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The role of zeotype catalyst support in the synthesis of carbon nanotubes by CCVD

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The effect of zeotype support on the selectivity of carbon nanotube formation in the catalytic decomposition of acetylene was investigated. Catalyst supports with various pore diameters were tested. Formation and the quality of carbon deposit were followed by transmission electron microscopy (TEM) and the state of supported catalyst particles was investigated by *in situ* X-ray photoelectron spectroscopy (XPS) measurements. It was found that only catalyst particles deposited on the external surfaces of porous support could efficiently take part in the catalytic carbon nanotube formation.

1. INTRUDUCTION

The catalytic chemical vapor deposition (CCVD) method for the production of carbon nanotubes is of great interest among researchers since it gives large quantity, good quality single- (SWNT) and/or multi- (MWNT) wall carbon nanotubes. In this procedure simple hydrocarbons as methane, ethylene, acetylene, or benzene, toluene

were used predominantly [1]. Transition metals, most frequently Fe, Ni or Co, supported on oxides or zeolites were the catalyst precursors [2]. When bimetallic catalyst was used, alloy phase was formed, which was supposed to be the active component of the catalyst. The relatively high yield and excellent quality of carbon nanotubes were explained by the peculiar behavior of this alloy phase [3].

Recently, several papers dealt with the mechanism of nanotube formation [4]. Particularly, the role of the catalyst support and the particle size of the metal have been discussed [5]. The most frequently used catalyst supports were silica, zeolites and alumina. Well-crystallized carbon nanotubes were formed on catalysts supported by these materials [6]. A part of these supports are molecular sieves having sharp pore diameter distribution in molecular dimensions (0.4-1 nm), pore diameter of the others 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 [7].

In this paper we present results on the role of zeotype catalyst support and the state of the metal in the CCVD production of MWNT.

2. EXPERIMENTAL

2.1. Preparation and characterization of catalysts

Zeolites (NaA: Hungalu Co., KL: Union Carbide, NaY: Union Carbide, 13X: Union Carbide) and mesoporous zeolite-like materials (MCM-41, SiMCM-48, AlMCM-48: synthesized in our laboratory [8-9]) were loaded with metal ions using ion exchange, impregnation and isomorphous substitution. After evaporating the solvent, the catalyst sample was dried at 400 K overnight. Catalyst samples prepared by the impregnation method contained 2-5 wt% of Co.

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

Ion exchange of AlMCM-41 in aqueous solution of Co acetate (0.1 mol/dm^3) was the preparation procedure for CoAlMCM-41(ex) catalyst. Ion exchange was performed twice at 343 K for 12 h each time (0.5 mmol metal ion/g silicate). CoMCM-41(iso) sample was prepared by isomorphous substitution of Si for Co

following the description in [10]. Co/AlMCM-41, SiMCM-48 and AlMCM-48 were prepared by impregnation. Calculated amount of Co salt was dissolved in distilled water, which was evaporated slowly under gentle heating.

The composition of the catalyst was checked by X-ray fluorescence (XRF) analysis. The transition metal content was determined by classical analytical methods. The zeolite samples and the MCM materials 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 samples, the pore size distribution was calculated by the Barett-Joyner-Halenda method [11] from the adsorption data.

2.2. Synthesis of carbon nanotubes

The catalytic reaction was carried out in a fix-bed flow reactor in the temperature range of 900-1100 K. The catalyst samples were placed in a quartz boat that was put into a horizontal tube reactor. Before introducing the reactant mixture (10% acetylene 90% N_2, with a flow rate of 300 ml/min) the catalysts were purged by nitrogen stream (300 ml/min) in order to remove water and pretreat the catalyst at 999 K. The reactions were carried out for reaction time of 30 min.

In situ XPS measurements were carried out to clarify the state of cobalt on the supported catalyst and the reaction was conducted in the sample preparation chamber of XPS instrument. [see details in ref. 12]

2.3. Characterization of the product MWNTs

Since the initial weight of catalysts introduced into the reactor was known, we measured the weight increase after the reaction. From these data the total carbon production was determined. For the charaterization of catalyst activity, carbon yield (ratio of carbon deposit and catalyst) calculated as following was used:

Carbon yield = $(m_{after\ reaction} - m_{catalyst}) / m_{catalyst}$ (g/g)

For TEM and HRTEM Philips CM20 and JEOL 200CX were used, respectively. For the preparation of sample holder grids, the glue technique was used described elsewhere in detail [2]. Nominal composition, surface area, pore diameter and activity data of the catalysts are given in Table 1.

