

## Formation of carbon nanotubes from the carbon monoxide disproportionation reaction over Co/Al<sub>2</sub>O<sub>3</sub> and Co/SiO<sub>2</sub> catalysts

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The ammonia method has been successfully used for preparing thermostable and well dispersed alumina-supported catalysts with a surface average size of cobalt particle  $D_s = 5.7$  nm. The disproportionation reaction of CO over this Co/Al<sub>2</sub>O<sub>3</sub> catalyst and a similar Co/SiO<sub>2</sub> catalyst leads to the formation of carbon nanotubes demonstrating the same morphology. The amount of nanotubes over Co/Al<sub>2</sub>O<sub>3</sub>, however, is much larger than that obtained over Co/SiO<sub>2</sub>, because of a faster ageing in the latter solid. Similar support effects have already been reported for other catalytic reactions involving carbon oxides.

**Keywords:** carbon nanotubes, CO dismutation, Co/SiO<sub>2</sub> catalyst, Co/Al<sub>2</sub>O<sub>3</sub> catalyst, support effect

### 1. Introduction

Solid carbons issued from the catalytic decomposition of gas-phase reactants demonstrate a great variety of shapes and nanostructures [1,2]. Since the discovery of nanotubes [3], attention has been focused on their possible growth by the catalytic way. The interests of the catalytic route are that these materials can be generated at moderate temperatures in large amounts and low cost and that their structure can be tailored by a control of a number of parameters such as the composition, the temperature of the gas-phase reactants, and the nanomorphology of the catalyst. As a reactant, acetylene has been extensively utilized [4–13] whereas fewer results have been reported for other gases: methane or benzene has led to nanotubes over Fe particles [14–17]. Hydrogen which is a by-product of the hydrocarbon dissociation can be associated with the hydrocarbon. The dismutation reaction of carbon monoxide (in the presence or in the absence of hydrogen or carbon dioxide) into carbon and carbon dioxide is also of special interest [18]: Smalley and co-workers [19] describe the nanotubes growth over molybdenum “preformed catalytic particles” at 1200 °C. At this temperature the calculated yield (related to CO) of the disproportionation reaction is lower than 0.1%. It is probably the reason why experiments reported by other authors were performed at much lower temperature (in the 300–800 °C range). Nolan [20] observed that, depending on the absence or the presence of hydrogen, CO disproportionation over supported Ni, respectively, led to nanotubes (with co-axial cylindrical graphene layers) or to filaments (consisting of stacked graphene con-segments). Consistent results were obtained by Chen et al. [21,22] on a Ni/MgO catalyst. Over a Co/MgO cata-

lyst, Khassin et al. [23,24] studied CO disproportionation in the absence of hydrogen and obtained nanotubes or “egg-shells”, depending on the size of cobalt particles.

The carbon nanostructure is strongly depending on the catalyst characteristics (e.g., cobalt particle size and shape, homogeneity of the size dispersion). It might also depend on the chemical nature of the cobalt support owing to its possible interaction with reaction intermediates and products. As far as we know, support effects related to this reaction have never been investigated in detail. This situation has led us to compare well defined silica- and alumina-supported cobalt catalysts for carbon nanotube preparation.

An inspection of literature data reveals that most of Co/Al<sub>2</sub>O<sub>3</sub> [25–33] and Co/SiO<sub>2</sub> catalysts [34] are prepared by the impregnation technique: this method consists in contacting supports with solutions of cobalt salts such as nitrates. Average diameters of cobalt particles thus obtained, however, are large ( $D_s > 10$  nm) and the size distribution is very far from uniform. Furthermore, the thermostability of these catalysts at 800 K is low. This probably results from the weak interaction between the active phase and the support brought about by this method of preparation. This has led us to explore the potential of the ammonia methods, initially proposed to prepare Ni/SiO<sub>2</sub> catalysts [35] involving a stronger interaction. We have shown elsewhere [34] that thermostable Co/SiO<sub>2</sub> catalysts, fully reduced with homogeneous cobalt particles as small as 3.8 nm in size, could be prepared according to this method. In this study we extend the field of the ammonia method to the preparation of novel Co/Al<sub>2</sub>O<sub>3</sub> catalysts, which demonstrate morphology characteristics very similar to those of their Co/SiO<sub>2</sub> counterparts, and we compare carbon materials obtained on both catalytic solids from CO disproportionation.

