

CATALYTIC SYNTHESIS OF CARBON NANOTUBES OVER ORDERED MESOPOROUS MATRICES

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Pyrolytic decomposition of acetylene over the surface of nickel-, cobalt- and iron-containing ordered mesoporous MCM-41 silicas has been studied. Catalytically active matrices have been prepared by chemisorption of volatile metal acetylacetonate complexes on the silica surface. Reduction of the supported metal-containing compounds was carried out in hydrogen or acetylene atmosphere. Acetylene is used not only as a source of carbon in synthesis of the nanostructures but also as a reagent capable of reducing metal ions in the surface chemical compounds. Formation of carbon nanotubes and nanofibers is shown to depend on the pyrolysis conditions.

Keywords: acetylene, carbon nanotubes, MCM-41 silica, mesopores, metal acetylacetonates, pyrolysis

Introduction

Since their discovery in 1991 [1], carbon nanotubes have shown many unique physical and chemical properties [2–4]. Depending on their structures, carbon nanotubes can be conducting, semi-conducting or insulating, which makes them the most promising materials for applications in nanoelectronics [5]. Due to their high mechanical strength they might become one of the best potential strengthening materials in polymer chemistry. The single-wall carbon nanotubes are excellent material for hydrogen storage, which would bring closer the use of hydrogen as a fuel [6].

Several methods are used for production of carbon nanotubes [7]. Generally the most frequently applied techniques differ either in the carbon source or the method to generate the high temperatures at which the carbon precursor converts to carbon nanotubes. Graphite, mixtures of transition metal compound and carbon, or various hydrocarbons and hydrocarbon derivatives in the vapour phase have been used as a carbon source. The high temperature is produced either by electric discharge [8] or laser ablation [9]. For catalytic syntheses, however, a lower temperature is required, which can be achieved in a conventional electric furnace by chemical vapour deposition methods [10]. Silicon or aluminium oxides are usually applied as catalyst supports. Metal clusters on a support function as nucleation centres for further growth of carbon nanotubes. The mechanism of pyrolytic growth of carbon nanotubes on such catalysts is assumed to include stages of catalyst formation, carbon deposition on the surface, and diffusion of carbon atoms to the free end of growing nanotubes [11].

Production of nanotubes by the method of thermal deposition of carbon from a gas phase generally includes three stages, namely preparation of a matrix; supporting of a catalyst; and, finally, synthesis of nanotubes. Usually, reduction of the supported metal-containing compounds is carried out in a hydrogen atmosphere followed by pyrolytic deposition of carbon [12]. In the case of pyrolysis of organic substances (benzene, acetone), hydrogen as a carrier gas is used so that reduction and pyrolysis stages proceed concurrently [13]. Thus, there is no necessity for primary reduction of metal nanoparticles since they are reduced in situ by the carrier gas (H_2) during the pyrolysis process.

The developed porous structure of a support generally provides a high density of catalytically active centres, and pore size provides accessibility of these surface sites to molecules of a decomposing gas. The latter condition is especially important because the rate of the nanotubes growth is limited by gas diffusion. The objective of our work is to employ the major advantages of mesoporous matrices of silicas (such as MCM-41). Of particular interest here is their high specific surface area and ordered structure of hexagonal mesopores, since these factors are very important in formation of nucleation centres for growth of carbon nanostructures. Besides, in order to attain the maximum possible uniformity of catalytically active surface, use was made of the volatile acetylacetonates of appropriate metals. Cobalt, nickel, and iron acetylacetonates were first anchored on the MCM-41 matrices through the chemical reaction with silanol groups of the silica surface. The subsequent synthesis of carbon nanostructures was carried out by the

