Carbon nanotubes production over Co / silica catalysts

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For the catalytic synthesis of carbon nanotubes having fullerene-like diameters, a detailed description of the catalyst preparation is given. Silica-supported catalyst samples (prepared from Co-acetate solution of different pH) were tested in the decomposition of acetylene. Catalysts with various pretreatments (different calcination temperature, time and atmosphere) were compared in the carbon nanotubes production and characterized by X-ray photoelectron spectroscopy (XPS). The quality and the quantity of the buckytubes were studied by transmission electron microscopy (TEM). As a final conclusion, it is possible that changing the pH of the solution during catalyst preparation allows control of the quality of the carbon nanotubes, namely the amount of turbostratic straight and helical tubes.

Keywords: carbon nanotube, catalytic synthesis, Co-catalyst, silica support

1. Introduction

An “unusual” form of carbon has already been discovered in 1953 on the investigation of carbon deposit in the brickwork of blast furnaces [1]. Since that time many papers have dealt with carbon filaments formed on transition metal catalysts. The prevention of deactivation of catalysts is dominant in the overwhelming majority of these works [2–4]. However, as a result of technological interest, the number of papers dealing with the formation mechanism, the structure, the properties, the possible uses, etc. of these filaments increased greatly [5–14].

The recent discovery of fullerenes, fullerenic onions and hollow turbostratic carbon tubes of nanometer diameter opened a new chapter in carbon chemistry. Because of their unique calculated chemical and physical properties [15–18], speculations about the possible applications of carbon nanotubes have been published [19–21]. For the synthesis of carbon nanotubes several methods have been reported. The arc-discharge method developed for C_{60} synthesis supplied a very surprising result, namely the growth of fullerene tubes was observed on the carbon cathode [22–26]. In this method carbon nanotubes are always grown out of the ends of carbon electrodes of the arc but they have never been found in the soot condensing from the vapour. Maybe this recognition led to the discovery of other nanotube synthesis methods such as plasma decomposition of hydrocarbons [27,28] and co-evaporating catalyst during a carbon arc-discharge [29–33]. Adopting these procedures it became possible to synthesize carbon nanotubes of different dimensions: The length of the tubes could be increased either by the electric field technique or single shell buckytubes could be produced by the catalytic method evaporating cobalt or iron in the system. According to Zhang et al. [34], multiwall nanotubes always have graphitic interlayer distance (0.34 nm) and typically turbostratic structure [35]. Recently, another catalytic process working under relatively mild conditions has been reported for carbon nanotube production [36,37]. Compared with other synthesis methods, the selectivity of this process to carbon nanotubes is significantly higher and, consequently the final product contains much less amorphous carbon [38]. Although many of these results have already come out [39–41], a detailed description of the catalyst preparation has not been published yet.

2. Experimental

Different silica-supported cobalt catalysts have been prepared and tested for the decomposition of acetylene at 700°C.

2.1. Catalyst preparation by pH-controlled ion-adsorption precipitation on silica gel

As a first step, 1.056 g of cobalt salt [$Co(H_3C–CO_2)_2 \cdot 4H_2O$, Riedel-de Haën] were dissolved in 60 ml of distilled water for each sample.

Catalyst preparation methods A, A′ and A″. Six as-made cobalt solutions were set to different pH values. (For checking the pH, Merck “Neutralit” pH-indicator strips were used.) The pH of the original Co-acetate solution was 7.0 and acetic acid or ammonia solution was used to set the pH of the solutions to 4, 5, 6, 8, 9, respectively. Above pH $= 7$ the colour of the solution turned to blue and at pH $= 9$ a slight precipitation was observed.

After this 2.0 g of silica (“SILICA GEL 60”, Merck, particle size: 15–40 μm) were added to each sample and they were let stand under occasional stirring. After two days the pH of the samples was shifted to the lower values. For, e.g., from solution pH = 9 (pH = 8) it became pH = 7 (pH = 6.5). Then the samples were filtered on a Büchner funnel, washed with 2 × 50 ml of distilled water and dried at 100°C. This procedure was followed by calcination in air at 450°C for 4.5 h. After this treatment the colour of the catalyst samples varied from light blue to olive and dark grey with increasing pH. A portion (0.4 g) of each sample was hydrogenated in H_2/N_2 (H_2 flow: 35 ml/min; N_2 flow: 75 ml/min) at 650°C for 8 h (*method A′*). One of the samples was treated in air (instead of hydrogen) under the same conditions (*method A″*).

Some other catalyst samples were also prepared with inversion of different steps, e.g. neutralize the solution just before filtration (method B), the calcination step in air at 450°C was omitted (method B′) or pretreating silica in ammonia solution first (method C).

Catalyst preparation method B. The Co/silica samples were prepared with the following sequence: Co-acetate + water + silica, was let for two days, then ammonia or acetic acid was added in order to set pH to the required value just before filtration. Further treatment of the catalyst samples was the same as in the method A.

Catalyst preparation method B′. The catalyst preparation method B′ was the same as in method B, except for the calcination step – in air at 450°C – which was not performed.

