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HDS of thiophene over CoMo/AlMCM-41 with different Si/Al ratios

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Abstract

A series of AlMCM-41 molecular sieves with different Si/Al ratios were synthesized followed by the deposition of cobalt and molybdenum oxides on these mesoporous supports by co-impregnation. Such materials were further calcined and catalysts with 15 wt.% of cobalt and molybdenum and a Co/(Co + Mo) atomic ratio of 0.30 were obtained. These materials were characterized by X-ray diffraction (XRD), transmission electron microscopy and selected area electron diffraction (TEM/SAED), X-ray fluorescence (XRF), and nitrogen adsorption. Hydrodesulphurisation (HDS) of thiophene was carried out at 350 °C in a fixed bed continuous flow micro reactor coupled on line to a gas chromatograph. The main XRD peaks of MCM-41 phase were observed in all samples and peaks due to MoO_3 and $CoMoO_4$ phases were also identified from XRD results. It was found that the as-synthesized catalysts presented reasonable conversion results for HDS of thiophene, when compared to other supported catalysts. The main products of HDS of thiophene were H_2S, isobutene, 1-butene, *n*-butane, 2-butene-trans, and 2-butene-cis. It was observed that the reactivity of the as-synthesized catalysts is a direct function of the Si/Al ratio, nature and concentration of the active species on the mesoporous supports.

Keywords: AlMCM-41; Si/Al ratio; Cobalt and molybdenum; Hydrodesulphurization

1. Introduction

Further emission reduction of sulfur and nitrogen compounds will require more severe hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) of petroleum fractions. Therefore, present day catalysts and operating conditions will have to be adapted to new requirements. Nowadays, the development of more active HDS catalysts is one of the main goals of the refining industry. However, considerable effort has already been applied to improve the activity of the HDS catalysts aiming to adapt the distillate fuels to the present environmental legislation. Since 1960's, cobalt and molybdenum on alumina or silica are the most studied systems in HDS of petroleum fractions [1]. The role of cobalt atoms is still under discussion, however, it is generally accepted that these atoms promote the activity of molybdenum through electron transfer, consequently lowering the oxidation state of molybdenum [2]. The nature of the active phase is determined by the structure of the oxide precursor species, which is strictly dependent on the preparation methods [3]. The most studied active phases consist of different materials based on transition metal oxides [4], sulphides [5], phosphides [6], nitrides, and carbides [7,8]. The most common metal loading on alumina based catalysts is around 15 wt.% [9]. The potential advantage of the use of mesoporous materials as supports for hydrotreating catalysts is the possibility to obtain high dispersion of the catalytic phase at high loadings that, depending on the nature of active phase, may surpass 15–30 wt.%, a composition that cannot be achieved with conventional supports, such as silica gel or precipitated alumina.

The silica based M41S materials, discovered by the *Mobil Company* in the early 1990's [10,11], are a very interesting class of mesoporous materials. The MCM-41 silica, which has pore

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structure hexagonally is ordered, is the principal phase of the M41S family. The hexagonal mesoporous system with high surface area opens possibilities of accepting the impurities of higher kinetic diameter contained in the oil fractions. The formation of the AlMCM-41 phase occurs according to the liquid crystal template (LCT) mechanism, in which SiO_4 and AlO_4 tetrahedral react with the surfactant template under hydrothermal conditions [12,13]. Some works have already been published in the literature concerning HDS over MCM-41 supported Co–Mo sulfides [14–16], demonstrating that this material has thermal and hydrothermal stabilities around 1000 °C and 600 °C, respectively.

In this paper, synthesis, characterization and catalytic properties for HDS of thiophene of a series of cobalt and molybdenum oxides precursors supported on SiMCM-41 and AlMCM-41 with different Si/Al ratios are reported.

2. Experimental

2.1. Supports preparation

The AlMCM-41 materials were synthesized from tetramethylammonium silicate (TMAS, Sigma–Aldrich, $P_A = 17.5\%$) as silicon source, sodium hydroxide (Vetec, $P_B = 99\%$) as sodium source, pseudoboehmite (Vista, $P_C = 30\%$) as aluminum source, cetyltrimethylammonium bromide (CTMABr, Vetec, $P_D = 98\%$) as template structure and distilled water as solvent. For the pH adjustment, 30% acetic acid in ethanol solution was used [17]. Table 1 shows the hydrogel composition and the respective mass values of the pure precursors: A, B, C, D, and E. The P_i value represents the purity to each precursor and should be used to correct the values of the pure precursors showed in Table 1 to obtain the final amount of starting materials.

