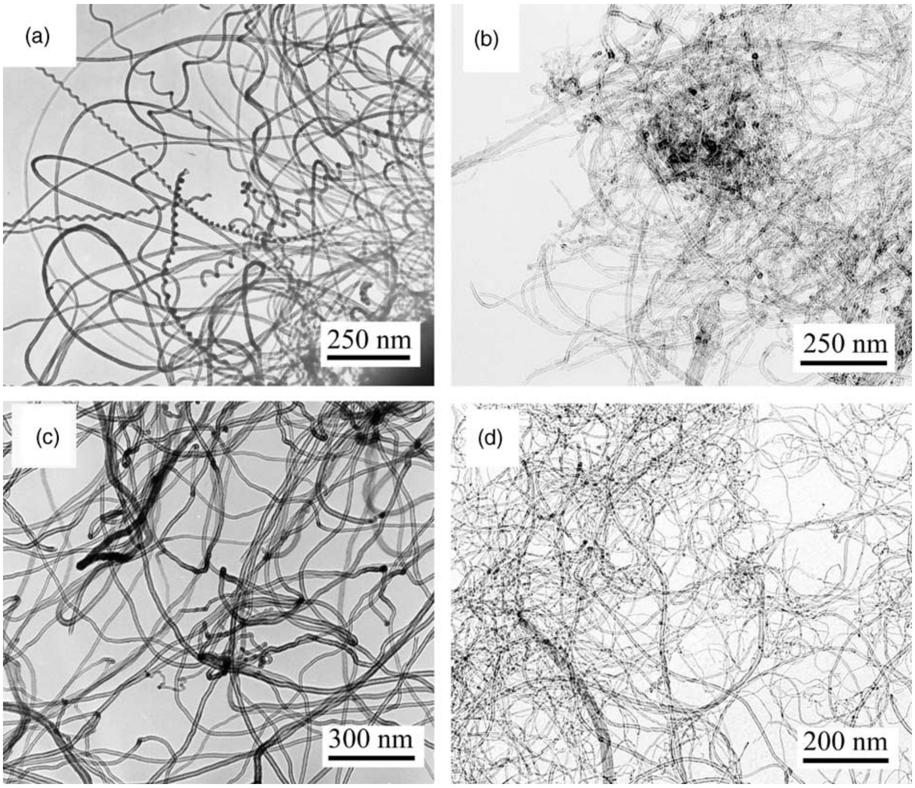

Fig. 1. Carbon nanotubes grown by CCVD on the surface: (a) Co/silica; (b) Co/alumina; (c) Co/NaY; (d) Fe/NaY.