Catalyst preparation method C. The components were added in the sequence: water + silica + ammonia (set pH to 7) + Co-salt, then it was let stand for two days followed by filtration at the end. Further treatment of the catalyst samples was the same as in method A.

2.2. Characterization of the catalyst samples

The cobalt content of the different catalyst samples was determined by titration of the cobalt content in the mother liquors of catalyst preparation with EDTA (J.T. Baker), at pH = 10.5 and using murexide (Vel) as an indicator. Better results (table 1) were obtained by proton-induced X-ray emission (PIXE) of the catalysts, using a Van de Graaff system (High Voltage Engineering N.V.), operating at 2.7 MeV proton beam.

Decomposition of acetylene was studied in a fixed-bed flow reactor (quartz tube of 14 mm in diameter in a Stanton Redcroft horizontal oven; ±0.5°C) at 700°C with a reaction time of 30 min. Each reaction was carried out using the same flow of acetylene (8 ml/min, Alphagas) and nitrogen (75 ml/min, Alphagas) and a catalyst amount of approximately 30 mg. The exact amount of the initial catalyst and the carbon deposit formed during the reaction was determined by weighing and the reproducibility was within 10%. After decomposition of acetylene, the carbon yield was calculated for each reaction as follows:

$$\text{carbon yield } (\%) = 100(m_{\text{tot}} - m_{\text{cat}})/m_{\text{cat}} \,,$$

where m_{cat} is the initial amount of the catalyst (before reaction), m_{tot} is the total weight of the product after reaction.

The nature of the carbon deposit on the catalyst surface was characterized by electron microscopy (SEM: Philips XL 20; TEM: Philips CM 20 and Jeol 200 CX). For sample preparation, the catalyst samples after reaction were glued on Rh–Cu grids. This method makes it possible to examine a representative sample of the product. In contrast, sonicating the material can result in a slight separation of different carbon deposits from the catalyst and is therefore not a good technique for judging the general quality of the sample. The gluing solution was made by suspending 0.5 m of tape (Scotch; 19 mm) in 100 ml of chloroform, then it was filtered.

The XPS measurements were carried out on a spectrometer SCIENTA ESCA 300, using the monochromatized Al K_α radiation ($h\nu = 1486.6$ eV) and equipped with a rotating anode X-ray source. Settings of pass energy 150 eV, slit width 0.8 mm, X-ray power 4.2 kW and take-off angle of 80° were used for spectra in this work.

Table 1
Co contents of the catalysts and carbon yields of acetylene decomposition at 700°C over different Co/silica catalyst samples

pH	Co content of the catalyst (wt%)				Carbon yield (wt% ±10 rel.%)			
	method A		method B		calc. at 450°C (air; 4.5 h)		hydr. at 650°C (H_2/N_2; 8 h)	not calcined
	EDTA	PIXE	EDTA	PIXE	method A	method B	method A′	method B′
4	< 0.1	< 0.01	< 0.1	< 0.01	7	64	15	66
5	< 0.1	< 0.01	< 0.1	< 0.01	9	90	23	87
6	0.5	0.04	< 0.1	< 0.01	51	99	45	112
7	0.9	0.82	< 0.1	0.22	71	90 (88[a])	76	84
8	2.3	1.74	0.5	0.70	74	82	83	97
9	12.5	11.64	3.0	2.66	47	98	65 (58[b])	86

[a] Different way of catalyst preparation (method C).

[b] Calcined 8 h at 650°C in air instead of H_2/N_2 (method A″).

