Structural properties of Carbides and Nitrides phases supported on SBA-15 y -16 from ammine salts precursors

E. C. Aguillón Martínez [a], J A Melo Banda [a], R. Silva Rodrigo [a], J M Domínguez [b], Aguilar E. J. [b]
[a] Instituto Tecnológico de Ciudad Madero, División de Estudios de Posgrado e Investigación, Juventino Rosas y Jesús Urueta S/N, Col. Los Mangos, CP 89440, Ciudad Madero, Tamps., México.
[b] Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas, 07730 México DF., México.

Introduction

The growing problems of environmental pollution due to the emission of toxic gases, generated by the increment in the concentration of pollutants as sulfur, nitrogen, and aromatic compounds in the heavy fractions of the petroleum. All problems have motivated the necessity to develop new catalysts that possess a bigger activity and better physical properties able to support more severe operation conditions.

After the family of material mesoporosos M41S woke up great interest from its discovery in 1992, new materials have been developed to be applied as mesoporous catalytic supports. In this way, the family of mesoporous silica SBA types, i.e. SBA-15 and SBA-16 because they are synthesized in friendly work conditions, micro and mesoporous intrinsic capacity[1]. They exhibit a wide variety of morphologies depending on the synthesis conditions, also they possess a wall thickness pore (2-6 nm), also they exhibit controllable pore sizes from 5 to 30 nm, involves them of excellent thermal, hydrothermal stability and mechanics properties [2, 3].

Ni, Mo phases unsupported phases and bimetallic combinations of those materials have been tested in many reactions with excellent results. Bimetallic nitrides, i.e. Ni_2Mo_3N, they have exhibited high catalytic activity in the synthesis and decomposition of ammonia, also these bimetallic nitrides phases have showed excellent active and selective properties in HDS[4]. Generally the Volpe and Boudart technique has been used as the principal synthesis route in the preparation of unsupported nitrides phases. On the other hand, the MoC/Al_2O_3 has shown a higher activity in HDS of the thiophene than a commercial catalyst of MoS/Al_2O_3. Recently carbides and nitrides of NiMo and CoMo have been obtained and promoted with phosphorous, where NiMo and CoMo carbides showed a high hydrogenation activity in HDS of the thiophene as long as in the nitrides were favored the hydrogenation and hydrogenolysis reactions[5].

Experimental

The SBA-15 was synthesized using Pluronic P-123 ([OE]20-[OP]70-[OE]20) as structure-directing agent and TEOS like silica source. Typically 3.01 g of P-123 was dissolved in 65.31 ml of deionized water and 44.04 ml of HCl (4 M) to 323 K with stirring during 1 h. Then 6.42 g was added from TEOS drop to drop without stirring for a period of 24 h. The mixture was taken to 333 K during 48 h. After drying to room temperature the product was calcined in air at 813 K by 6 h. Pluronic F-127 ([OE]106-[OP]70-[OE]106) for the synthesis of SBA-16 was used with similar procedure as SBA-15. 3 g of F-127 was dissolved in 8.69 g of HCl (12 M) and 140.14 ml of H_2O, 12.5 g was added from TEOS to 308 K with stirring during 15 minutes. The mixture it was taken then to extraction with ethanol and HCl solution. The solid was filtered and drying to 373 K, finally, the solid was calcined in air at 813 K during 6 h.

The Ni-Mo carbides supported in SBA-15 and SBA-16 was synthesized using $[Ni(NO_3)_2\ 6H_2O]$ and $[(NH_4)_6Mo_7O_{24}]$ by incipient wetness technique with atomic ratios Ni/(Ni+Mo) =0.3 and later drying to 393 K. Phosphorous was incorporated using aqueous solutions of $(NH_4)_2HPO_4$ after drying the impregnated solids at 393 K. After, the materials were calcined at 773 K by 4 h. Finally, the samples were heated up to 823 K (1 K/min) in CH_4/H_2 flow and later on up to 973 K (0.666 K/min). The Ni-Mo nitrides supported in SBA-15 and SBA-16 was synthesized by means of the impregnation of same salts like carbides synthesis, hexamethylenetetramine (HMT) as nitrogen precursor was used. Similar procedure for phosphorous incorporation was used, finally impregnated solids were calcinated at 393 K. The precursor was heated (10 K/min) up to 923 K during 2 h with flow of Ar. Finally structural and textural properties were characterized by X ray diffraction (XRD) using a diffractometer BRUKER-AXS, model D800 ADVANCE and nitrogen adsoption performed using an AUTOSORB – 1 apparatus (QUANTA CHROME), respectively.

Results and discussions

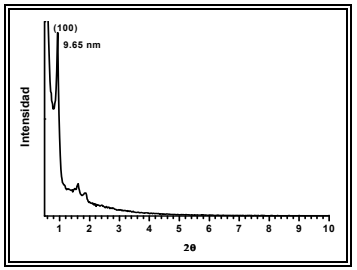

Figure 1. XRD pattern of SBA-15 sup

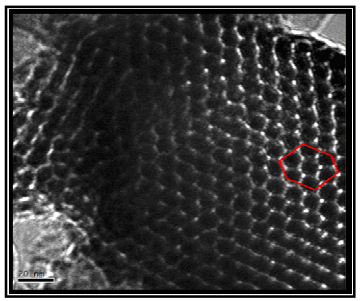

Figure 2. TEM image from SBA-15 particle.

Characteristical peak SBA-15 support was determinated by XRD in the 1.2 grades in the 2θ scale. Carbides and nitrides phases not were detected, in order at low metallic concentration of phases in the surface. Textural properties showed high surface areas from 800 to 1000 m^2/g also attributable to the presence of mesoporous of IV type were founded. TEM images showed a similar hexagonal arrangement as MCM-41 types in all materials after and before synthesis of nitrides and carbides supported phases.

References

[1] Van Der Voort P; Benjelloun M; Vansant E F; *J Am. Chem. Soc.* (2002), 106, 9027-9032.
[2] Zhao D Y; Sun J; Li Q; Stucky G D; *Chem. Mater.* (2000), 12, 275.
[3] Sayari A; Han B H; Yang Y J; *J Am. Chem. Soc.* (2004), 126, 14348.
[4] Diaz, B.; Sawhill, S. J.; Bale, D. H.; Main, R.; Phillips, D. C.; Korlann, S.; Self, R.; Bussell, M. E. *Catal. Today* (2003), *86*, 191.
[5] Santillan Vallejo L A; Melo Banda J A; Reyes de la Torre A I; Sandoval Robles G; Montesinos-Castellanos A; De los Reyes Heredia J A; *Catalysis Today* 109 (2005) 33–41.