In a typical synthesis the reagents were mixed in order to obtain a gel with the following molar composition: 4.58 SiO_2:(0.437 + X) Na_2O:1 CTMABr:X Al_2O_3:200 H_2O. The value of X represents the molar coefficient of the aluminum source. The value of X varied from 0.114, 0.0570, 0.0380 to 0 in order to prepare MCM-41 with Si/Al atomic ratios of 20, 40, 60, and SiMCM-41, respectively. The procedure used to obtain ca. 1 g of calcined SiMCM-41 and AlMCM-41 with different Si/Al compositions was: (i) (A/P_A) grams of TMAS, (B/P_B) grams of NaOH, (C/P_C) grams of pseudoboehmite and (E/2) grams of water were placed into a 100 mL Teflon beaker and stirred at 60 °C for 2 h in order to obtain a clear solution; (ii) a solution prepared from (D/P_D) grams of cethyltrimethylammonim bromide and (E/2) grams of distilled water was added to the mixture (i), and aged for 30 min at room temperature. The hydrogels were placed into 45 mL teflon-lined autoclaves and heated at 100 °C for four days. Their pH was measured each day and adjusted to 9–10. In the last day sodium acetate (Carlo Erba) was added in a 1:3 molar proportion of CH_3COONa/CTMABr in order to stabilize the silica [17]. The as-prepared materials were filtered, washed and dried at 100 °C in a stove for 2 h. The elimination of the template species was performed by calcination. First, the samples were heated from room temperature to 450 °C, at a heating rate of 10 °C min^{-1}, in nitrogen dynamic flow of 80 mL min^{-1} and left at this temperature for 1 h in nitrogen and in air for an additional hour.

2.2. Impregnation of the active phases

The cobalt and molybdenum species were deposited on MCM-41 materials by co-impregnation of $(NH_4)Mo_7O_{24}{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ ethanol excess solutions. All samples were impregnated to obtain a total metallic percentage of 15 wt.% and a Co/(Co + Mo) atomic ratio of 0.3. After impregnation the samples were dried for 1 h at 80 °C and after that at 100 °C in a stove for 10 h. In the calcination step the samples were heated from room temperature up to 450 °C, at a heating rate of 10 °C min^{-1} in air dynamic flow of 80 mL min^{-1} and kept at this temperature for 1 h.

2.3. Chemical and structural characterization

The structural characterization was performed in order to evaluate the surface properties of the SiMCM-41 and AlMCM-41 mesoporous materials. X-ray diffraction (XRD) measurements were carried out on a Shimadzu equipment using Cu Kα radiation in the 2θ ranges: 1–9° and 10–60°, with step of 0.01°. Transmission electron microscopy and selected area electron diffraction (TEM/SAED) together with qualitative Energy Dispersive Spectroscopy (EDS) were performed using a Jeol 2010 instrument with an electron beam accelerating voltage of 200 kV. The sample was dispersed ultrasonically in 2-propanol, and a drop of the suspension was deposited on a holey carbon copper grid. The experimental chemical composition of the supports and metallic phases were obtained via X-ray fluorescence (XRF) (EDX-800, Shimadzu) with uranium X-ray based tube. The specific surface area was determined according to the standard Brunauer–Emmett–Teller (BET) method [18] while pore size distribution was evaluated by

Table 1
Molar compositions of gels and respective amounts in grams of the pure starting materials in order to obtain ca. 1 g of final calcined MCM-41

Si/Al	Gel molar composition									
	A	B	C	D	E	A	B	C	D	E*
20	4.58SiO_2:0.550Na_2O:0.1140Al_2O_3: 1CTMABr:200H_2O					1.747	1.159	0.042	1.318	13.019
40	4.58SiO_2:0.494Na_2O:0.0570Al_2O_3:1CTMABr:200H_2O					1.751	0.143	0.021	1.321	13.049
60	4.58SiO_2:0.475Na_2O:0.0380 Al_2O_3:1CTMABr:200H_2O					1.752	0.138	0.014	1.322	13.058
∞	4.58SiO_2:0.437Na_2O:0.0000 Al_2O_3:1CTMABr:200H_2O					1.758	0.127	0.000	1.326	13.101

* The final value of E can be approximated by: $E_{final} = E - A((1 - P_A)/P_A)$.