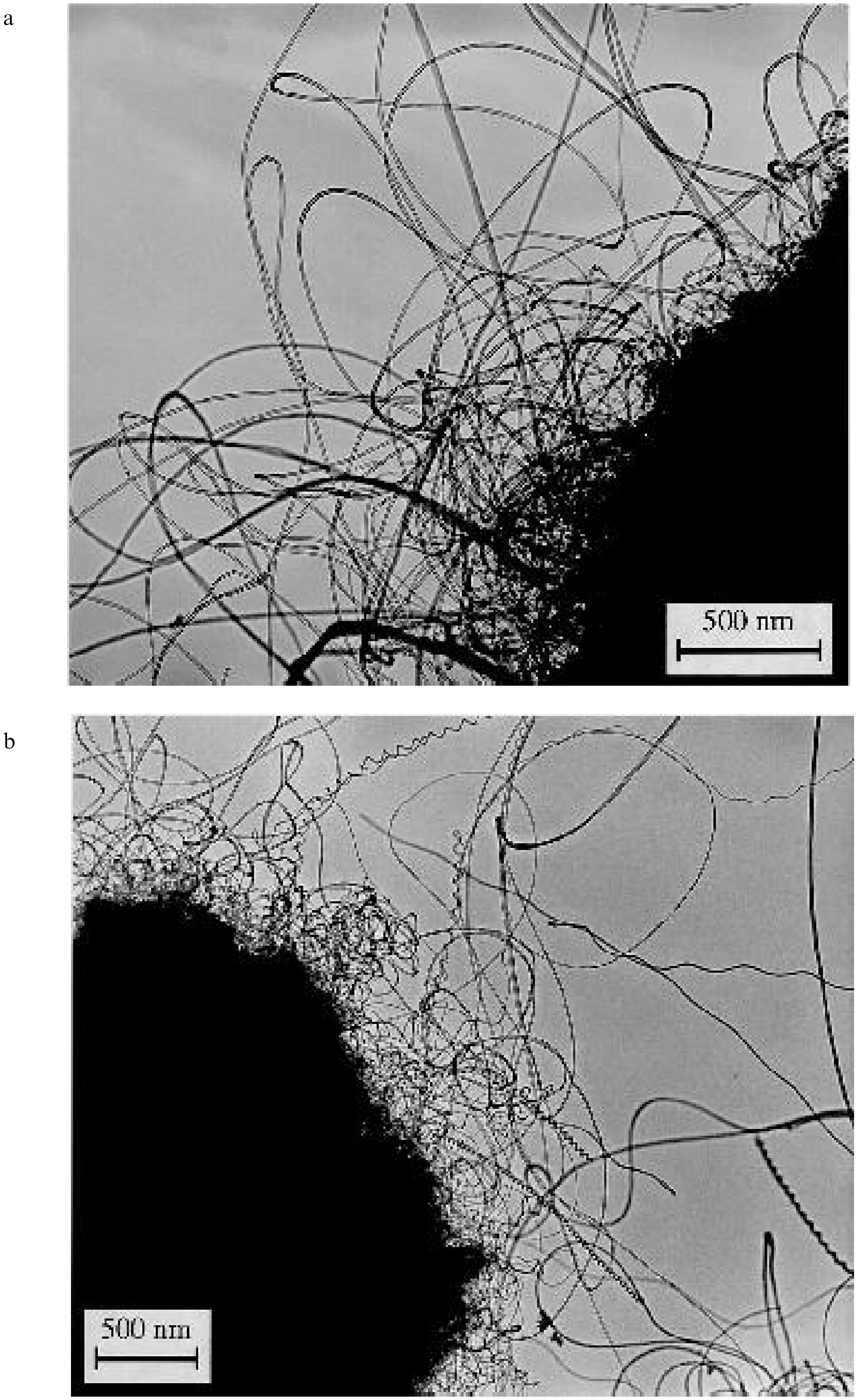

Figure 1. TEM images of carbon nanotubes formed in the decomposition of acetylene at 700°C over Co/silica prepared by method A (pH = 8): (a) and (b) low magnification; (c) high resolution. (Continued on next page.)

3. Results and discussion

Both quantitative and qualitative analysis of carbon formation over different Co/silica catalysts are given in this paper. The cobalt content of the different fresh catalyst samples presented in table 1 was first determined by titration with EDTA and secondly by PIXE with more precision. In the same table, carbon yields of acetylene decomposition over different Co/silica catalyst samples prepared by different methods are also given.

3.1. Using catalyst preparation method A

The highest activity was observed in the presence of catalyst prepared from the Co-acetate solution of pH = 8, both for the original and the hydrogenated samples (methods A and A′ in table 1). It is interesting to remark that according to carbon yield data, there is no significant difference between catalysts prepared from solutions of pH = 7 and pH = 8. Otherwise decreasing or increasing the pH of initial Co-acetate solutions results in a decreasing carbon yield. Making a comparison between the original and the hydrogenated samples (table 1), it can be concluded that the latter ones yield carbon in a somewhat higher amount. This tendency and the carbon yields of the sample calcined at higher temperature for a longer time will be interpreted together with the qualitative observations obtained by electron microscopy.

Concerning the quality of the catalytically obtained carbon deposit (figure 1), a large amount of well-turbostratic carbon nanotubes covered only with a very small

