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Synthesis, characterization and catalytic properties of NiMoP/MCM41-γAl_2O_3 catalysts for DBT hydrodesulfurization

R. Silva-Rodrigo[a,*], H. Castillo Jimenez[a], A. Guevara-Lara[b], J.A. Melo-Banda[a], A. Olivas Sarabia[c], A.I. Reyes de la Torre[a], F. Morteo Flores[a], A. Castillo Mares[a]

[a] Instituto Tecnológico de Cd. Madero, División de Estudios de Posgrado e Investigación, Juventino Rosas y Jesús Urueta S/N, Col. Los Mangos, 89440 Cd. Madero, Tam., Mexico
[b] Universidad Autónoma del Estado de Hidalgo, Ciudad Universitaria Carretera Pachuca-Tulancingo, Mexico
[c] Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Km. 107 Carretera Tijuana-Ensenada, Baja California, Mexico

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ABSTRACT

NiMoP/MCM41-γAl_2O_3 (NiMoP/AMx) supported catalysts have been investigated as a modification of MCM41 by using the sol–gel alumina incorporation method. Different catalysts were synthesized varying the Si/Al molar ratio (5, 10, 25 and 50). The aqueous solution method was used to impregnate the metallic species (NiMoP) on the AMx supports. A surface area high mesoporous solid was synthesized by using an organic template method. The incorporation of sol–gel alumina did modified the hexagonal array of the mesoporous material MCM41 when the preparation of AMx supports was carried out. The XRD patterns of the catalytic supports show that phases, MCM-41 and γ-Al_2O_3 exist, indicating the presence of the two materials in the synthesized solids. Raman spectroscopy also indicates the formation of $NiMoO_4$ and MoO_3 which are more difficult to sulfide and produce MoS_2 and Ni_3S_2 as separated sulfides instead of the NiMoS phase. The symmetries of the materials were determined through UV–vis where octahedral NiO as well as tetrahedral and octahedral Mo were found. The main reaction products were biphenyl (BP), cyclohexylbenzene (CHB) and bicyclohexyl (BCH) when the materials were tested in the HDS of DBT.

1. Introduction

The most common industrial process for sulfur removal is catalytic hydrodesulfurization (HDS) and considerable efforts have been made in the last few years to develop better catalysts for this process working at high temperatures and pressures. It has been demonstrated that the sulfured products more difficult to remove from intermediate fractions are dibenzothiophene (DBT) and its derivatives. In HDS reactions it is necessary high surface areas in order to remove the complex sulfured molecules, it is for this reason that researchers of Mobil Oil Company together with Japanese scientists developed the family of mesoporous materials called MCM40s. Mobil catalytic materials of number 41 (MCM41) belong to the family of the mesoporous molecular sieves discovered in the 1990s [1]. These highly ordered pore systems with tunable pore sizes [2], large surface areas and pore volumes, and high density of surface silanols [3] provide excellent opportunities in chemistry [4,5].

Typical hydrodesulfurization catalysts are alumina-supported sulfides of molybdenum or tungsten with either nickel or cobalt "promoter" [6,7] and often contain phosphorus as a secondary promoter. When γ-Al_2O_3 is introduced into the network of the MCM41 a support is created with adequate mechanical and thermal properties as well as a large surface area with mesopores. In addition the material must be able to support the severe conditions of the HDS reactions, without having deactivation problems. Nickel and molybdenum catalysts supported on alumina, present disadvantages of small surface areas but excellent stability to severe conditions, reason why they are the present industrial catalysts. Transition metal phosphides have recently been reported as a new class of high activity hydroprocessing catalysts that represent a substantial promise as a new generation catalysts. They are regarded as a group of stable, sulfur-resistant, metallic compounds that have exceptional hydroprocessing properties [8,9]. The primary role of phosphorus is, to promote the formation of well dispersed active species and hence improved catalytic activity, but at the same time another study found a poisoning effect of P in the HDS activity. The objective of this paper is to get a better understanding of the different species present on the catalytic support. This was done by a careful characterization of the Ni and Mo entities of a

* Corresponding author. Tel.: +52 833574820x3110; fax: +52 833574820x3110.
E-mail address: rebsilva_2000@yahoo.com.mx (R. Silva-Rodrigo).

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Table 1
Molar compositions of supports.

Supports	Si/Al molar ratio	Molar composition			
		CTAB	NH_4OH	TEOS	Sol–gel alumina
AM5	5	0.2	0.92	0.049	12.30
AM10	10	0.2	0.92	0.049	6.15
AM25	25	0.2	0.92	0.049	2.46
AM50	50	0.2	0.92	0.049	1.23

A = Sol–gel γ-alumina; M = MCM41.

NiMoP supported on MCM41-Al_2O_3 using BET, XRD, FTIR, Raman and UV–vis spectroscopies with the purpose of taking advantage of the properties that each of these techniques contribute with the aim to use these catalysts in the HDS reaction of dibenzothiophene (DBT).