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## 2. Experimental

### 2.1. Catalyst preparation

The preparation method of Co/SiO<sub>2</sub> catalysts has been described elsewhere [34]. Let us recall that a solution of cobalt ammine ions was obtained by dissolving 15 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O into 150 ml of water and adding 150 ml of solution of ammonia (28 wt%). While stirring, 10 g of silica (Aerosil 200 from Degussa, specific surface area 200 m<sup>2</sup> g<sup>-1</sup>) were added to the solution. The contact time between the support and the solution was 2 h. The system was centrifugated and washed five times. The solid was dried in a vacuum oven at 352 K for one night. The precursor was reduced in flowing hydrogen (the flow was comprised between 40 and 80 lNTP h<sup>-1</sup> per gram of catalyst) by increasing slowly the temperature at a heating rate of 1.3 K min<sup>-1</sup> for 8 h; the final temperature was 873 K. The weight of catalyst was 0.1 or 0.3 g for characterization and dismutation experiments, respectively.

The alumina-supported catalyst was prepared according to a similar procedure, using the same amounts of water, cobalt nitrate and ammonia solution. As for the Co/SiO<sub>2</sub> precursor preparation, dissolved oxygen was removed by boiling the water and the system was protected from air by an argon blanket. 10 g of  $\gamma$ -alumina from Degussa (non-porous, specific surface area 100 m<sup>2</sup> g<sup>-1</sup>) were added to this solution. The system was stirred continuously for a time which was varied from 3 to 120 min. After centrifugation, the precursor was dried in a vacuum oven at 353 K for one night. After drying, the system was washed and subsequently dried a number of times. Co/Al<sub>2</sub>O<sub>3</sub> precursors were reduced according to the same procedure as that used for Co/SiO<sub>2</sub>. The weight of catalyst was 0.1 or 0.5 g for characterization and dismutation experiments, respectively.

### 2.2. Characterization of reduced catalysts by magnetic measurements

Magnetic measurements give information [34] on the amount of reduced cobalt present in the catalyst by comparing the saturation magnetization per gram of total cobalt in the sample with the specific saturation magnetization of bulk cobalt (the ratio,  $F$ , yields the extent of reduction). When superparamagnetism occurs (no remanence) the metal particle size can be calculated: average diameters can be obtained from  $\sigma$  vs.  $H$  curves at low fields ( $D_1$ ) and  $\sigma$  vs.  $1/H$  curves at high fields ( $D_2$ ), where  $\sigma$  and  $H$  are magnetization and field strength, respectively [36,37]. It has been shown that the surface mean diameter,  $D_s$ , is equal to  $D_s = (D_1 + D_2)/2$ .

When the cobalt particle size is larger than a critical value,  $D_c$ , a remanence  $\sigma_r$  is brought about after saturation at zero field strength. The weight fraction of cobalt particles giving rise to remanence is given by  $\gamma = 2\sigma_r/\sigma_s$ , where  $\sigma_s$  is the saturation magnetization. The critical diameter  $D_c$

has been found to be 15–20 nm [34] for Co/SiO<sub>2</sub> catalysts; it is supposed that this value is the same for Co/Al<sub>2</sub>O<sub>3</sub> catalysts. It is also suggested that, so long as this fraction does not exceed a few percent, mean sizes calculated assuming superparamagnetism are significant. For the case of Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> catalysts a good agreement between diameters obtained from magnetism and transmission electron microscopy was achieved [34]. Magnetic measurements were performed by the Weiss extraction method in an electromagnet providing fields up to 21 kOe (2.1 Tesla) at 300 K [34]. Magnetic experiments were carried out *in situ*, without contacting the reduced sample with air. Results were shown to be little altered by hydrogen outgassing so that most of experiments were carried out under hydrogen.

