# Synthesis of carbon nanotubes by acetylene decomposition in MCM-41 and SBA-15 materials modified with Ni, Fe & Co for $H_2$ adsorption

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## OBJECTIVES AND NOVELTY

The severe pollution problems in urban areas due to the burning of fossil fuels and greenhouse gases, in particular the Metropolitan Zone of the Valley of Mexico, affect the population, the ecosystem and the economy. Recently, higher energy consumption, the decline of conventional reserves and the dramatic increase in the price of gasoline, have activated research to find new sources of energy. Hydrogen is an ideal fuel: it is abundant, renewable and clean combustion (by producing only water vapor as a byproduct, it is environmentally friendly). In addition, this gas has three times more heat energy per unit mass than other fuels such as gasoline, and even better than biofuels. Although rapid progress has been made in the methods of production, its use is limited, since the main concern is the efficient storage and transport of this highly flammable gas. The $H_2$ storage methods are high-pressure tanks, cryogenic liquefaction and adsorption in solid materials. Among these, adsorption in solid materials is the safest and most efficient. The adsorption capacity of $H_2$ has been studied on complex and metal hydrides, zeolites, carbon materials and in metal-organic networks (MOF's). Therefore, the main objective of this work was to synthesize carbon nanotubes (CNT's) for the adsorption and storage of $H_2$ from mesoporous supports MCM-41 and SBA-15, modified with Ni, Fe and Co at different concentrations.

The mesoporous materials MCM-41 and SBA-15 were obtained by direct synthesis and impregnation, MCM-41 with an extremely low surfactant concentration, while in SBA-15 the pH was adjusted by approximation, the first one was obtained at 30 °C in basic medium and the second at 95 °C in acidic medium. Both were modified with Fe, Ni and Co (Si / Metal = 10, 20 and 50). Carbon nanotubes (CNTs) were synthesized by the chemical vapor deposition (CVD) method using as support the previously synthesized and calcined mesoporous materials, and as a source of acetylene and toluene carbon. All materials were characterized by different techniques: XRD, HRTM, SEM, UV-Vis, Raman and fisisorción of $N_2$ and $H_2$ (BET and BJH).

## RESULTS

Low-angle DRX patterns showed that the highly ordered hexagonal structure was obtained in materials MCM-41 and SBA-15 synthesized directly (Figure 1); calcination did not affect these patterns. Microscopy images (HRTEM and SEM) show that ordered one-dimensional channels constitute the structure of the same materials and the morphology of both is well defined with characteristic shapes for each of them (Figure 2).

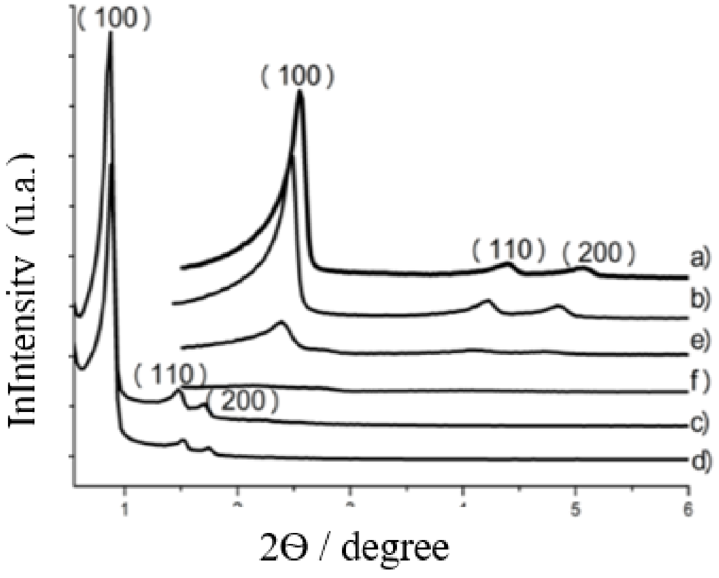

**Figure 1.** XRD patterns of calcined mesoporous materials: a) MCM-41, b) FeM-CM-41(50), c) SBA-15, d) FeSBA-15(50), e) FeMCM-41(20) and f) FeMCM-41(10).