2. Experimental

2.1. Synthesis of the γ-alumina support (sol–gel method)

The synthesis of sol–gel alumina was prepared in a similar procedure as was reported by Silva et al. [10]. In a free oxygen atmosphere, a quarter of a total used volume of ethanol (C_2H_5OH) was added to a volumetric flask. On the other hand, a trisecbutoxide mixture of aluminum [Aldrich 97%], $[C_2H_5CH(CH_3)O]_3Al$ was prepared with the three quarters of the remaining volume of ethanol in constant stirring. This solution was added to the volume of existing ethanol in the reactor, and was warmed up to 343 K for 30 min. Once homogenized, the mixture was added little by little partial volumes of deionized water, to obtain the gel of viscous consistency, which will stay in agitation for 3 h. Later it was aged at room temperature for 24 h, in order to permit the formation of the alumina structure and avoid the loss of its homogeneity. Later the remaining water was poured off and it was dried at 353 K. Finally it was calcined in a dynamic atmosphere of N_2 for 3.5 h and in air atmosphere for 12 h at 873 K to form the gamma alumina phase. After the gamma phase was obtained, this was dissolved in nitric acid before incorporating it during the synthesis of the MCM41.

2.2. Synthesis of the MCM41

The MCM41 materials were prepared following a conventional method described by Terres et al. [11]; Cetyltrimethyl ammonium bromide (CTAB) ($C_{19}H_{42}NBr$; Aldrich, 99%) was tenso-active materials which together with ammonium hydroxide (NH_4OH; Aldrich, 28% de NH_3 in water) were added to deionized water at room temperature. Both were stirred at varied time from 20 to 45 min, later tetraethyl orthosilicate (TEOS) ($C_8H_{20}O_4Si$; Aldrich 99.9%) was added to the mixture as a source of silicon. Supports were dried at 343 K and calcined at 813 K in a dynamic air atmosphere.

The incorporation of the γ-Al_2O_3 into the network of the MCM41 was during the preparation of the MCM41, before the addition of the ammonium hydroxide NH_4OH, to obtain the series of supports MCM41-γ-Al_2O_3 named AM, with a Si/Al ratio of 5, 10, 25 and 50. Table 1 presents the molar compositions used for the preparation of the supports along with the Si/Al ratio.

Table 2 presents the nomenclature used for the supports and catalysts. In this table, sol–gel alumina is represented by A, MCM41 by M, the series of supports MCM41-γ-Al_2O_3 by AM, molybdenum by Mo, nickel by Ni, phosphorus by P, Si/Al molar ratio by x and the Ni/(Ni + Mo) = 0.3. The same notation is used for the NiMo/AMx catalysts.

Table 2
Nomenclature of supports and catalysts.

Supports	Si/Al molar ratio (x)	Catalysts[a]
A	–	NiMoP/A
M	–	–
AM5	5	NiMoP/AM5
AM10	10	NiMoP/AM10
AM25	25	NiMoP/AM25
AM50	50	NiMoP/AM50

A = Sol–gel γ-alumina; M = MCM41; P = Phosphorus. x = Si/Al.
Mo = Molybdenum; Ni = Nickel.
[a] Reference catalysts; Ni/(Ni + Mo) = 0.3.

2.3. Synthesis of catalysts

The method of preparation of the catalysts was carried out by means of successive impregnation of ammonium heptamolybdate ($H_{24}Mo_7N_6O_{24}{\cdot}4H_2O$) [Aldrich] and nickel nitrate ($NiNO_3{\cdot}6H_2O$) [Aldrich], with a Ni/(Ni + Mo ratio) of 0.3 and impregnated at the same time with ammonium phosphate with the purpose of obtaining a 1 wt.% of phosphorus in the catalysts [12]. Ammonium phosphate [Aldrich] was used as the phosphorous source [13]. The compositions of NiMo catalysts are given in Table 3.

2.4. Characterization

2.4.1. X-ray diffraction

The structural properties of the catalysts were characterized by X-ray diffraction using a Bruker AXS diffractometer, model 8000 Advance, with Cu Kα radiation and continuous scanning of $0.6^\circ\ min^{-1}$, without rotation, within the range of $1.5 < 2\theta < 10$ and $40 < 2\theta < 70$ with a scan constant rate.

2.4.2. N_2 physisorption (BET)

Textural properties (surface area, pore volume and average pore diameter) of the supports were determined by N_2 physisorption (BET) at 78 K, using a Quantachrome AUTOSORB-1 equipment. Surface area was calculated from the BET equation, while pore and average pore diameters were determined from the desorption isotherm using the BJH method. Before the N_2 physisorption measurements, samples were degassed at 623 K for 2 h.

Table 3
Actual metallic contents and atomic ratio of the synthesized catalysts.

Catalysts*	Composition[a] wt.%		
	Ni	Mo	Ni/(Ni + Mo)
NiMoP/AM5	2.3	11	0.173
NiMoP/AM10	2.2	10	0.180
NiMoP/AM25	2.3	12	0.161
NiMoP/AM50	2.1	11	0.160
NiMoP/A	2.4	12	0.160

* These results were obtained by the technique of atomic absorption.
[a] By atomic absorption.