### 2.3. CO disproportionation and carbon observation

After reduction, the reactor was flushed with He for 6 h and cooled down to 785 K, the temperature of the disproportionation reaction. A mixture of carbon monoxide and carbon dioxide with a ratio making the reaction  $2\text{CO} \rightarrow \text{CO}_2 + \text{C}\downarrow$  thermodynamically possible was then introduced at a flow rate of 8 lNTP h<sup>-1</sup> at atmospheric pressure. Both gases were of high-purity grade (CO: 1 ppm H<sub>2</sub>, 2 ppm hydrocarbons, 3 ppm H<sub>2</sub>O, 5 ppm O<sub>2</sub>; CO<sub>2</sub>: 1 ppm H<sub>2</sub>, 5 ppm hydrocarbons, 7 ppm H<sub>2</sub>O, 10 ppm O<sub>2</sub>). This mixture was used instead of pure CO in order to slow down the catalyst deactivation. The dismutation reaction was performed at 785 K since this temperature has previously been shown to be the most favourable for the tubular growth of carbon [38].

On-line chromatographic analyses of the gaseous mixture above and below the reactor allowed calculation of the disproportionation rate and of the total amount of deposited carbon at different times. The reaction was stopped after times varying from 2 to 17 h by flushing the reactor with helium and quenching it to room temperature. Weighing the amount of carbon after each experiment allowed us to check the chromatographic measurements.

The carbon deposits were first observed under a scanning electron microscope (SEM) which revealed their arrangement over the support. As a second step, samples of carbon were dispersed into ethanol by ultrasonication, deposited on a copper grid covered with an amorphous carbon film and observed by high-resolution transmission electron microscopy (HRTEM) in a Jeol 200 CX microscope.

## 3. Results and discussion

### 3.1. Characterization of reduced Co/Al<sub>2</sub>O<sub>3</sub> catalysts

Figure 1 shows the variation of the ratio  $2\sigma_r/\sigma_s$ , proportional to the fraction of cobalt particles with size larger than 15–20 nm, with the contact time and the number of washings. As can be seen, this fraction decreases, goes

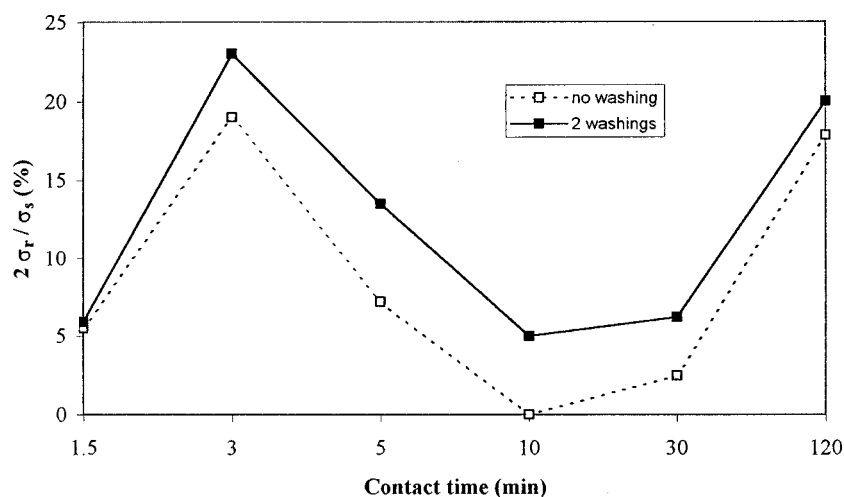


Figure 1. Characterization of reduced  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts by magnetic measurements: weight fraction of cobalt particles with size larger than 15–20 nm ( $2\sigma_r/\sigma_s$ ) as a function of the contact time between the cobalt solution and the alumina support, and of the number of washings of the precursor.

Table 1  
Morphological characteristics of  $\text{Co}/\text{SiO}_2$  and  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts.

Catalyst	BET surface area support ( $\text{m}^2 \text{g}^{-1}$ )	Co loading (wt%)	Reduction temp. (K)	$F^a$ (%)	$\gamma^b$ (%)	Mean diameters (nm)		
						$D_1$	$D_2$	$D_s$
$\text{Co}/\text{SiO}_2$	200	6.1	873	88	0	4.6	6.1	5.4
$\text{Co}/\text{Al}_2\text{O}_3$	100	4.76	873	92	0	4.8	6.7	5.7

<sup>a</sup> Extent of reduction as deduced from magnetic measurements.