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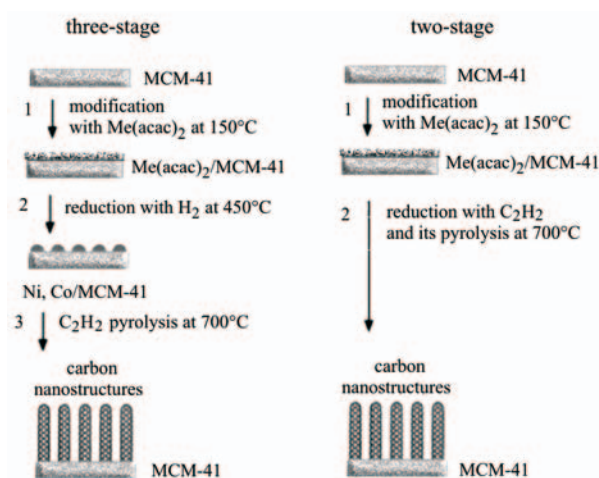
method of pyrolytic decomposition of acetylene which was simultaneously used as a source of carbon and for in situ reduction of a metal in the surface chemical compounds; and catalytic nanoparticles of metals were obtained by common reduction with hydrogen with following application as catalysts for synthesis of carbon nanotubes.

Experimental

Synthesis of ordered mesoporous silica, such as MCM-41, was carried out according to recommendations [14] in a reaction mixture with a molar ratio of reagents 1.0TEOS:0.52CTMABr:16NH₃:39H₂O in the following way. Cetyltrimethylammonium bromide (8.3 g) (CTMABr, Aldrich) was introduced into aqueous ammonia (25 mass%, 126 cm³), then tetraethoxysilane (9 g) (TEOS) was added and the mixture was heated at 70°C under stirring before formation of the gel structure. The sample obtained was calcined at 540°C for 6 h in air. Structural characteristics of silica were studied by nitrogen ad(de)sorption measurements at 77 K (Micromeritics ASAP-2000 system) and X-ray powder diffraction (DRON-4-07, CuK_α-radiation).

The synthesis of carbon nanotubes was carried out by two routes: (1) MCM-41 treatment with Ni(acac)₂ or Co(acac)₂ vapour at 150°C, metal reduction with H₂ at 450°C, C₂H₂ pyrolysis over the catalyst at 700°C; (2) MCM-41 treatment with Co(acac)₂ or Fe(acac)₂, reduction of supported metal complexes with C₂H₂, and pyrolysis at 700°C (in situ reduction).

The processes necessary to prepare a catalyst and to effect pyrolysis of acetylene on the silica matrix surface were carried out according to the following schemes of the two-stage and three-stage procedures (Scheme 1).



Scheme 1

Three-stage synthesis of carbon nanotubes

Stage 1 (modification of MCM-41 with volatile metal acetylacetonates)

Modification of mesoporous silica surface was carried out in a flow-type reactor at atmospheric pressure using argon as a carrier gas. The procedure of Ni(acac)₂ or Co(acac)₂ deposition on MCM-41 surface was as follows. Powdered MCM-41 (0.6 g) was dehydrated at 250°C for 1 h in air. Then this dehydrated MCM-41 sample was placed in the reactor, which was heated up to 150°C for 30 min and treated upstream with the modifying reagent – acetylacetonate of the appropriate metal (0.1 g). Subsequently the reactor was cooled in a stream of argon to room temperature.

Stage 2 (reduction of deposited metal)

A sample of mesoporous silica modified with acetylacetonate of the appropriate metal was placed into a horizontal quartz reactor (with an inner diameter of 42 mm). Process of reduction of metal in surface compounds was carried out at 450°C for 2.5 h in a flow of hydrogen and argon (1:1 volume ratio). At this stage formation of the large quantity of metal nanoparticles on the surface of support was observed.

Stage 3 (pyrolysis of acetylene)

Silica containing nanoparticles of the reduced metal were used as an active template for the carbon nanostructures growing by pyrolysis of C₂H₂ in quartz reactor in a mixture of C₂H₂ (6 cm³ min⁻¹) and Ar (103 cm³ min⁻¹) at 700°C for 1 h. During pyrolysis of acetylene a deposition of black decomposition products on silica matrices was observed.

Two-stage synthesis of carbon nanotubes

Stage 1 (modification of MCM-41 with volatile metal acetylacetonates)

Ordered mesoporous matrices were modified with Ni(acac)₂, Co(acac)₂ or Fe(acac)₂ as was described above.

