Comparison and performance of different sulphided Ti-loaded mesostructured silica-supported CoMo catalysts in deep HDS

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ARTICLE INFO

ABSTRACT

Ti-loaded mesostructured silica materials (HMS, MCM-41 and SBA-15), with Si/Ti atomic ratio of 40, were used for the preparation of supported CoMo catalysts. The catalysts were tested in the reaction of HDS of 4,6-DMDBT carried out in a continuous-flow microreactor in the liquid-phase. The samples were characterized by DRS UV-Vis, XPS, Micro-Raman spectroscopy, S_{BET}, XRD, TPR, FT-IR of adsorbed NO and pyridine. The type of mesostructured material has an important effect on the dispersion of both Mo and Co species. The highest catalytic performance in the HDS of 4,6-DMDBT was observed for the catalysts prepared on the Ti-HMS material. The superior performance of this sample was related to the following factors: (i) larger specific area value, (ii) higher acidity, (iii) higher dispersion of the Co and Mo species, and (iv) the lower reduction temperature of the supported species. Traditional reaction pathways for the HDS of 4,6-DMDBT were observed on the conventional CoMo/γ-Al$_2$O$_3$ and CoMo/Ti-SBA-15 samples, while the CoMo/Ti-MCM-41 and CoMo/Ti-HMS samples show some dealkylation of the alkyl groups in the 4,6-DMDBT molecule (producing DBT). Additionally, the CoMo/Ti-HMS sample recorded the isomerization of the one alkyl group in the 4,6-DMDBT molecule. The differences observed in the reaction pathways via the HDS of 4,6-DMDBT are related to the acidity of the samples.

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1. Introduction

The environmental challenges for producing sufficient and better quality liquid hydrocarbon fuels to meet the world's spiralling transportation needs are accentuated by demands for clean and less polluting fuels. Today, strict environmental regulations on the sulphur content of diesel fuels is leading refiners to develop novel catalysts for the production of ultra-low sulphur diesel. The threshold limit for sulphur in diesel fuel is now expected to be restricted to 50 ppm [1]. Moreover, sulphur-content removal in heavy petroleum fractions is receiving interest due to new environmental legislation requiring the further reduction of such content. Accordingly, it is considered that by 2009 the sulphur content in petroleum fractions needs to be lower than 10 or fewer ppm [2]. To confront this problem, the hydrodesulphurization (HDS) of petroleum feedstocks has been an essential reaction for producing clean fuels with lower sulphur content [3–5]. Molybdenum-based hydroprocessing catalysts promoting by Co and Ni are usually supported on γ-Al$_2$O$_3$ [6]. Unfortunately, these catalysts do not comply with new environmental legislation in the hydroprocessing of heavy petroleum fractions, especially

regarding the complex petroleum fractions as Maya-México oil. The need to produce clean engine fuels, combined with the prospect of processing poor-quality petroleum feedstocks, has stimulated the interest in synthesizing novel and effective catalysts for deep hydrodesulphurization of diesel and gas-oil [7,8]. Recently, the novel unsupported NEBULA® catalysts developed jointly by Akzo Nobel, Nippon Ketjen and Exxon Mobil and commercialized in 2001 are many times more effective for the deep hydrotreating HDS reaction than traditional hydroprocessing catalysts [9]. However, this catalyst is more expensive than the supported ones. Thus, the challenge is to design novel cost-effective catalysts. The use of novel structured materials as supports for hydrotreating catalysts could probably help to alleviate the problem.

Many studies have reported that the support has an important role in the performance of hydrotreating reactions. The use of different materials as support for the preparation of hydrotreating catalysts, such as γ-Al$_2$O$_3$ [10,11], SiO$_2$-Al$_2$O$_3$ [12–14], ZrO$_2$ [15–16], TiO$_2$-ZrO$_2$ [17], TiO$_2$-Al$_2$O$_3$ [18–20], TiO$_2$-SiO$_2$ [18,19], has shown that the morphological and chemical composition of the support has a significant effect on the electronic properties of the supported metallic hydrotreating catalysts, and its effect is reflected in the catalytic activity of the samples. However, these materials have low surface area values, with this being an important restriction for the preparation of catalysts with high

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loads of active phases and with a higher dispersion of supported components.

In recent years, the mesoporous silicate materials with ordering pore structure, in particular with hexagonal ordering of the pores, such as HMS, MCM-41 and SBA-15 materials, which have large pore diameters and higher surface areas than the Al_2O_3 material [21,22] have attracted widespread attention as new potential materials for the preparation of novel supported hydrotreating catalysts [21,22]. Several reports have been made to develop high performance supported hydrotreating catalysts on HMS, MCM-41 and SBA-15 materials. Principally, the HMS material prepared by a neutral template pathway offers certain advantages for the preparation of supported hydrotreating catalysts over the MCM-41 material that is synthesized by electro-statically templated [21]. This advantage could be because the HMS material shows higher thermal and hydrothermal stability than the MCM-41 material. Unfortunately, the HMS material has low mechanical and thermal stability in comparison with the γ-Al_2O_3 material [21,22]. In this sense, several solutions have been reported in open literature in order to enhance the stability of mesoporous materials. The modification of the mesoporous siliceous molecular sieves by incorporating heteroelements provides the silica framework with high structural stability in comparison with the counterpart heteroelement-free molecular sieves [21–23].