<sup>b</sup> Fraction of Co particles with size larger than 15–20 nm as deduced from remanence measurements.

through zero and increases as the contact time increases beyond 3 min. This trend is apparently at variance with that observed for  $\text{Co}/\text{SiO}_2$  precursors [10], where a monotonic increase was observed. It should be noted, however, that in the latter case the contact time was varied over a range in excess of 2 h, whilst in the former case the minimum was observed at a shorter contact time (10 min). Figure 1 also shows that washing is not beneficial to cobalt dispersion. This behaviour is also at variance with that observed for  $\text{Co}/\text{SiO}_2$  precursors for still unexplained reasons. Cobalt loadings and extents of reduction do not vary over a large range with the contact time and the number of washings: they are comprised between 5.7 and 4.5 wt%, 90 and 107%, respectively. From this series of data, it can be concluded that, in terms of Co dispersion and of size homogeneity, the best catalyst is obtained after a contact time of 10 min and without washing. In the following, this solid will be termed standard  $\text{Co}/\text{Al}_2\text{O}_3$  catalyst. Its main features are summarized in table 1, where they can be compared to those of the  $\text{Co}/\text{SiO}_2$  catalyst.

The thermostability of the standard  $\text{Co}/\text{Al}_2\text{O}_3$  catalyst was put to the test by varying the final reduction temperatures without changing the other reduction parameters. The extent of reduction observed at 673, 873 and 1073 K is found to be 56, 92 and 114%, respectively. The occurrence of reduction, as deduced from magnetic measurements, in excess of 100% has been discussed elsewhere [34]: it might result from the presence of a small amount of unreduced

$\text{Co}^{2+}$  ions located at the cobalt–alumina interface, participating in the ferromagnetism of reduced cobalt. This experiment also shows that  $\text{Co}/\text{Al}_2\text{O}_3$  precursors are more reducible than  $\text{Co}/\text{SiO}_2$  precursors prepared by the ammonia method: as a matter of fact, in the latter case no reduction occurs at 673 K.

When the reduction of  $\text{Co}/\text{Al}_2\text{O}_3$  precursors is performed at 1073 K, no remanence is observed and surface average diameters are found to be 5.0, 5.7 and 6.5 nm at 673, 873 and 1073 K, respectively. In other words, the cobalt particle size does not increase to a large extent when the temperature of reduction increases substantially. This behaviour illustrates the high thermostability of  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts prepared by the ammonia method.

### 3.2. Carbon deposition over the catalysts

In the case of  $\text{Co}/\text{Al}_2\text{O}_3$ , a first experiment was performed with an equimolar mixture of CO and  $\text{CO}_2$  which was flowing for 17 h. The variations of the disproportionation rate with time are reported in figure 2. At the end of the experiment, the total amount of carbon was 0.8 g. SEM demonstrated the filamentous nature of the deposit (figure 3) and HRTEM showed the arrangement of carbon layers (figure 4). Further characterization (Raman spectra and diffraction of the synchrotron radiation) of this deposit was performed and will be published [39] in comparison with that of other filamentary carbons.