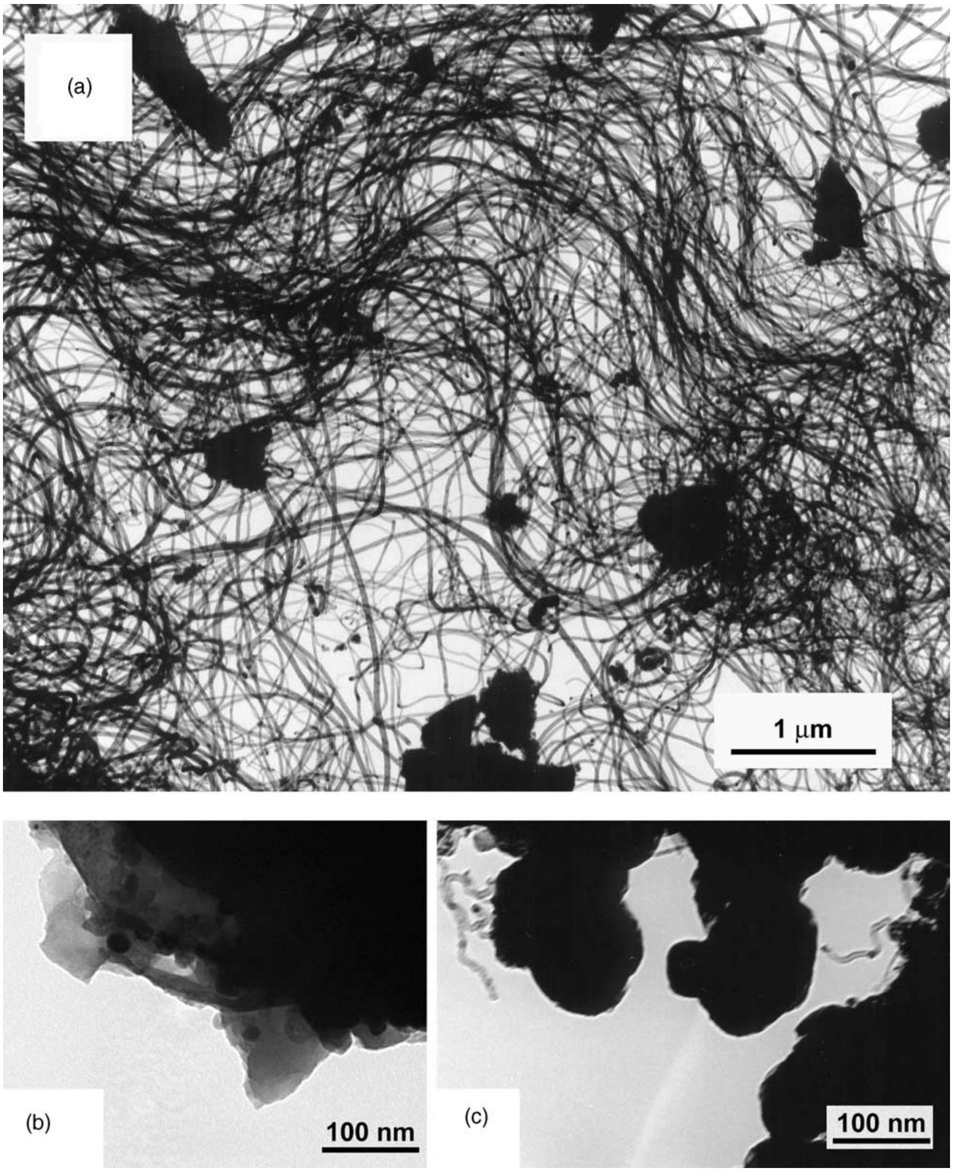

Fig. 2. MWNT grown on Co-containing MCM-41 samples: (a) Co/MCM-41; (b) Co-MCM-41(iso); (c) Co-MCM-41(ex).

Si/Al ratio of the framework varies, but its upper limit is around 5 mmol g^{-1} dry zeolite. This 5 mmol g^{-1} Co ion is bound to particular positions in the cage system and are accessible only for molecules of kinetic diameter less than 0.7 nm. This is true for the reverse way as well. Though, only those molecules can leave the pores whose diameter is smaller than the pore exit that is identical to the entrance. From this follows that the carbon nanotube formation takes place on those metal particles which are generated from ions sitting on the outer surface of zeolite crystals, since the outer diameter of the thinnest MWNT is much bigger than 0.7 nm pore size of zeolite.

For the MCM-41 the situation is similar. Here, MWNT formation was observed neither on Co-MCM-41(ex) nor on Co-MCM-41(iso). The case of the former is identical to that mentioned above for the ion-exchanged zeolites. Here the pore opening is bigger (∼3 nm); however, the Co ions are in the channels, but the pores are too small to be the nests of MWNT generation.

The case of an isomorphous substituted sample is even simpler. Presumably, all Co ions are chemically bound in the wall of MCM-41 in this sample. These Co ions are immobile, almost irreducible; therefore, there is no or a very small chance to form clusters on the outer surface of the material. Therefore, they cannot act as active sites in the MWNT generation.

3.3. *Reducibility of Fe^{3+} under reaction conditions*

As far as the reducibility of iron ions is concerned detailed in situ XPS investigations were carried out. All binding energies were referenced to Al(2p) at 74.7 eV. The use of proper