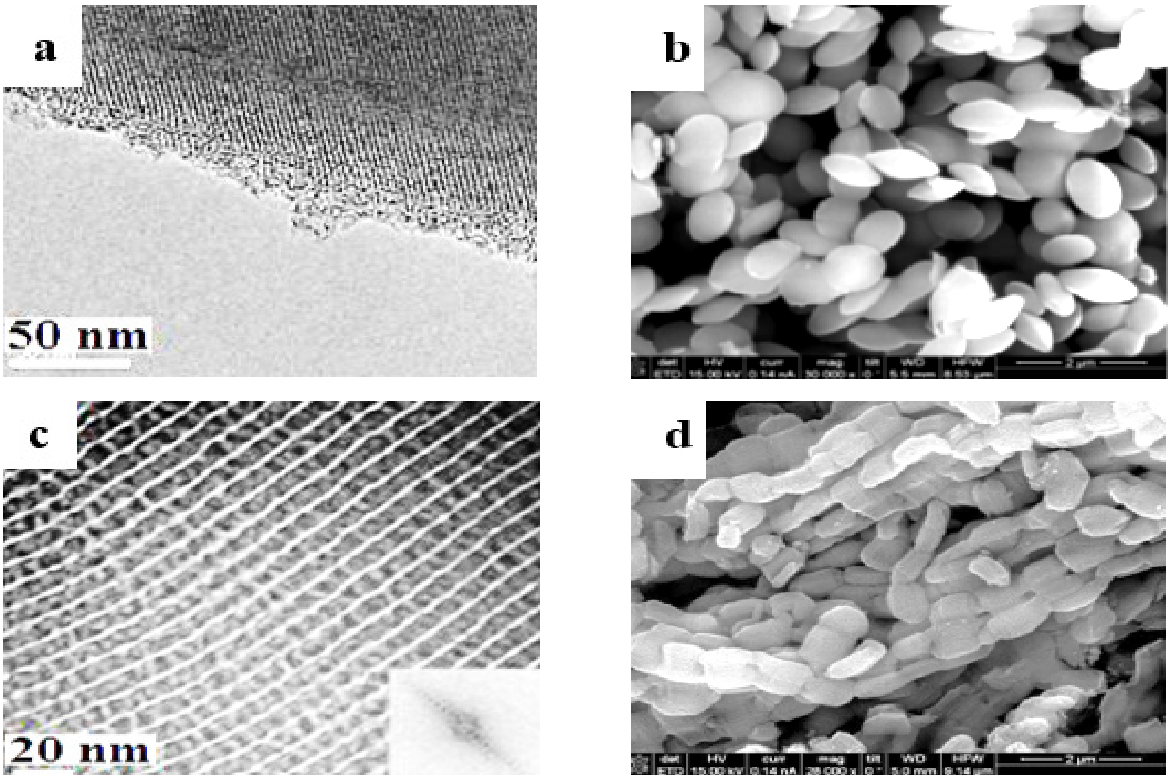

**Figure 2.** HRTEM images for a) MCM-41 and c) SBA-15. SEM images for b) MCM-41 and d) SBA-15.

The adsorption isotherms of $N_2$ (-196 °C) showed that the materials have high specific areas (> 1000 m$^2$g$^{-1}$ for MCM-41 and 500 m$^2$g$^{-1}$ for SBA-15). This may be because the SBA-15 phase has thicker walls, (~ twice as thick (3 nm). MCM-41 materials presented a very narrow hysteresis loop, type H4. Meanwhile, type materials SBA-15 have a unimodal pore distribution and the hysteresis loop is wider (H1) attributed to filling of uniform mesopores and cylindrical geometry. The synthesis of MCM-41 materials was optimized, the best hexagonal structures were obtained for those materials in which high concentration $NH_4OH$ was used, added at the beginning of the synthesis, which conditioned the obtaining of a crystalline phase.

Carbon nanotubes (CNTs) were synthesized using the pristine MCM-41 and SBA-15 materials as support as modified by Ni, Fe and Co using the CVD method, using different carbon sources, once obtained they were purified with strong acids and subsequently calcined. Raman spectra showed the two corresponding typical bands, G and D of carbon. The first (1600 cm$^{-1}$) indicates the formation of the crystalline graphite phase. The second (1300 cm$^{-1}$) the presence of amorphous carbon that causes structural defects. In addition, in the case of the presence of the G´ band, it was observed in the materials that showed a long-range order.

The adsorption of $H_2$ was carried out in both the MCM-41 and SBA-15 materials, as well as in the CNT's synthesized in the different materials modified with Ni, Co and Fe. Table 1 shows the best results.