Stage 2 (reduction of deposited metal and pyrolysis of acetylene)

A sample of mesoporous silica modified with acetylacetonate (0.6 g) of the appropriate metal was placed into a horizontal quartz reactor through which a mixture of C₂H₂ (6 cm³ min⁻¹) and Ar (103 cm³ min⁻¹) were passed for 40 min at 700°C. Deposition of black decomposition products on silica matrices was observed during the pyrolysis of acetylene, similar to stage 3 above.

For removal of the silica phase the synthesized composite was treated with 44 mass% hydrofluoric acid at ambient temperature. As a result, an insoluble carbon fraction was obtained; it was used for the subsequent studies.

Identification of carbon structures was made by the transmission electron microscopy (JEM-100CXII, Japan).

Results and discussion

X-ray powder diffractogram of the prepared silica sample (Fig. 1a) exhibits (100), (110) and (200) reflections in a small-angle range of $2\theta=2-8^\circ$, which is characteristic of the hexagonal ordered structure.

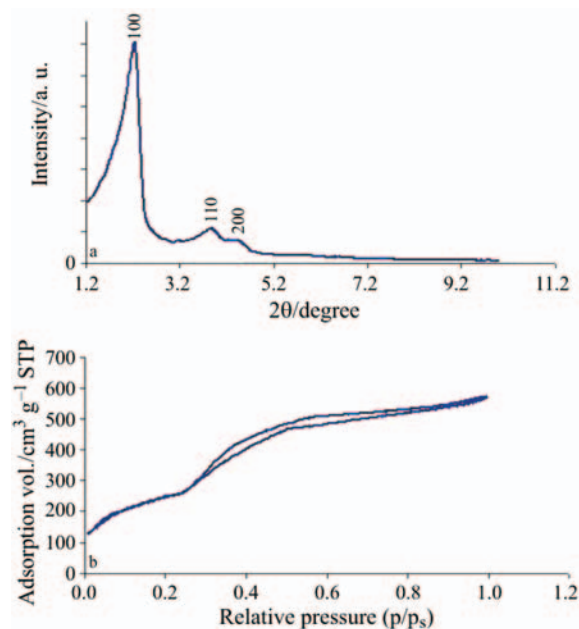


Fig. 1 a – X-ray powder diffractogram and b – sorption isotherm of nitrogen at 77 K for the synthesized MCM-41 silica

The sorption isotherms of nitrogen on synthesized silica recorded at 77 K provide information about the mesostructure of the material (Fig. 1b). The specific surface area of the sample determined from the linear part of the BET equation [15] (at $p/p_0=0.03-0.20$) is $905 \text{ m}^2 \text{ g}^{-1}$. The specific volume of pores calculated from the BET equation (desorption branch of the isotherm of nitrogen) reaches a value of $0.87 \text{ cm}^3 \text{ g}^{-1}$ (at $p/p_0=0.98$); average diameter of pores determined by the Barret–Joyner–Halenda method [16] is about 3.9 nm.

The thermal stabilities of acetylacetonates of divalent metals increase in sequence from cobalt to nickel $\text{Ni} > \text{Fe} > \text{Co}$ [17, 18]. The temperatures of sublimation of $\text{Ni}(\text{acac})_2$, $\text{Fe}(\text{acac})_2$ and $\text{Co}(\text{acac})_2$ are 132, 97 and 112°C , respectively. Elimination of

ligands is observed under conditions close to the onset temperatures of decomposition. All β -diketonates of metals of the general formula $\text{Me}(\text{acac})_n$ studied by differential thermal analysis are decomposed within the temperature range, $150-400^\circ\text{C}$ [19]. To prevent a premature decomposition of metal acetylacetonates the chemical modification of the silica surface was effected at 150°C .

After chemisorption of acetylacetonates of the iron-subgroup metals on the mesoporous support, IR spectra of the corresponding surface compounds were recorded. The IR spectra of the $\text{Co}(\text{acac})_2$, MCM-41, and corresponding cobalt-containing compounds anchored on the MCM-41 surface are shown in Fig. 2. According to Nakamoto *et al.* [20] and Dismukes *et al.* [21] asymmetric and symmetric stretching vibrations of the chelate group (C=C) and (C=O+CH) in $\text{Co}(\text{acac})_2$ appear at $1570-1575$ and $1460-1513 \text{ cm}^{-1}$, respectively. In our case in the spectrum of $\text{Co}(\text{acac})_2$ these absorption bands are observed at 1546 and 1481 cm^{-1} (Fig. 2).