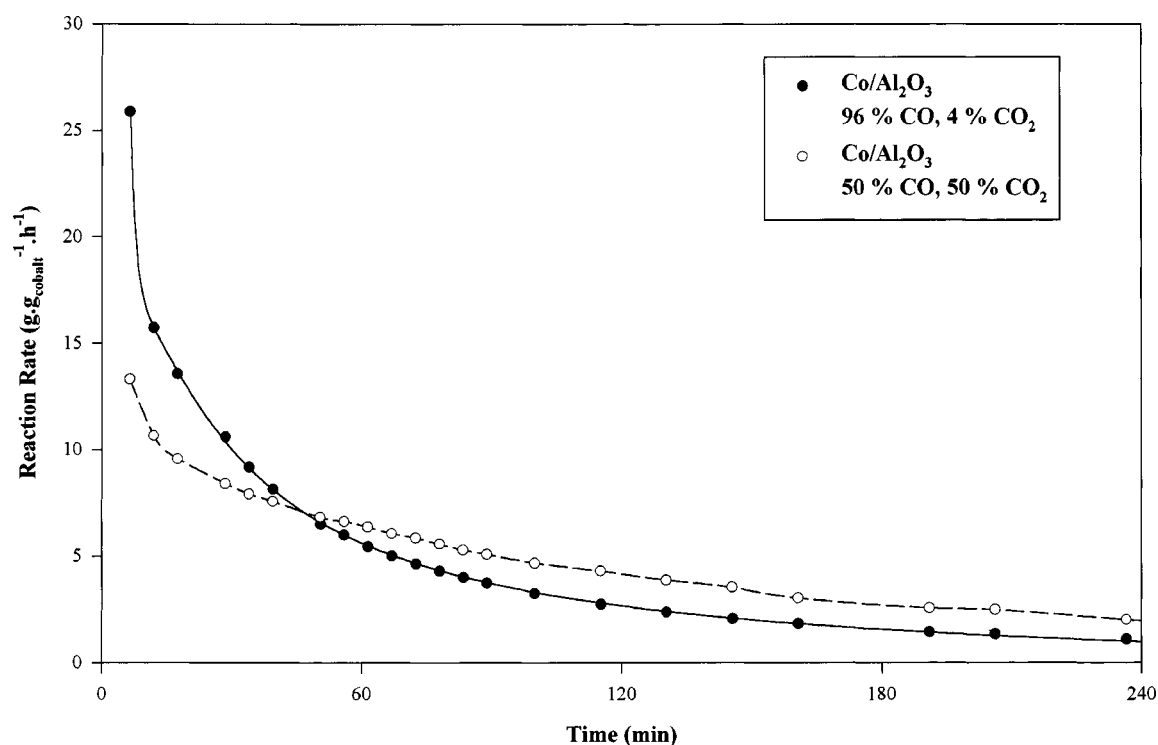


Figure 2. Reaction rate of carbon deposition over Co/Al<sub>2</sub>O<sub>3</sub> from two different CO/CO<sub>2</sub> mixtures.

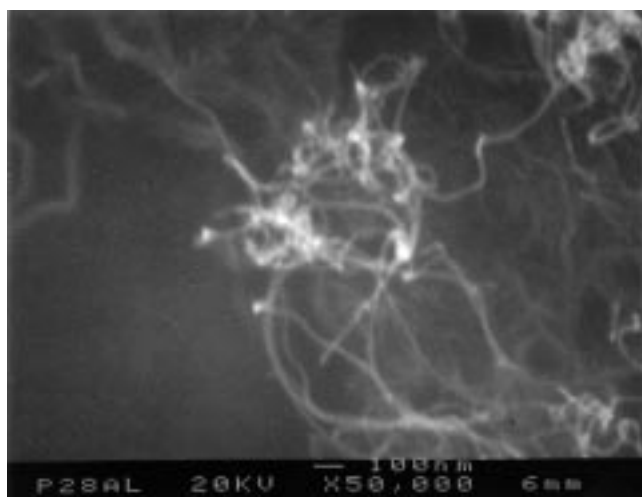


Figure 3. SEM of carbon deposit from equimolar CO/CO<sub>2</sub> mixture over Co/Al<sub>2</sub>O<sub>3</sub>.

In a second experiment, the disproportionation of CO was performed from a 96 mol% CO mixture with CO<sub>2</sub> at the same total flow of 8 lNPT h<sup>-1</sup>. As expected from the composition, the initial rate was higher but the deactivation faster (see figure 2), then the total amount of deposition carbon after the same time (17 h) was only 0.6 g. The carbon had the same appearance as that obtained from the first experiment.

Two tests were performed over silica-supported catalysts, both with the 96 mol% CO mixture. The deposits demonstrate also a nanotubular structure (figures 5 and 6), whereas their amounts were much smaller than over

Co/Al<sub>2</sub>O<sub>3</sub> (around 0.05 g in each experiment). The reason was a poisoning of Co/SiO<sub>2</sub> much faster than that of Co/Al<sub>2</sub>O<sub>3</sub>: the rate of reaction measured after 2 h of reaction over Co/SiO<sub>2</sub> (figure 7) is nearly equal to zero.