| **Muestra** | NT-CoMCM41 (8%)<br>Impregnation | NT-CoMCM41 (20)<br>Direct synthesis | NT-CoSBA15 (8%)<br>Impregnation | NT-CoSBA15 (20)<br>Direct synthesis |
|---|---|---|---|---|
| **$H_2$ cm$^3$** | 27.98 | 47.94 | 66.27 | 40.29 |
| **Muestra** | NT-FeMCM41 (8%)<br>Impregnation | NT-FeMCM41 (20)<br>Direct synthesis | NT-FeSBA15 (8%)<br>Impregnación | NT-FeSBA15 (20)<br>Direct synthesis |
| **$H_2$ cm$^3$** | 50.86 | **137.68** | **407.33** | 55.34 |
| **Muestra** | NT-NiMCM41 (8%)<br>Impregnation | NT-NiMCM41 (20)<br>Direct synthesis | NT-NiSBA15 (8%)<br>Impregnation | NT-NiSBA15 (20)<br>Direct synthesis |
| **$H_2$ cm$^3$** | 27.10 | 85.70 | 64.66 | 101.73 |

**Table 1.** Maximum $H_2$ adsorption in the CNT's synthesized in the Metal-Modified Materials.

## CONCLUSIONS

MCM-41 mesoporous materials synthesized and modified with Fe, Ni and Co directly, showed by DRX a highly ordered hexagonal structure; the addition at the beginning of the synthesis of high concentration $NH_4OH$ conditioned the obtaining of a crystalline phase. In addition, it was confirmed that it is feasible to synthesize them at a low concentration of surfactant and at a low temperature (close to the environment) with moderate inclusion of metal. Thus, the parameters that influence the synthesis are the control of the temperature and the pH, the size of the agitator, the speed and the maturation time.

SBA-15 materials were normally synthesized in extremely acidic pH (pH <1), so that in the modified modifications with metals by direct route, adjustment and control of the pH is required. On the contrary, in the impregnation modification, the best option to incorporate the metal is by using metallic solutions in ethanol, which affects the structure to a lesser extent. However, subsequent calcination may have an adverse effect on the structure, but even when the amount of metal (4% to 8%) was increased, the hexagonal phase in both types of materials remained.

Although MCM-41 materials have a greater specific area than SBA-15, these modified with iron, showed greater adsorption capacity, wall diameters and thicknesses than those of MCM-41, therefore they are more stable. The adsorption isotherms of $H_2$ showed that the inclusion of iron in the materials increases the adsorption capacity of $H_2$. It is observed that a higher proportion of iron improves adsorption (FeMCM-41: Si / Fe = 20), slightly above FeSBA-15 (50).

The synthesis of CNT's was carried out under different conditions (gas flow, temperature and time); it was observed that at a lower temperature the formation of metal nanoparticles is favored. The length and diameter of the CNT's are related to the synthesis time, the flow of the carbon precursor and the type of cation, as well as the concentration of the latter. The iron-based materials were the most suitable for the synthesis of CNT's.

The adsorption of hydrogen at -196 °C is governed by the physisorption mechanism, while at room temperature the mechanism is chemisorption. The values of $H_2$ adsorption are congruent with those reported in the literature. In the present work, several hydrogen adsorption tests were performed on the CNT's, and it was found that they are capable of adsorbing it even at room temperature. Several adsorption-desorption cycles showed their stability at cryogenic temperature, even at room temperature without seeing any impairment in their adsorption capacity.

It is inferred that the purification step is key to the removal of impurities and the catalyst. Purification can influence the pore size distribution and contribute to improving hydrogen capture capacity. It was observed that impurities occluded in the materials, in this case the residual cations of Ni, Co and Fe can generate a beneficial effect on the adsorption of $H_2$.

## RELATED PUBLICATIONS

Soto Soto, L, Rojas García E, Maubert Franco M, Estudio comparativo de la síntesis y modificación con Fe de materiales mesoporosos MCM-41 y SBA-15, su caracterización y evaluación, Superficies y vacío, Sociedad Mexicana de Ciencia y Tecnología de Superficies y Materiales A.C., 2016, 29, 1, 19-23.

Soto Soto L, Maubert Franco A M, Estudio de la capacidad de adsorción de $H_2$ en materiales mesoporosos y modificados con metales, XIV Congreso Mexicano y V Congreso Internacional de Catálisis XIV-CMC-2015, abril 19-24, 2015, Valle de Bravo, Estado de México,

Castillo Mínguez Brianda Marcela, Evaluación de la capacidad de captura del dióxido de carbono mediante materiales mesoporosos de sílice modificados, Tesis de Licenciatura Ing. Química, 2015, Universidad Autónoma Metropolitana, Asesora: Dra. Ana Marisela Maubert Franco

Maubert F A M, Soto Soto L, León Choreño A M, González R L, Ortiz Landeros J, Materiales mesoporosos silíceos modificados con Fe para la captura de $CO_2$, XXIV Congreso Iberoamericano de Catálisis, 15-19 de septiembre, 2014, Medellín, Colombia.

Full Thesis can be downloaded from: http://148.206.79.169/F/?func=find-b-0&local_base=tesis