

Influence of silica precursor on the cobalt incorporation on mesoporous silica MCM-41 used for the synthesis of single wall carbon nanotubes

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SUMMARY

In this work several silica precursors have been used for synthesis of MCM-41 mesoporous silica, i.e. Cab-O-Sil, sodium silicate and TEOS with incorporation of cobalt in-situ during the synthesis of the molecular sieves. The materials have been characterized by TPR, nitrogen adsorption and XRD. The synthesized catalysts were employed in the chemical vapor deposition of methane at 800 °C for 30 minutes in order to obtain single wall carbon nanotubes. The reaction products were characterized by RAMAN, TGA and TEM. The results show an important effect of synthesis pH and silica precursors on the final selectivity and yield to SWCNTs. Although all the precursors gave way to uniform mesoporous silica type MCM-41, the selectivity to SWCNTs was higher for the catalysts prepared with Cab-O-Sil, followed for the silica prepared with silicate and the catalyst prepared with TEOS shows the lowest activity to SWCNTs. This behavior is related with the TPR profile for each catalyst. It showed that cobalt ions are reduced at higher temperatures for the support prepared with Cab-O-Sil as precursor. The higher is the reduction temperature the inner is the cobalt species into the silica walls, then sinterization process is less feasible, giving way to single wall carbon nanotubes with more uniform diameters and high yield.

Keywords: carbon nanotubes, mesoporous support, MCM-41, catalysis, silica precursor.

1 INTRODUCTION

Many efforts are currently being carried out to develop catalysts with high selectivity and yield to single walled carbon nanotubes (SWCNTs)[1, 2], i.e. carbon nanotubes with uniform and predesigned diameters. Even though parameters as temperature of reaction, pressure and hydrocarbon source can affect this selectivity, the main focus for those proposes has to be the catalysts design in CCVD process[3]. The catalysts consist of an active metal and the support[1, 4]. The mesoporous silica are widely used as a support due to the high surface area, and pore volume[5, 6]; However, these parameters are not enough to ensure an adequate dispersion of metal and small cluster size after reduction process, therefore it is necessary to pay attention to the interaction among the metal species and

silica precursors during the catalysts preparation. The electrostatic and covalent interaction between the metal and silica play an important role in the final properties of the catalysts. If the interaction of cobalt ions with the silica monomers is enhanced during the sol-gel formation, the polymerization of silica over the surfactant micelles will include cobalt species incrustated in the silica layer, this species might be in a tetrahedral way or not depending on the concentration and electrostatic repulsion with the silica.

2 EXPERIMENTAL

Materials: Colloidal silica Cab-O-Sil, tetramethylammonium silicate (TMASiO₂) and tetraethylortosilicate used as a silica sources and cetyltrimethylammonium bromide (CTMABr), ammonium solution was purchased from Sigma-Aldrich. The ion interchange resin Ambersep 900 (OH) was from Alfa-Aesar. Sodium silicate (15-20 wt% SiO₂), acetic acid and cobalt nitrate were from Merck.

Synthesis of Co-MCM-41/Cab-O-Sil: 2.5g of Cab-O-Sil and 10 g of TMASiO₂ were dissolved in 50 mL deionized water and mixed for 30 minutes under magnetic stirring. After that, the cobalt salt at 3.0 wt% in Co was added with two drops of antifoam A[7]. 27.89 g of CTMAOH (Obtained by ion exchange) surfactant solution at 20 wt % were added to the previous solution, then pH was adjusted to 11.5 using acetic acid. The gel was heated in an autoclave at 100 °C for 3 days. After that the gel was filtrated and washed with deionized water and dried in an oven at 80 °C overnight. In order to obtain the mesoporous catalyst, the silica was calcined at 540 °C for 3 hours in air.

Synthesis of Co-MCM-4/sodium silicate: 2.8 g of CTMABr were dissolved in 10 mL of HCl 1.0 M and 15.0 mL of deionized water by means of magnetic stirring. After that, the cobalt precursor was added with Co 3.0 wt % by stirring for 30 minutes. Separately 8.0 g of Sodium silicate were dissolved in 30.0 mL of water, this solution was added drop by drop the former solution. The pH is adjusted to 10.0 using ammonium solution[8]. The hydrothermal

treatment and calcinations were carried out with the same procedure described before.

Synthesis of Co-MCM-41/TEOS: 2.8 g of CTMABr were dissolved in 60 mL of deionized water with magnetic stirring. After that, 8.0 mL of ammonium solution (28-30 % wt) were added. The cobalt precursor was introduced with Co 3.0 wt % by stirring for 30 minutes. Five grams of TEOS were added drop by drop to the former solution adjusting the final pH to 11.5 with ammonium solution[9]. The same hydrothermal and calcinations treatment were used.