Table 1
Characterization of catalyst samples

Sample	Metal content (wt%)	Surface area (m^2g^{-1})	Pore diameter (nm)	Activity (g/g)
Co/A	2	435	0.51	0.03
Co/L	2	216	0.60	0.20
Co/Y	2	632	0.74	0.19
Co/13X	2	615	0.74	0.21
Co/AlMCM-41	5	931	3.4	0.73
CoAlMCM-41(ex)	0.29	931	3.4	0.82
CoMCM-41(iso)	0.01	931	3.4	0.96
Co/SiMCM-48	5	1078	3.1	0.67
Co/AlMCM-48	5	994	3.0	0.71

3. RESULTS

3.1. Formation of MWNTs

There are obvious differences between these catalysts concerning both the quantity and the quality of MWNT formed. Using impregnated zeolite-supported catalysts of pore diameter less than 1 nm, well-graphitized carbon nanotubes could be grown almost independently of the type of the support. Neither surface area nor pore diameter affected significantly the quality and the quantity of carbon nanotubes. For illustration, Fig. 1 shows electron microscopy images of carbon nanotubes grown over various zeolite-supported cobalt catalysts.
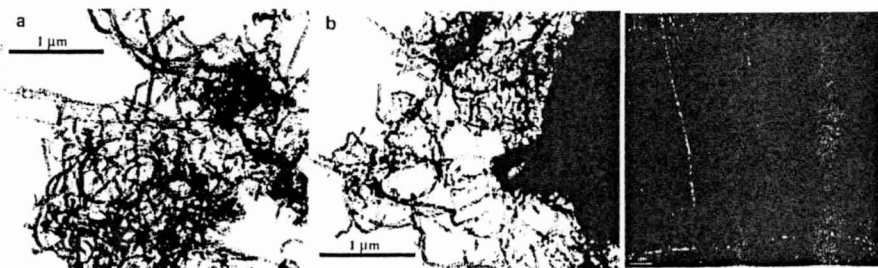

Figure 1. Carbon nanotubes formed on the surface of a) Co/NaY; b) Co/13X catalysts; c) high resolution image of a carbon nanotube.

similar dimension would be able to regulate the inner or the outer diameter of the forming carbon nanotubes. Close scrutiny of our samples (Figs. 2 and 3a) revealed, however, that the pore size of the mesoporous supports and the diameter of carbon nanotubes showed no correlation.
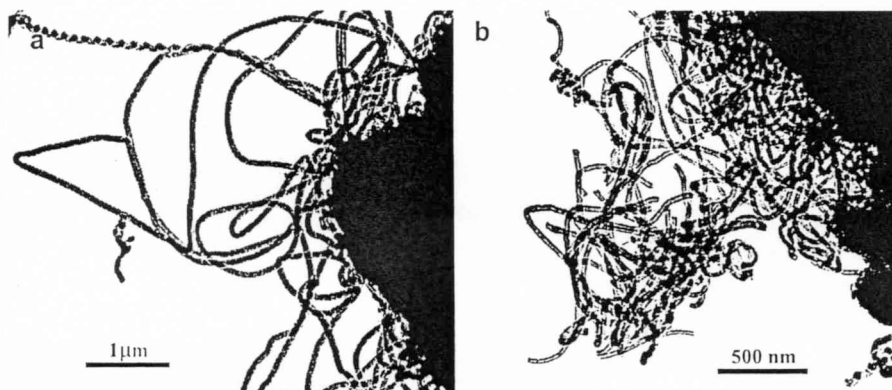

Figure 2. Carbon nanotubes formed on the surface of a) Co/SiMCM-48 and b) Co/AlMCM-48 catalysts.

No nanotube could be detected on CoAlMCM-41(iso) (Fig. 3b) and only a slight indication of nanotube formation is seen on CoMCM-41(ex). Numerous, well-graphitized nanotubes formed on Co/AlMCM-41 (Fig. 3a). It is worth to emphasize here that the samples proved to be inactive in the production of MWNTs were prepared by isomorphous substitution and ion exchange, not by impregnation.

