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Influence of the activation atmosphere on the hydrodesulfurization of Co-Mo/SBA-15 catalysts prepared from sulfur-containing precursors

G. Alonso-Núñez[a,*], J. Bocarando[a], R. Huirache-Acuña[b], L. Álvarez-Contreras[c], Z.-D. Huang[d], W. Bensch[d], G. Berhault[e], J. Cruz[f], T.A. Zepeda[a], S. Fuentes[a]

[a] Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Ensenada, Baja California, C.P. 22860, Mexico
[b] Universidad Michoacana de San Nicolás de Hidalgo. Morelia, Michoacán, Mexico
[c] Centro de Investigación en Materiales Avanzados S. C., Chihuahua, Chih., C.P. 31109, Mexico
[d] Institut für Anorganische Chemie, Christian-Albrechts University of Kiel, Max-Eyth-Str. 2, D-24118 Kiel, Germany
[e] Institut de Recherches sur la Catalyse et l'Environnement de Lyon, CNRS Université Lyon I, 02 Av. A. Einstein, 69100 Villeurbanne, France
[f] Facultad de Ciencias Químicas e Ingeniería, Universidad Autónoma de Baja California, Tijuana, B. C., Mexico

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ABSTRACT

Mesoporous SBA-15 material was used as support of binary Co-Mo hydrodesulfurization (HDS) catalysts prepared using a novel approach based on the use of already sulfided precursors (ammonium tetrathiomolybdate and cobalt diethyldithiocarbamate). The effects of atmosphere and activation temperature were studied to optimize the preparation of highly active CoMo/SBA-15 hydrodesulfurization catalysts. Two sets of catalysts were synthesized using either a N_2/H_2 (10% H_2) or a H_2/H_2S (15% H_2S) atmosphere at three different temperatures of activation (723, 773 and 823 K). The catalysts were tested in the HDS of dibenzothiophene (DBT) and the catalysts were characterized by N_2 physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The use of already sulfided precursors leads to a homogeneous dispersion of the active phase inside the SBA-15 channels. Moreover, the N_2/H_2 activation procedure at 723 K allows obtaining optimized HDS active catalysts. Finally, a confinement effect of MoS_2 slabs inside the SBA-15 channels leads to a high selectivity along the direct desulfurization pathway.

1. Introduction

Nowadays, the processing of "more dirty" feeds containing larger amounts of sulfur has become more and more urgently needed and a new generation of transition metal sulfide-based catalysts with higher activities, greater selectivity, and better resistance to poisoning is required. Using high-performance hydrodesulfurization (HDS) catalysts is then necessary to achieve lower sulfur concentration levels satisfying environmental restrictions [1].

Typically, hydrotreatment (HDT) reactions are catalyzed by sulfided Co(Ni)Mo(W) catalysts supported on alumina [2]. The origin of the almost exclusive use of alumina as support has been ascribed to its outstanding textural and mechanical properties and its relatively low cost [3]. However, the presence of undesirable strong metal–support interaction when using alumina has triggered research devoted to the development of new supports for HDT applications [4–13]. Thus, more recently, research concerning the development of highly dispersed active phase on zeolites or mesoporous materials has been very intense in order to respect the stringent regulations concerning the maximum amount of sulfur admitted in fuels. Some results have been presented before in publications concerning the effect of support in hydrotreating catalysts for ultra clean fuels [12,14].

On the other hand, the catalyst activation is also a crucial step for the physicochemical properties (nature, composition and dispersion of the active phase) and consequently for activity and selectivity properties. In this respect, the temperature of treatment used during this step can affect the degree of reduction and sulfidation as well as the dispersion of the active phase. The influence of activation over the HDS of dibenzothiophene (DBT) on $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, Ru/MgF_2 materials has been investigated extensively [15–23].

The influence of atmosphere during the decomposition of ammonium tetrathiomolybdate for the activation of unpromoted and cobalt-promoted alumina-supported MoS_2 catalysts was also investigated by Pawelec et al. [24]. This study showed a strong influence of the activation procedure. For the unpromoted catalyst, the most efficient treatment was related to the use of a 10% H_2S/H_2 atmosphere while the cobalt-promoted catalyst needed

* Corresponding author. Tel.: +52 646 174 46 02.
E-mail address: galonso@cnyn.unam.mx (G. Alonso-Núñez).

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