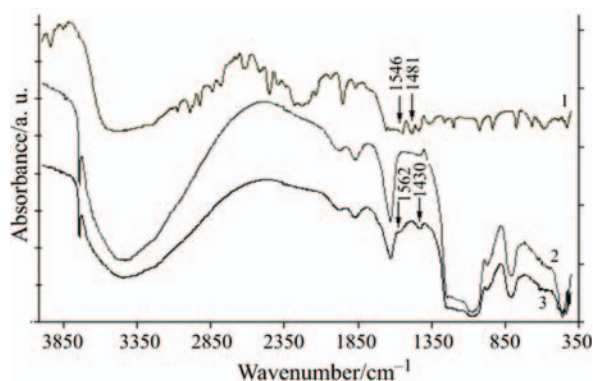
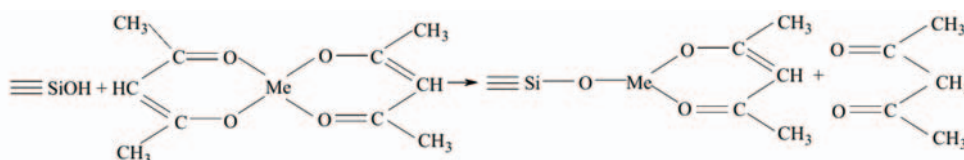


Fig. 2 IR spectra: 1 – $\text{Co}(\text{acac})_2$, 2 – MCM-41 modified with $\text{Co}(\text{acac})_2$ and 3 – MCM-41

Absorption bands at 1562 and 1430 cm^{-1} in the spectrum of the modified silica could provide evidence for the fact that the chelate ring structure of the bound ligands is retained. According to Mazurenko *et al.* [22], the ring-opening reaction for pure $\text{Cr}(\text{acac})_3$ occurs at 280°C and is accompanied by an increase in the intensity of the absorption bands at 1780 and 1800 cm^{-1} . Since the above-mentioned absorption bands for the supported cobalt-containing complex in this frequency range were not observed, it is plausible that the ring-opening reaction does not proceed under the experiment conditions. These observations are in agreement with the data published by Kenvin *et al.* [23], who made a conclusion that no ring-opening process occurred for $\text{Fe}(\text{acac})_3$ and $\text{Mn}(\text{acac})_3$ after removal of one or two of acetylacetonate ligands as a result of reaction with silanol groups of the silica surface.

As reported earlier [24], under these conditions nickel acetylacetonate enters into a chemical interaction with free silanol groups of the silica surface (ab-



Scheme 2

sorption band of 3750 cm^{-1} in the IR spectrum) with elimination of one ligand. These observations and deductions may be extended to other volatile metal acetylacetonates so that it is possible to assume that in the case of $\text{Co}(\text{acac})_2$ and $\text{Fe}(\text{acac})_2$ (whose sublimation temperatures are lower) their chemisorption takes place on the silica surface according to the mechanism of the electrophilic substitution of a proton in surface $\equiv\text{SiOH}$ groups according to Scheme 2.

Possibly, such chemical modification of the silica surface with the volatile acetylacetonates of nickel, cobalt, and iron leads to a quite homogeneous distribution of a metal in the surface layer in comparison with impregnation of matrices with solutions of the corresponding metal salts.

Gravimetric studies of processes of the thermal decomposition of acetylacetonate complexes of cobalt or iron attached to mesoporous matrices showed (Fig. 3) that the mass loss due to destruction of acetylacetonate groups retained after the reaction with surface silanol groups was observed over the temperature range $350\text{--}450^\circ\text{C}$. The heating rate was $10^\circ\text{C min}^{-1}$. As a result, complex oxides of the corresponding metals of cobalt and iron had formed on the silica surface. Similar results were achieved earlier for the thermal decomposition of $\text{Cr}(\text{acac})_3$ [25] and $\text{Cu}(\text{acac})_2$ [23] supported on the silica matrix. The destruction of the formed chromium- and copper-containing surface compounds took place at 295 and 315°C , respectively.