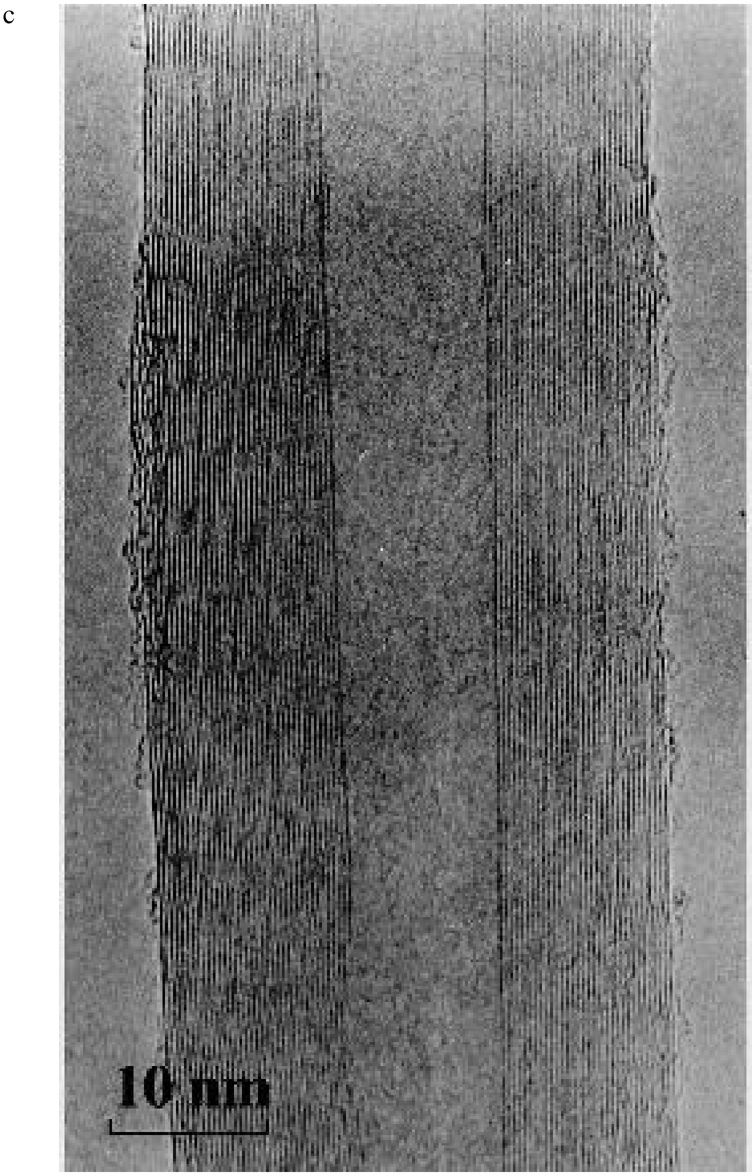

Figure 1. (Continued.)

amount of amorphous carbon (figure 1c) could be observed over the catalyst prepared from a Co-acetate solution of pH = 8 (method A). The dimensions of the carbon nanotubes were quite regular with outer diameters of 20–30 nm and inner diameters of approximately 5–10 nm. The length of the nanotubes was found to be of the order of 10 μm at the end of the reaction of 30 min. Over Co/silica (pH = 8; method A) we could also observe helices in relatively high percentage (figure 1b).

For the catalyst prepared from Co-acetate solution of pH = 9 (method A), the quality of the deposit has been found also very good, similar to the previous one. The only difference observed by electron microscopy was the definitely higher amount of helices, as illustrated on figure 2.

While the activities of the catalysts prepared from solutions of pH 7 and 8 were about the same (table 1), there was a significant difference between the qualities of carbon deposit formed on them. While in the case of samples pH 8 and 9 every catalyst particle was covered by regular carbon nanotubes after the reaction (figures 1 and 2), the composition of the product obtained over the catalyst pH 7 was more heterogeneous. Much fewer particles were covered by well-turbostratic tubes, while the relative amount of irregular tubes and fibers increased considerably.

Observing the catalyst samples prepared from Co-acetate solution of lower pH, the surface was mostly covered by amorphous carbon and fibers. On Co/silica pH 4 only very few soot-like clusters could be observed by electron microscopy. The decreasing amount of carbon deposit at lower pH values (table 1) can be related to the very low cobalt content of the catalysts prepared at acidic pH. In the absence of metal particles, only the homolytic decomposition of carbon occurs, producing amorphous carbon and fibers.

3.2. Using catalyst preparation method A′

On the hydrogenated catalyst samples a definite difference was observed in the quality of carbon deposit, which was especially conspicuous for samples pH 8 and 9. While over the original catalysts almost no amorphous carbon, soot and fibers were found, the amount of these "by-products" was significantly higher on the hydrogenated samples. Figure 3 shows clearly that especially the amount of thick tubes and fibers (over 50 nm in diameter) increased with the hydrogenated Co/silica (method A′). Many encapsulated cobalt particles are also observed on the hydrogenated catalysts [37].

During the catalyst calcination at 450°C thermal decomposition of Co-acetate takes place and gives CoO.