Similar support effects have already been reported for the case of other reactions: the rate of the methanation reaction ( $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + 3\text{H}_2\text{O}$ ) over Ni-based catalysts decreases much more rapidly for silica-supported solids whilst Ni/Al<sub>2</sub>O<sub>3</sub> catalysts demonstrate a much more stable activity [40]. Furthermore, the total amount of carbon deposits obtained from chemical analysis after 15 h of reaction varies in the order Al<sub>2</sub>O<sub>3</sub>  $\gg$  SiO<sub>2</sub>, in agreement with the results of this work. The carbon dioxide reforming of methane ( $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ ) over nickel- and ruthenium-based catalysts [41,42] leads to the same situation: a fast ageing of silica-supported materials is observed. This behaviour is attributed to a large residence time of surface carbon intermediates favouring the formation of noxious compounds situated near the active metal surface. Over alumina support the stability is much better. It is speculated that hydroxyl groups of the alumina support could play a role in the detoxication of the metal surface [43]. Interestingly, lanthana has been found to be the best support in terms of catalytic stability for methane reforming [40]. It could be of interest to examine to what extent this observation could be extrapolated to the disproportionation reaction of carbon monoxide. This strongly suggests that the ageing mechanism of these three reactions, which involve carbon oxides transformation, share common steps and intermediates.

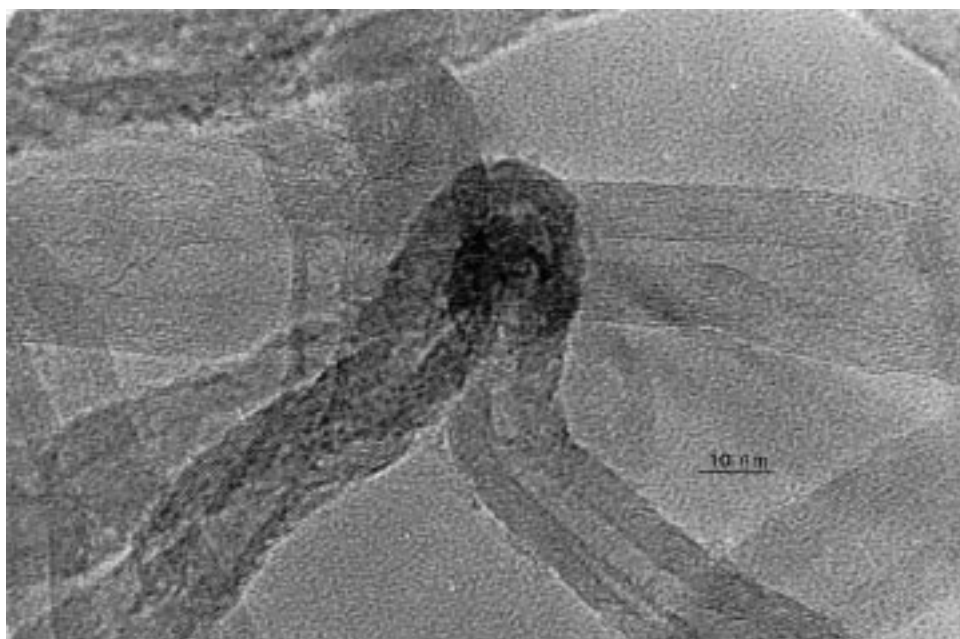


Figure 4. HRTEM of carbon deposit from equimolar CO/CO<sub>2</sub> mixture over Co/Al<sub>2</sub>O<sub>3</sub>.