Application of matrices with the supported metals as catalysts enabled us to attain rather high content of carbon nanostructures (20–30% of the process product). Content of nanotubes in pyrolytic deposi-

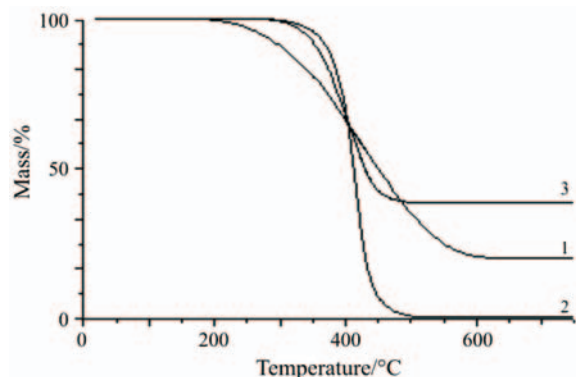


Fig. 3 TG curves of 1 – $\text{Ni}(\text{acac})_2$, 2 – $\text{Co}(\text{acac})_2$ and 3 – $\text{Fe}(\text{acac})_2$ complexes supported on the MCM-41 surface

tion was determined by subtraction of the mass of amorphous carbon from the mass of resulting product (amorphous carbon plus nanotubes). According to electron microscopic data, in the three-stage synthesis for obtaining of carbon nanostructures, many nanotubes were formed with external diameters in the range $35\text{--}52\text{ nm}$ for the cobalt catalyst (Fig. 4a) and, $10\text{--}35\text{ nm}$ for the nickel catalyst (Fig. 4b). Formation of small quantities of carbon fibres of diameter of $50\text{--}70\text{ nm}$ was also observed.

In the use of acetylene as a source of carbon and as a reducer of metals in the two-stage process, electron microscopy data provided evidence for formation of nanotubes with an external diameter of $42\text{--}84\text{ nm}$ in the case of the cobalt catalyst (Fig. 5a) and $14\text{--}24\text{ nm}$ in the case of the iron catalyst (Fig. 5c). Formation of carbon fibres, with diameters in the range, $80\text{--}110\text{ nm}$, for the nickel catalyst (Fig. 5b) was also observed. Observation of presence of nanotubes with large diameter for the nickel catalyst (Fig. 5d) is depended with enhanced dimensions of reduced nanoparticles of metal. Comparison of nanotubes growth using the cobalt catalysts by two methods show that nanotubes in Fig. 4a are more curved. Catalysts that were prepared in an atmosphere

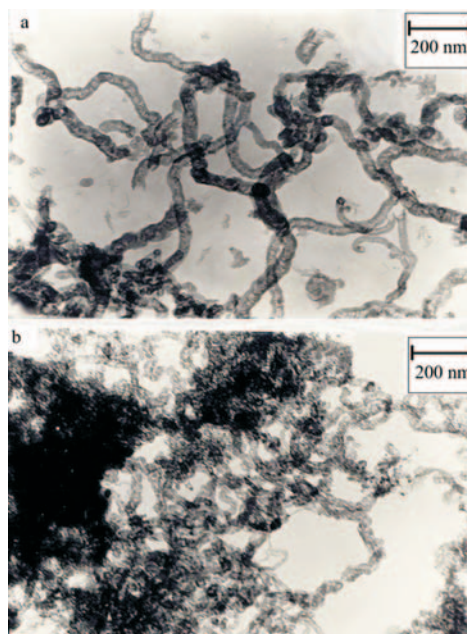


Fig. 4 TEM micrographs of carbon nanotubes obtained on MCM-41 matrices with a – cobalt and b – nickel catalysts prepared by reduction in hydrogen