Previous studies made in our research group and by other researchers showed that the selected pH for each synthesis gave way to the mesoporous silica MCM-41 with structural regularity and good metal incorporation[10].

Carbon nanotubes synthesis: Two hundred mg of each catalyst were placed in a quartz tube with a fritted disc of 25x5 mm using a vertical oven at 700 °C for 30 minutes in flowing hydrogen and nitrogen mixture of 50:150 sccm respectively at 1 atm. After reduction, the hydrogen is displaced with nitrogen and the carbon nanotubes were synthesized by conversion at 800 °C for 30 minutes with methane and nitrogen mixture 50:150 sccm. The oven is cooled in a nitrogen flow and the material is recovered. The Raman spectra of nanotubes were recorded in a Horiba Laser Raman Spectrophotometer model LabRAM HR with an excitation radiation at 736 cm⁻¹.

CHARACTERIZATION

The nitrogen adsorption-desorption studies were carried out at -196 °C in a Micromeritics ASAP 2010 to examine the mesoporous properties of the catalysts. The catalysts were preheated at 250 °C for 2 hours in vacuum.

The X-ray analyses were performed at room temperature in a Siemens D5000 equipped with a Cu-K α source ($\lambda=1.54\text{\AA}$), with a 0.048 step.

The thermogravimetric analyses were carried out in air from room temperature up to 800 °C at 10 °C/minute.

The reduction temperature analyses were made in an AutoChem II 2920 Micromeritic with TCD detector. Fifty milligrams of each catalyst are preheated up to 250 °C for 1 h in argon flow in order to eliminate any absorbed gas. The catalyst is heated again in a flow of 5% of hydrogen in argon from room temperature up to 1000 °C and hold at this temperature for 1h more in order to ensure the complete cobalt reduction.

3 RESULTS AND DISCUSSIONS

3.1 Catalyst characterization

Figure 1 shows the nitrogen adsorption isotherms for all the catalysts employed in the study. All the catalyst show a defined mesoporous adsorption profiles with isotherm type IV with large surface area ranging from 970 to 990 m²g⁻¹ determined with BET model, and BJH pore size distribution with uniform range from 2.6-2.7 nm for all the samples.

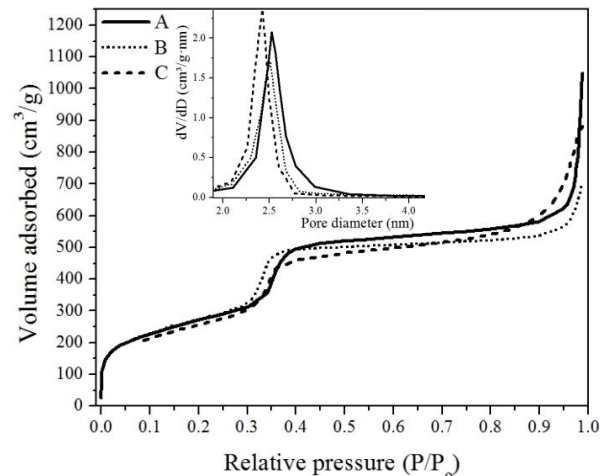


Figure 1. Adsorption isotherm of nitrogen at 77 K for the catalyst Co-MCM-41 prepared using Cab-O-Sil (A) sodium silicate (B) and TEOS (C) as precursors.

Silica precursor	BET area (m ² /g)	PD (nm)	a ₀ (nm)	WT (nm)
TEOS	990	2.43	4.91	2.45
Sodium silicate	975	2.29	5.21	2.54
Cab-O-Sil	978	2.53	4.50	1.84

Table 1. XRD and nitrogen physisorption summary. WT = wall thickness; PD = Pore diameter; a₀ = Cell parameter

As it is summarized in table 1, there are not significant differences among the surface areas for all the catalysts, but catalyst synthesized by using Cab-O-Sil shows the higher pore diameter distribution and textural porosity.

X-ray diffraction experiments show diffractograms with a typical profiles corresponding to the reflections (100), (110) y (200) for a MCM-41 silica structure (Figure 2). The incorporation of the cobalt into the silica walls has not a significant effect in the structural regularity in relation to the pure silica. However, catalysts prepare using TEOS as precursor showed the highest structural ordering due to the reflection at the plane (210) and higher intensity in the diffractogram. The wall thicknesses for the mesoporous catalysts were determined as the differences among the cell parameter (a₀) from de XDR results and BJH pore size distribution. As a result, the catalyst prepared using sodium silicate as precursor has the biggest wall thickness, which could be related to the pH synthesis. A reduction in the pH synthesis promotes the polycondensation of silica species.