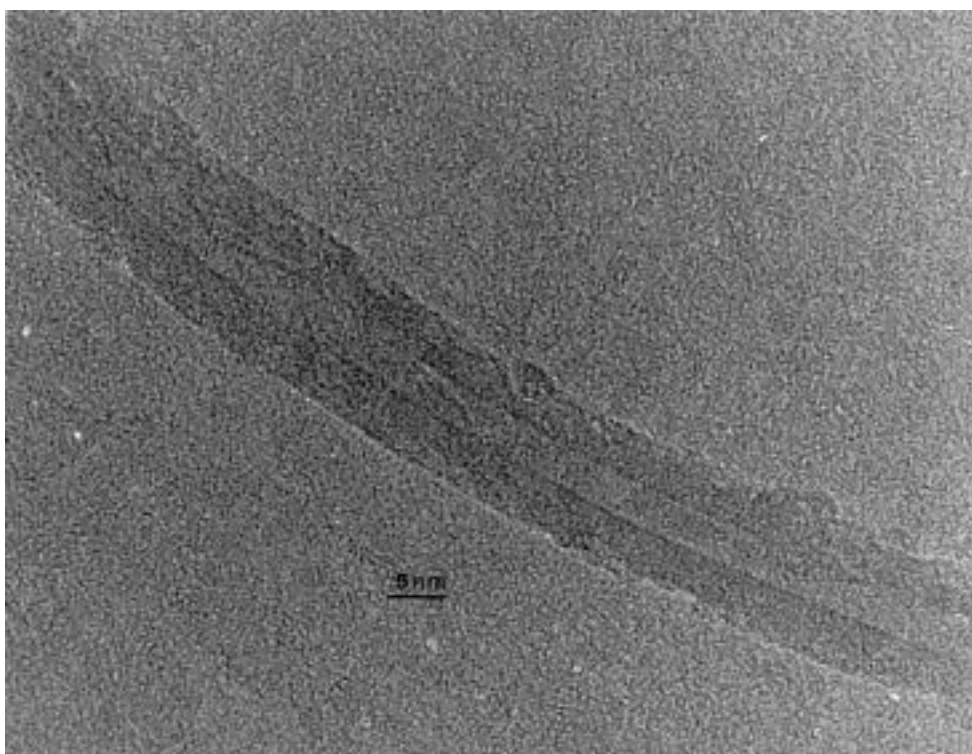


Figure 5. HRTEM deposit from 96 mol% CO mixture over Co/SiO<sub>2</sub>.

#### 4. Conclusion

This study has demonstrated that the ammonia method, initially proposed for preparing stable and well dispersed Ni/SiO<sub>2</sub> catalysts, and successfully extended to the preparation of Co/SiO<sub>2</sub>, can be used for obtaining novel Co/Al<sub>2</sub>O<sub>3</sub> catalysts which demonstrate characteristics similar to those of the Co/SiO<sub>2</sub> catalysts. Silica- and alumina-supported

cobalt catalysts, with comparable metal dispersion, were shown to be active towards the carbon monoxide disproportionation reaction which leads in both cases to the deposition of carbon layers into nanotubular arrangements. Over the alumina support the stability is much better than over silica. This results in a larger amount of carbon nanotube formation (0.8 gram per gram of catalyst). This