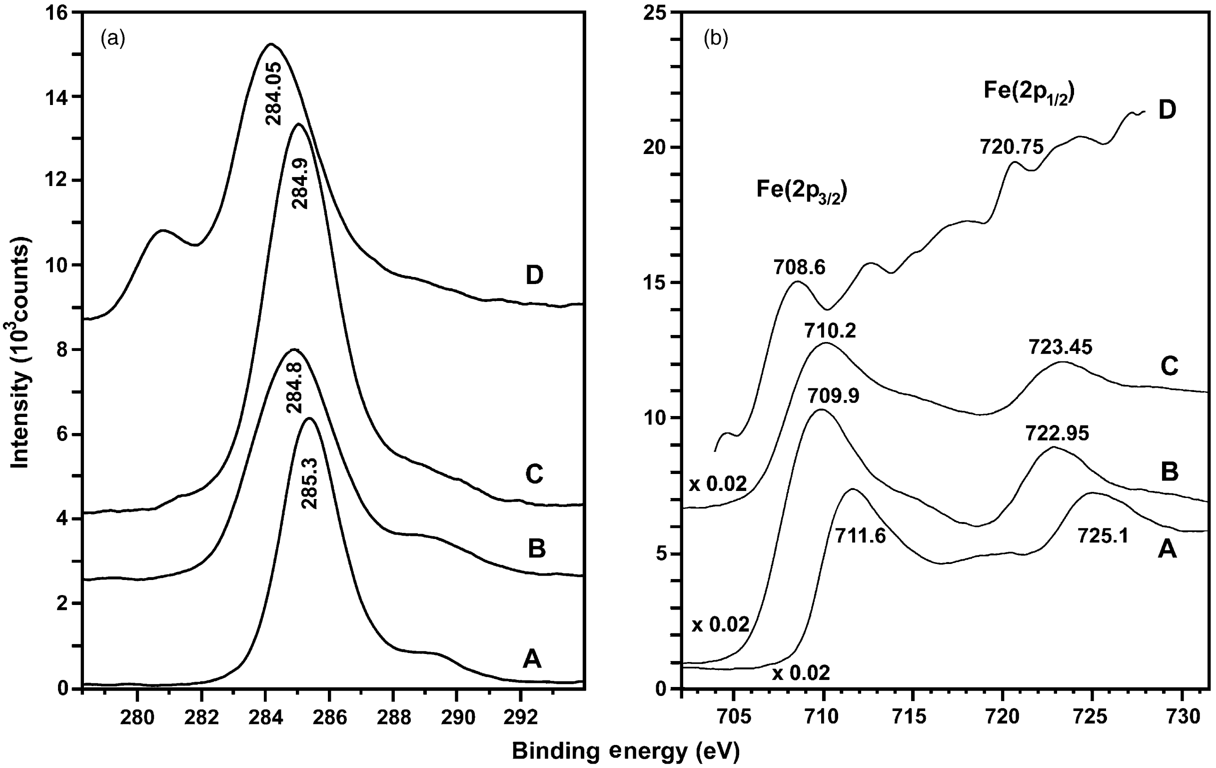

Fig. 3. Core binding energies of C (a) and Fe (b) of Fe/alumina catalyst. Curve A: after evacuation at 300 K for 60 min; curve B: after calcination at 1000 K for 20 min; curve C: after 20 Torr C_2H_2 at 300 K for 60 min; curve D: after 20 Torr C_2H_2 at 1000 K for 60 min.

reference is very important in the case of the fabrication of carbon nanotubes. The structure and electronic environment of carbon could be quite different from substrate to substrate; its structure may change with temperature, reaction time or carbon concentration, not mentioning the formation of nanotubes or fullerene. The general picture in the literature is that graphite-like carbon has a higher binding energy than carbidic carbon [13]. The core binding energies of C and Fe of Fe/alumina catalyst taken at different stages of pre-treatment are displayed in Fig. 3. In Fig. 3a we would like to present that during the different treatments the carbon signal changes significantly. As we mentioned above this carbon signal cannot be used for a standard reference to determine the position of the binding energies of other elements when we investigate the catalytic formation of carbon nanotubes on different substrates. It is seen in Fig. 3b that Fe emissions shifted to lower binding energies after calcination at 1000 K compared to the "as-received sample". Significant changes were also observed after the sample was kept at 1000 K in an acetylene atmosphere for 60 min. The most important observation is that in such a strong reduction atmosphere we could detect only a small, if any, photo-emission at 707.0 eV, which is characteristic of bulk metal Fe. The main peak at 708.6 eV can be attributed to the formation of carbide instead of some kind of remaining oxide. (We mention here that in the case of Co/Al_2O_3 after C_2H_2 treatment at 1000 K, metallic Co formation was detected with the deposition of graphitic carbon.) The reduction in the intensity of oxygen and the position of C(1s) may also support this conclusion.

4. Conclusions

1. We proved that both Co- and Fe-containing samples are good catalysts in the generation of MWNT from acetylene via CCVD.
2. The activity differences found for the various supports can be explained by the necessary localisation of the catalytically active components on the outer surface, at those places of support where a MWNT can easily accommodate, i.e., in the big pores like the silica has.
3. No indication was found suggesting that formation of MWNT starts in the pores of MCM-41 type catalysts. Actually, their pore diameter is much smaller than that of the MWNT. From this it follows that the explanation given by Jiang et al. [12] to the formation of nanotubes on MCM-41 catalyst from acetylene should not be accepted.
4. Our in situ XPS experiments showed that Fe ions are easily reduced by the reactant acetylene and we found no indication of any kind of Fe oxide after treatment the sample at 1000 K. This finding is also in contradiction to the statement of Jiang et al. [12].

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