3.1. *In situ* XPS characterization

As far as the reducibility of cobalt ions is concerned detailed *in situ* XPS investigations were carried out. XPS spectra of the catalyst samples were taken under vacuum at both ambient and reaction temperatures, then, measurements were performed in acetylene atmosphere. Significant changes were observed after the sample was kept at 1000 K in acetylene atmosphere for 60 min. In such a strong reducing atmosphere we could detect reduction of cobalt ions.
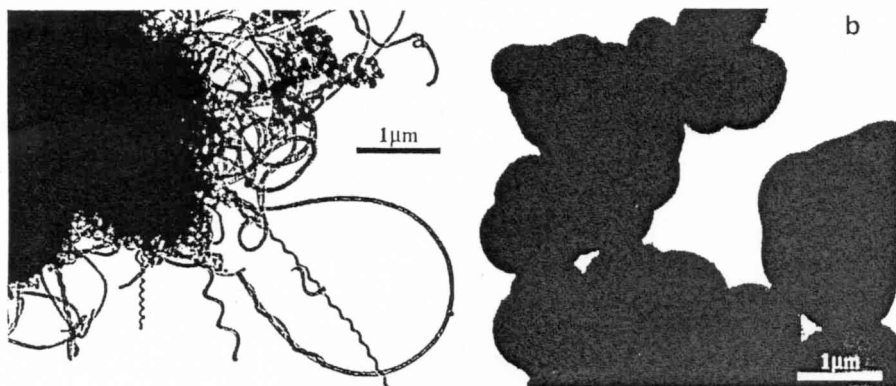
Figure 3. Electron microscopy image of samples a) Co/MCM-41 and b) CoMCM-41(iso) after CCVD.

4. DISCUSSION

Zeolites have a relatively small pore size, typically a few Å. Mesoporous molecular sieves have uniform hexagonal (MCM-41) and cubic (MCM-48) pore systems ranging from 10 Å to more than 100 Å. This significant difference inspired us to test these materials as catalyst support in the formation of carbon nanotubes having similar dimensions.

As it is known from zeolite chemistry, the ion exchange positions of zeolites are situated in their pore system, which is of 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 Si/Al ratio of the framework varies, but its upper limit is around 5 mmol/g dry zeolite. This 5 mmol/g Co^{2+} ion is bound to particular positions in the cage system and is 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 carbon nanotube formation takes place on those metallic 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, the pore size of the zeolite. Similar consideration can be done for the other zeolitic supports applied in our system. Their pore diameter is lower than or equal to that of NaY.

For the MCM structures the situation is similar. Here, MWNT formation was observed neither on CoAlMCM-41(ex) nor on CoMCM-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^{2+} 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.

We proved that cobalt-containing samples prepared by impregnation are good catalysts for the generation of MWNT from acetylene *via* CCVD. The activity differences found for the various supports can be explained by the necessary localization 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 a silica gel has [13]. Interaction between cobalt particles and catalyst support seems to be of significant importance. Catalyst activity may slightly vary with Si/Al ratio. Since carbon yield determined after reaction is only an approximate measure of the synthesis (MWNT content of carbon deposit varies in wide range), quantitative considerations cannot be done.

Concerning the characteristics of zeotype support materials listed in Table 1, no correlation was found between these data and catalytic activity in carbon nanotube formation. Increasing amount of deposited carbon with larger pore diameter is due to stuffing the pores with non-graphitic carbon. This activity is independent of the selectivity of carbon nanotube formation for which exclusively catalyst particles on the outer surface was found to be responsible. Consequently, using mesoporous material as catalyst support, instead of presumable controlling effect, the overwhelming part of carbon deposit is composed of amorphous carbon. No indication was found suggesting that formation of MWNT starts in the pores of MCM type catalysts. Actually, their pore diameter is much smaller than that of the MWNT. From this it follows that only those catalyst particles, which are deposited on the outer surfaces can have a role in the formation of carbon nanotubes.

Our *in situ* ESCA experiments showed that cobalt ions are reduced by the reactant acetylene and we found no indication of any kind of cobalt oxide after treatment the sample at 1000 K.

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