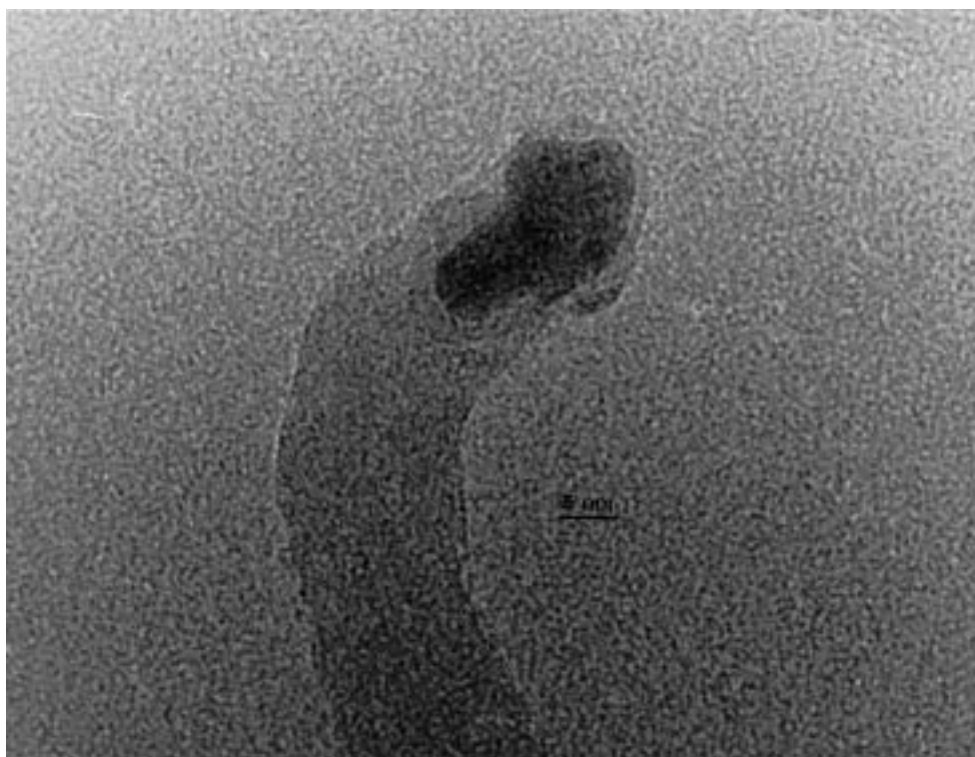


Figure 6. HRTEM deposit from 96 mol% CO mixture over Co/SiO<sub>2</sub>.

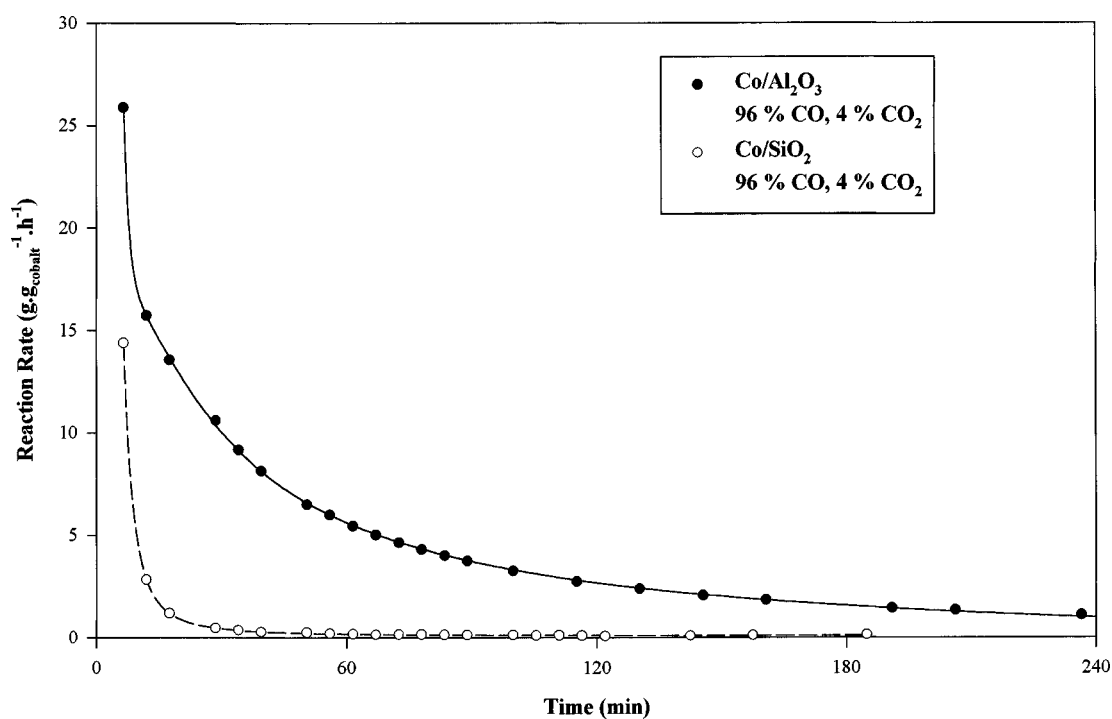


Figure 7. Reaction rates of carbon deposition from 96 mol% CO mixture over Co/Al<sub>2</sub>O<sub>3</sub> and Co/SiO<sub>2</sub>.

support effect has already been observed for other reactions involving carbon oxide transformation over nickel- and ruthenium-based catalysts, suggesting similarities in ageing process and giving clues for the design of new catalysts.

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