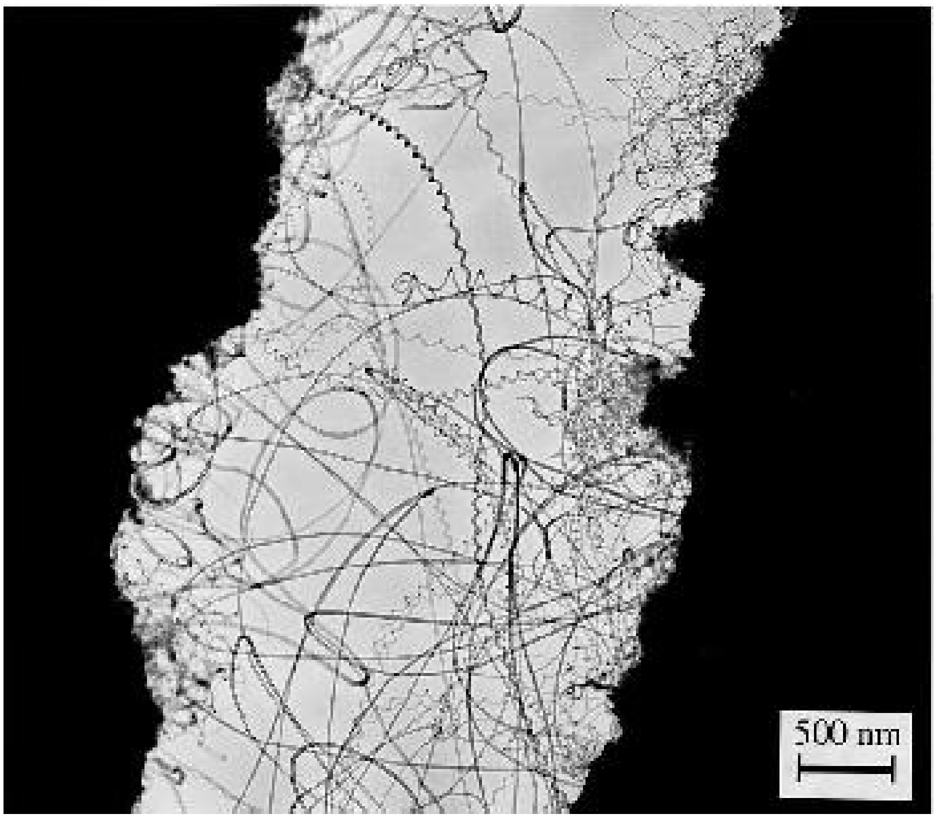

Figure 2. TEM image of helical carbon nanotubes formed in the decomposition of acetylene at 700°C over Co/silica prepared by method A (pH = 9).

Figure 3. TEM image of carbon nanotubes formed in the decomposition of acetylene at 700°C over Co/silica (method A′; pH = 8) reduced by hydrogen before reaction.

As a result of the applied calcination treatment the first series of catalyst samples (method A in table 1) should contain well-dispersed Co-oxide particles on the silica support, mainly in the inner pores. The hydrogenated series (method A′ in table 1) contain cobalt particles in a reduced form. Since the reactant acetylene is able to reduce the catalyst itself under the above-mentioned reaction conditions, reduction alone explains neither the higher catalytic activity leading to a higher carbon yield nor the appearance of amorphous carbon and thick fibers. According to our previous results [36], the diameter of the carbon nanotubes growing on a Co/silica particle depends mainly on the dispersion of the catalyst. During the hydrogenation treatment the catalyst was exposed to high temperature for a long time (compared to the average reaction time of 30 min). As a consequence, cobalt particles had a chance to migrate from the inner pores to the outer surface and to assemble reducing dispersion. These particles outside the pores can be reached by the reactant molecules more easily, which gives an explanation for the higher catalytic activity. At the same time, increasing particle size can result in the higher amount of amorphous carbon and thick tubes obtained over the hydrogenated catalyst samples.

3.3. Using catalyst preparation method A″

In order to prove the effect of the heat treatment, one sample was pre-treated in air at 650°C for 8 h without hydrogenation (method A″ in table 1). The behaviour of this catalyst has been intermediate between the original and the hydrogenated samples considering both carbon yield and the quality of carbon deposit. On the TEM image (figure 4) it can be seen that the quality of the tubes is almost as good as those obtained over Co/silica calcined at 450°C (figures 1 and 2) but more amorphous carbon and thick tubes could be observed on the surface of the support. This shows that beside long calcination at high temperature, hydrogenation also has a disadvantageous effect on the catalyst performance. Since acetylene is able to reduce CoO particles to a required extent and even fortunate if the active sites are being formed in situ at the beginning of acetylene decomposition [42,43]. It means that the most selective catalyst can be obtained during the induction period of the reaction. As a result of the electron microscopic observations it can be concluded that catalyst samples calcined at 450°C for 4.5 h give better results in nanotube production than the other ones which were reduced prior to acetylene reaction.

XPS-measurements also gave some confirmation of this interpretation. While in catalyst samples before reaction, only Co^{2+} could be detected, 20% of the cobalt content was Co^0 in the sample after reaction, as illustrated in figure 5. This data shows clearly that acetylene was indeed able to reduce the catalyst under the reaction conditions but the degree of reduction is far from having