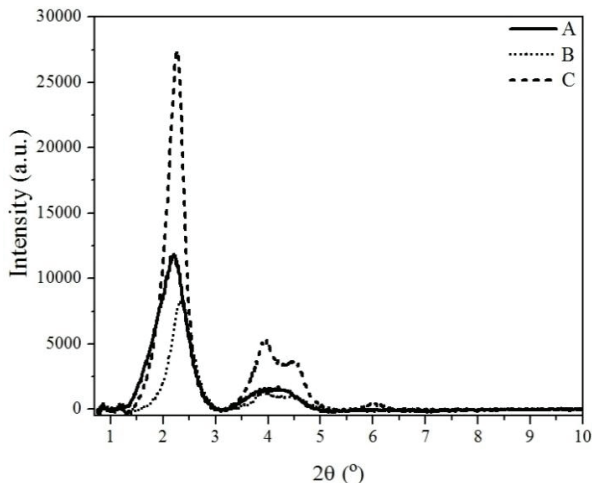


Figure 3. Diffractograms for catalysts of Co-MCM-41 prepared using Cab-O-Sil (A), Sodium silicate (B) and TEOS (C) as precursors.

The temperature programmed reduction (TPR) profiles are shown in figure 3. According to the TPR profiles, the catalyst prepared with sodium silicate as precursor shows the highest reduction temperature which could be related with his large wall thickness, in this case cobalt ions can be in an inner place far from the surface, for that reason more temperature is required to promote the reduction and migration of cobalt clusters. In the catalyst prepared with TEOS as silica precursor more heterogeneous species are on the silica with cobalt outside the walls as it is shown by the lower reduction peak about 500 °C. According to the TPR, the catalyst prepared with Cab-O-Sil shows the most homogeneous distribution of cobalt on the silica walls with a maximum temperature reduction at 750 °C.

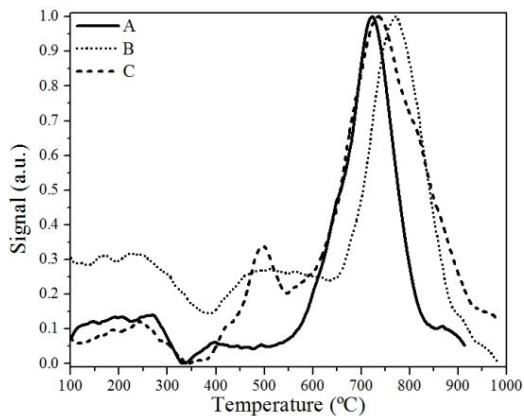


Figure 3. TPR profile for the catalyst Co-MCM-41 prepared using Cab-O-Sil (A) sodium silicate (B) and TEOS (C) as precursors.

During the reduction pretreatment in the carbon nanotubes synthesis the catalyst is heated below the maximum reduction temperature, thus the sintering process is not completed because the cobalt atoms that leave the silica

wall will stay anchored with the cobalt cations that remain into the silica wall by electrostatic interaction[11].

2.1 Catalysts performance

Figure 4 and 5 show the Raman spectra of the SWNT growth on the different catalysts. The three most important signals in the spectra are the radial breathing mode (RBM) that gives information about the tubes diameter distribution, and the D band at about 1350 cm^{-1} that is related with the presence of amorphous carbon and structural disorder of the graphite sheet. The G band about 1570 cm^{-1} is related to the graphite sheet order thus the relative intensity D/G gives information about the order of the SWNT[12], i.e. the lower the ratio D/G the highest is the order in the SWNT structure. According to the RBM the single carbon nanotubes obtained have diameters from 0.8 up to 1.5 nm.

In our results it is clear that the precursor plays an important role in the selectivity to the formation of SWNT. The catalyst prepared with Cab-O-Sil as precursor showed the highest selectivity to single wall carbon nanotubes compared to the others supports prepared with sodium silicate and TEOS as precursors, despite of the highest structural regularity the catalyst prepared using TEOS precursor, for the last case the deposition of SWNT was only 1.2 wt% according to the thermogravimetric analysis (TGA). On the other hand sodium silicate gave the most disordered carbon nanotubes in all the samples due to his highest D/G intensities ratio as it is shown in figure 4. This catalyst gave only 1.6 wt% of carbon deposition, showing low selectivity to SWCNTs, This effect could be related to sodium effect on the cobalt incorporation. Some studies have demonstrated that the presence of sodium during the metal incorporation could displace metal cations to the silica surface.