Several reports have shown that the heteroatom-containing HMS [23–34], MCM-41 [25–46] and SBA-15 [47–53] materials offer certain advantages over the preparation of new hydrotreating catalysts that are more active than the typical hydrotreating catalysts supported on alumina. However, the simultaneous comparative study of these three materials as support for hydrotreating catalysts is not reported.

Within this framework, this work was undertaken in order to evaluate the performance and catalytic stability of the hydrotreating CoMo catalyst supported on Ti-containing HMS, SBA-15 and MCM-41 materials. The catalysts were tested in the reaction of HDS of 4,6-DMDBT carried out in a continuous-flow microreactor in the liquid-phase. The supports and catalysts were characterized by UV-Vis diffuse reflectance spectroscopy (DRS UV-Vis), X-ray photoelectron spectroscopy (XPS), Micro-Raman spectroscopy, N_2 adsorption–desorption (S_{BET}), X-ray diffraction (XRD), FTIR spectroscopy of adsorbed NO and pyridine and temperature programmed reduction (TPR).

2. Experimental

2.1. Synthesis of the supports

The Ti-HMS support (Si/Ti molar ratio of 40) was prepared following a procedure similar to that described by Gotier and Tuel [54] using dodecylamine ($C_{12}H_{25}NH_2$, Aldrich 98%) as surfactant. The procedure followed during preparation has been described elsewhere [55]. The material obtained was dried at room temperature for 16 h and then at 378 K for 2 h, and finally calcined in air at 773 K for 4.5 h, reaching this temperature in 3.5 h.

The Ti-MCM-41 support (Si/Ti molar ratio of 40) was synthesized by following a similar procedure to that described by Schmidt [56]. The incorporation of Ti into the MCM-41 mesostructure was synthesized by a similar procedure to that described in ref. [57]. The solid product obtained was filtered, dried at room temperature for 36 h and then at 383 K for 4 h, and finally calcined in air at 773 K for 5.5 h at a heating rate of 0.8 °C/min.

The Ti-SBA-15 support (Si/Ti molar ratio of 40) was synthesized by following a similar procedure to that described by Zhao et al. [58] and Yue et al. [59]. The incorporation of Ti into the SBA-15 mesostructure was carried out by the direct-synthesis method

using tetrabutyl orthotitanate as the Ti source following the published procedure [59]. The solid product obtained was filtered, dried at room temperature for 24 h and then at 393 K for 3 h, and finally calcined in air at 773 K for 6 h with a heating rate of 1 °C/min.

2.2. Preparation of the catalysts

The CoMo/Ti-HMS, CoMo/MCM-41 and CoMo/SBA-15 catalysts were prepared by successive impregnation method using the pore filling method. All supported CoMo catalysts on the Ti-HMS material were prepared with nominal composition of 3.0 and 9.0 wt.% of Co and Mo, respectively (Co/(Co + Mo) atomic ratio = 0.35). Molybdenum was impregnated first from an aqueous solution of $(NH_4)_6Mo_7O_{24}$ (Aldrich 99%). The impregnate samples were dried at room temperature for 6 h followed by drying at 378 K for 1 h. The samples were then calcined at 773 K for 4.5 h, reaching this temperature within 3.5 h, whereupon the $Co(NO_3)_2$ (Aldrich 98%) solution was added. The samples were dried at room temperature for 6 h and then at 378 K for 1 h followed by calcination at 773 K for 4.5 h, reaching this temperature within 3.5 h. The chemical composition and denomination of the catalysts are given in Table 1.

2.3. Characterization methods

2.3.1. UV-Vis diffuse reflectance spectroscopy

The UV-Vis diffuse reflectance spectra (DRS UV-Vis) of the pure supports and the catalysts in their oxide state were recorded using a Cary 5_E spectrophotometer with a specially designed Praying Mantis diffuse reflection attachment (Harrick) for in situ measurements. All spectra were recorded after heating the samples at 523 K in He flow for 1 h. Decomposition of each spectrum was performed by non-linear fitting of multiple Gaussian peak functions sharing a common baseline.

2.3.2. X-ray photoelectron spectroscopy

The X-ray photoelectron spectra of the supports, calcined, sulphided and used catalysts were recorded to study the effect of Ti-HMS, Ti-MCM-41 and Ti-SBA-15 on the dispersion and the degree of sulphidation of the supported species. A VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Mg Kα ($h\nu$ = 1253.6 eV) X-ray source was used. The samples were first placed in a copper holder mounted on a sample-rod in the pre-treatment chamber of the spectrometer and then outgassed at 403 K for 1 h before transfer to the analysis chamber. The freshly sulphided catalysts (ex-situ sulphidation to 673 K with a flow of 60 ml min^{-1} of the mixture H_2/H_2S; 10 vol.% H_2S for 2 h) were kept under i-octane in order to avoid exposure to air, and then introduced to the preparation chamber. All supports and catalysts were outgassed at 10^{-5} mbar and then transferred to the ion-pumped analysis chamber, where residual pressure was kept below 7×10^{-9} mbar during data acquisition. The binding energies (BE) were referenced to the C 1s peak (284.9 eV) to account for the charging effects. The areas of the peaks were computed after fitting the experimental spectra to Gaussian/Lorentzian curves and

Table 1
Nominal composition of the samples

Catalysts	Mo (wt.%)	Co (wt.%)	Theoretical Si/Ti atomic ratio
CoMo/Ti-HMS	9	3	40
CoMo/Ti-SBA-15	9	3	40
CoMo/Ti-MCM-41	9	3	40
CoMo/γ-Al_2O_3	12	3.4	0