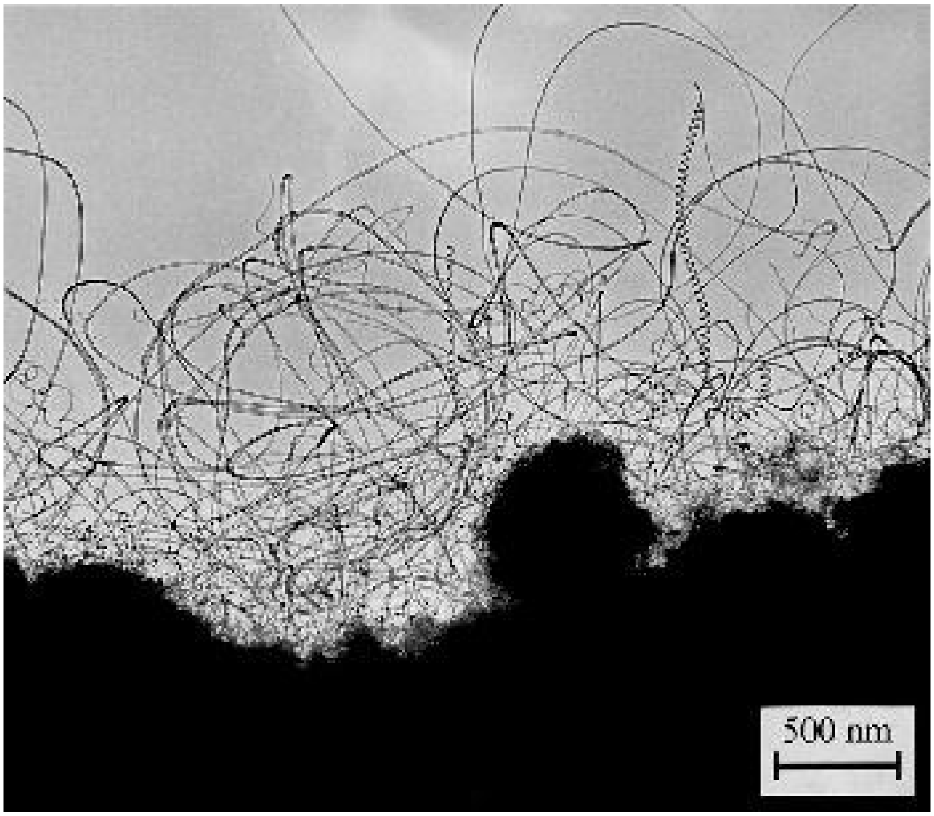

Figure 4. TEM image of carbon nanotubes formed in the decomposition of acetylene at 700°C over Co/silica (method A″; pH = 9) calcined at 650°C for 8 h.

a homogeneous Co-carbide particle, which was supposed to be the active phase previously [44]. Samples reduced by hydrogen contained also some Co^{2+}. Since they were exposed to air before the XPS measurements, oxygen could reoxidize metal particles very easily due to the high dispersion of the samples. For verification of the possible migration and aggregation of Co-particles in the samples which where exposed to high temperature for a longer time, unfortunately no confirmation could be obtained by the XPS measurements.

3.4. Using catalyst preparation method B

Since the catalysts which had pH-value of 6.5–7 before

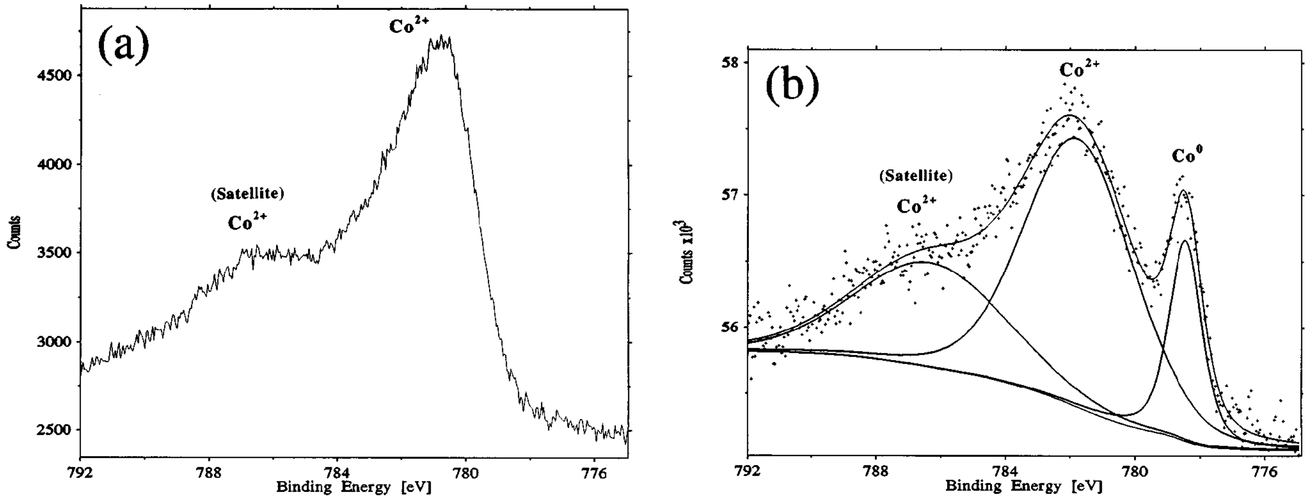

Figure 5. Co $2p_{3/2}$ XPS spectra of catalyst sample Co/silica (pH = 9): (a) before and (b) after reaction with acetylene.

filtration (method A), produced carbon nanotubes of the best quality, in method B the solution was neutralized only before filtration. In the decomposition of acetylene over the samples prepared by this method, not only has the formation of carbon nanotubes with regular structure been observed (figure 6) but the carbon yield was found to be somewhat higher than over those prepared by method A. As far as carbon deposition activity is concerned, the catalysts (method B) had quite constant activity (approximately 87%) throughout all of the studied pH range.