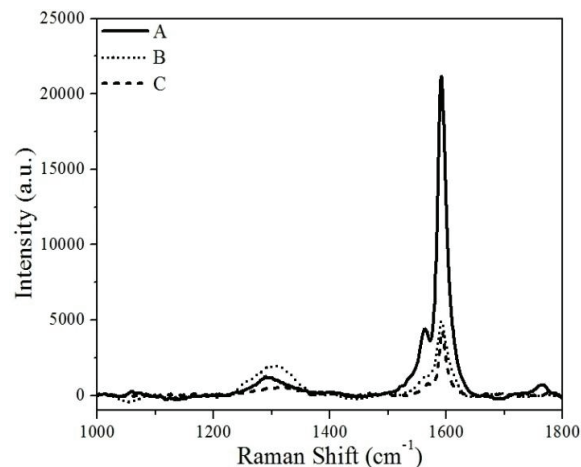


Figure 4. RAMAN spectra for D and G bands of the carbon synthesized on Co-MCM-41 prepared using Cab-O-Sil (A) sodium silicate (B) and TEOS (C) as precursors.

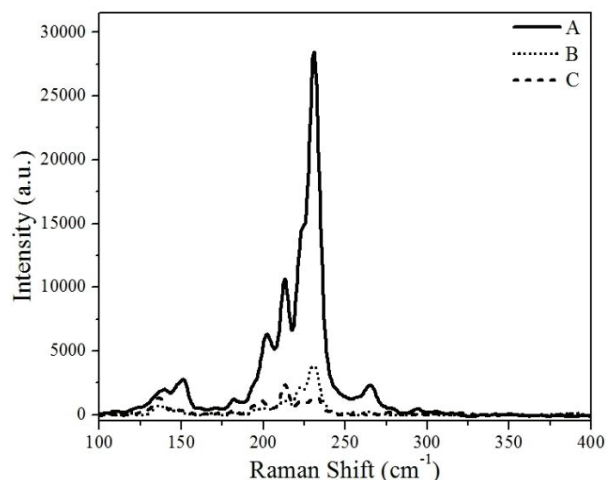


Figure 5. RAMAN spectra for the RBM region of the carbon synthesized on Co-MCM-41 prepared using Cab-O-Sil (A) sodium silicate (B) and TEOS (C) as precursors.

The Cab-O-Sil gave the highest selectivity and deposition, about 3.8 wt% under the reaction conditions. Even when all the samples have almost the same physical properties, with almost the same surface area and pore distribution, the performance is quite different for all the catalysts prepared with the precursors, therefore is not only important a high surface area and uniform pore size distribution, but also the interaction between the silica and cobalt precursors.

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REFERENCES

- [1] G. L. Haller, "New catalytic concepts from new materials: understanding catalysis from a fundamental perspective, past, present, and future", *Journal of Catalysis*, 216, 12-22, 2003.
- [2] S. Lim, et al., "Improved synthesis of highly ordered Co-MCM-41", *Microporous and Mesoporous Materials*, 101, 200-06, 2007.
- [3] J. E. Herrera, et al., "Relationship between the Structure/Composition of Co-Mo Catalysts and Their Ability to Produce Single-Walled Carbon Nanotubes by CO Disproportionation", *Journal of Catalysis*, 204, 129-45, 2001.
- [4] A.-C. Dupuis, "The catalyst in the CCVD of carbon nanotubes--a review", *Progress in Materials Science*, 50, 929-61, 2005.
- [5] J. Liu, et al., "Pore size control of mesoporous silicas from mixtures of sodium silicate and TEOS", *Microporous and Mesoporous Materials* 106, 62-67, 2007.
- [6] L. F. Giraldo, et al., "Mesoporous Silica Applications", *Macromol. Symp.*, 258, 129-41, 2007.
- [7] Y. Chen, et al., "Synthesis of uniform diameter single-wall carbon nanotubes in Co-MCM-41: effects of the catalyst prereduction and nanotube growth temperatures", *Journal of Catalysis*, 225, 453-65, 2004.
- [8] L. F. Giraldo; M. Echeverri, and B. L. López, "Reinforcement of Polyamide 6 with Nanoparticles", *Macromol. Symp.*, 258, 119-28, 2007.
- [9] M. Grün, et al., "Novel pathways for the preparation of mesoporous MCM-41 materials: control of porosity and morphology", *Microporous and Mesoporous Materials*, 27, 207-16, 1999.
- [10] S. Lim, et al., "The effect of synthesis solution pH on the physicochemical properties of Co substituted MCM-41", *Topics in Catalysis*, 34, 2005.
- [11] S. Lim, et al., "Evidence for anchoring and partial occlusion of metallic clusters on the pore walls of MCM-41 and effect on the stability of the metallic clusters", *Catalysis Today*, 123, 122-32, 2007.
- [12] M. S. Dresselhaus, et al., "Raman spectroscopy of carbon nanotubes", *Physics Reports*, 409, 47-99, 2005.