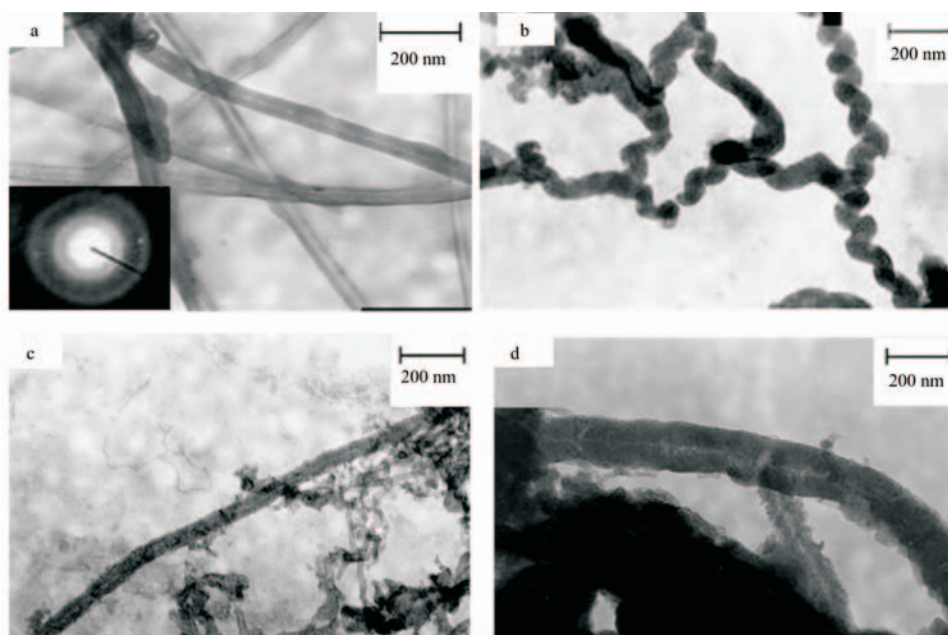


Fig. 5 TEM micrographs of carbon nanotubes obtained on MCM-41 matrices with a – cobalt, c, d – iron catalysts and carbon nanofibres obtained with b – nickel catalyst. All catalysts were prepared by reduction in acetylene

of acetylene (without reduction with hydrogen) (Fig. 5a) promote formation of more aligned nanotubes. Here it is noted that in the absence of a catalyst on such matrices small yields (up to 2%) of carbon nanotubes were obtained [26].

The inset in Fig. 5a, which exhibits an electron diffraction pattern, gives of metallic cobalt. The value of an interplanar crystal spacing ($d_{hkl}=0.125$ nm) calculated from the diffraction ring diameters is in good agreement with the standard ASTM value for bulk Co ($d_{110}=0.1252$ nm). Thus, during the course of acetylene pyrolysis, surface compounds of nickel, cobalt, and iron were probably reduced to the corresponding metals, which initiated the growth of carbon nanotubes on the matrix surface. Hence, the above-outlined simultaneous application of acetylene as a source of carbon and as a reducer of metals allows one to replace hydrogen, which is traditionally used for reduction of metals before the pyrolysis stage.

The average diameter of the carbon nanotubes obtained exceeds greatly the average pore size of the initial silica matrix. Because under the above-mentioned conditions of pyrolysis of C_2H_2 , any noticeable formation of nanotubes with diameters close to sizes of MCM-41 pores is not observed, it is possible to assume that growth of carbon nanostructures occurs on those sites of matrices where the corresponding nanoparticles of metal are formed (on an external surface of the support) or on sites where probable destruction of walls of hexagonal pores takes place. Also, it should be noted that with increasing duration of pyrolysis (more than 1 h) the yield of amorphous carbon increases.

Conclusions

Efficient methods for producing catalysts that can also be used to synthesize carbon nanostructures have been developed. Two methods are described: (a) chemisorption onto MCM-41 silica of acetylacetonates at $150^\circ C$, followed by reduction of the supported metal acetylacetonates with hydrogen at $450^\circ C$ and subsequent treatment with acetylene at $700^\circ C$; (b) direct treatment of the supported metal acetylacetonates with acetylene at $700^\circ C$. Both routes, depending on the metal and conditions, leads to carbon deposition either in the form of nanotubes (diameter, 14–84 nm) or carbon fibres (diameter, 86–111 nm). Longer pyrolysis with acetylene increases the yield of amorphous carbon particles.

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