For pH $\leqslant 7$, the percentage of cobalt and then the carbon deposition activity of these catalysts could be governed by pH $= 7$ during the two days treatment, that was constant for the method B. According to the cobalt content of sample pH $= 7$ in method A, the maximum cobalt content of the fresh catalysts made by method B should be approximately 0.8 wt%.

For pH > 7, the percentage of cobalt deposited on the fresh catalyst was found to be 0.7 and 2.7 for pH $= 8$ and pH $= 9$, respectively. The high cobalt content observed for sample pH $= 9$ is due to the precipitation of cobalt hydroxide on the silica support.

Using method B, TEM observations of the deposited carbon revealed that much more nanotubes are formed on the samples set to higher pH before filtration. It behaves as if the carbon deposition activity would depend mainly on the percentage of cobalt remaining on the catalyst after the set of pH and washing steps, while the nanotube formation selectivity would depend exclusively on the degree of basicity of the final cobalt species. Moreover, it is interesting to point out that on certain bad samples – not selective in nanotube formation – it is possible to have a very high carbon yield (deposited in the silica pores) and still no carbon nanotubes at all when observing the samples by TEM. As it concerns mainly the samples pH $= 4$ and pH $= 5$, the cobalt concentrations of wich are very low (< 0.01 wt%), it can be concluded that when there is not enough cobalt on the catalyst surface to form clusters big enough to have the nanotube formation selectivity, the low cobalt content of the catalyst will only contribute to a very high carbon deposition activity. The fact, that the carbon deposition is originated from the cobalt centers is in agreement with the absence of carbon deposition activity for pure silica.

3.5. Using catalyst preparation method B″

Above a certain temperature, the soot and fibers formation activity increases with increasing calcination temperature, as it was observed from comparison of the result of the single sample calcined at 650°C (sample [b] in table 1) to that of the original catalyst calcined at 450°C (method A in table 1). This result suggests a harmful effect of the calcination and/or hydrogenation steps on

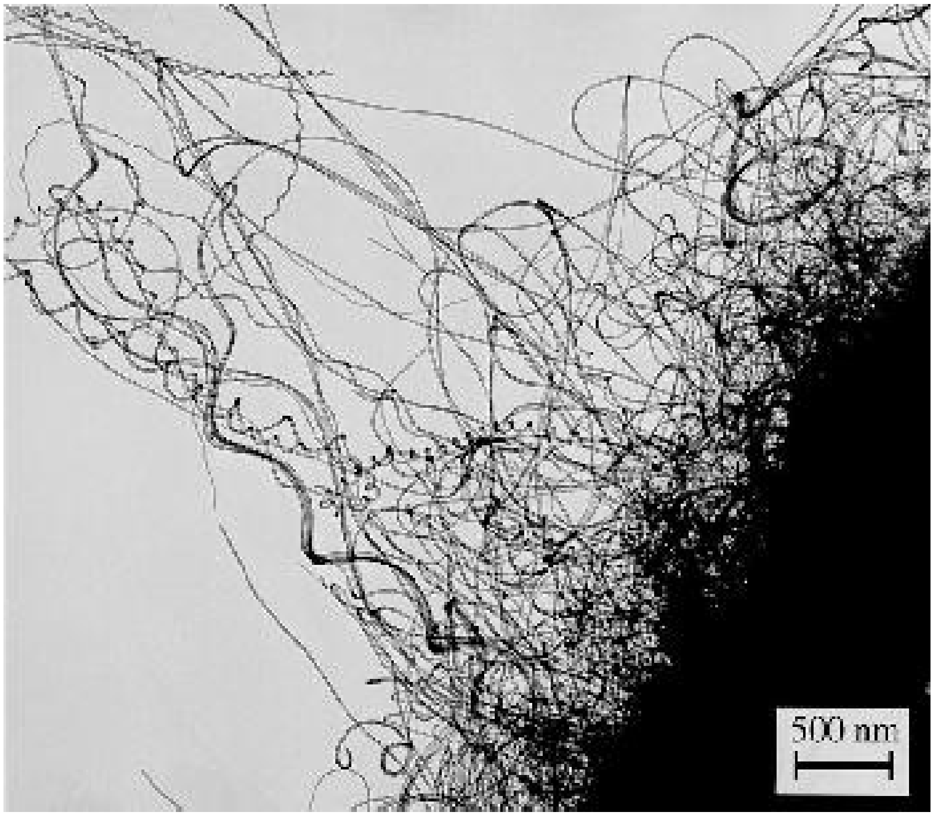

Figure 6. TEM image of carbon nanotubes formed in the decomposition of acetylene at 700°C over Co/silica prepared by method B (pH $= 9$).

the nanotube formation selectivity of the catalyst. Calcination was then omitted in method B′ and the non-calcined catalysts were found at least as active as those calcined at 450°C (method B′ compared to method B in table 1). It means that the short pre-treatment before reaction – at 700°C under N_2 flow for 10 min – is sufficient for the decomposition of Co-acetate on the surface of the silica. In other words: CoO can form in a few minutes at 700°C. Again, fortunate that the active sites for nanotube production are generated in situ by the reaction of the hydrocarbon and the CoO particles during the initiation reaction [37].

3.6. Using catalyst preparation method C

On the basis of observation that during catalyst preparation (method A), interaction between Co-acetate and silica resulted in a shift of pH to the lower values, catalyst samples were prepared in such a way that the components were added in different sequences. To exclude the role of acidic centres of silica support, ammonia was first added to the silica (method C). Catalysts prepared by the latter method also showed high activity with the carbon yield of 88%. According to the TEM observations (figure 7), the carbon nanotubes kept their good quality.

3.7. Generally

The carbon deposition activity reflects the cobalt content of the catalyst. This enhances the effectiveness of method A since it seems to be the pH of the two days treatment that is of importance to determine the cobalt content of the catalyst. Furthermore, using method A, the pH is set constant during all of the catalyst preparation, so that the precipitated cobalt species on the silica support can be more homogeneous in nature and size. Homogeneous in sizes (inner and outer diameters), shapes (straight, coils and helical) and structures (amorphous or turbostratic) are also the carbon nanotubes formed on these catalysts.

4. Conclusions

It is established that Co/silica catalysts which were prepared by method A can produce carbon nanotubes of well-turbostratic structure with high activity. The calcination and/or hydrogenation steps of the catalyst preparation is not necessary and can even have an unfavourable effect on the catalyst performance.

With changing the pH of the original solution (between 7 and 9; method A), the quality of the carbon

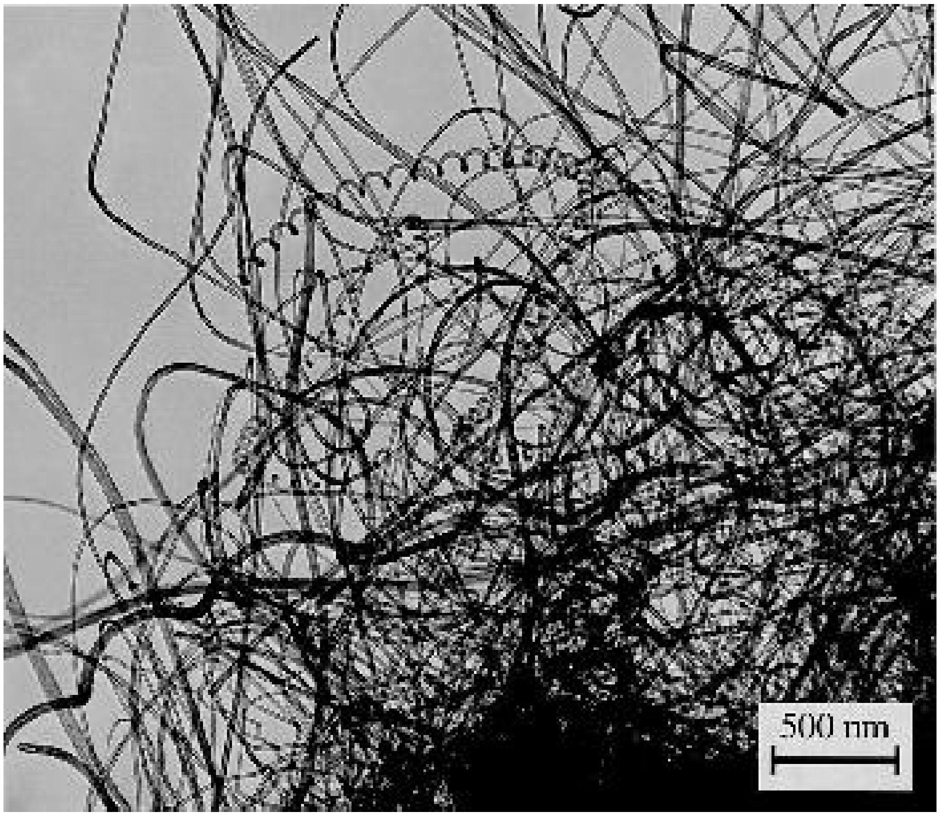

Figure 7. TEM image of carbon nanotubes formed in the decomposition of acetylene at 700°C over Co/silica prepared by method C (pH = 7).

nanotubes, namely the amount of turbostratic straight and helical tubes can be controlled to a certain extent.

It is established that Co/silica catalysts which were only set to the required pH at the final stage of preparation and not calcined (method B′) can also produce carbon nanotubes of well-turbostratic structure with high activity.

It is also very important to remark that reduction of Co-particles by hydrogenation is not favourable for the selectivity. From our results, it can be assumed that acetylene is able to reduce Co-oxide under reaction conditions to the required extent.

With controlling the pH during catalyst preparation and omitting the ‘‘traditional’’ reduction step, a catalyst sample can be obtained which produces carbon nanotubes with high activity and selectivity. The carbon deposition activity seems to be related to the cobalt content of the catalyst while the interesting nanotube formation selectivity seems to be function of the pH of catalyst preparation.

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