



Comparison of the morphology and reactivity in HDS of CoMo/HMS, CoMo/P/HMS and CoMo/SBA-15 catalysts

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ABSTRACT

Mesoporous HMS and SBA-15 materials were synthesized using dodecylamine and pluronic triblock copolymer as surfactants, respectively. The P-modified HMS material (P/HMS) was prepared by incipient wetness impregnation of calcined HMS substrate with aqueous solutions of H₃PO₄. The influence of support (HMS, P/HMS, SBA-15) and metal loading on both bulk and surface structures of calcined and sulfided CoMo catalysts were studied by a variety of techniques (N₂ adsorption–desorption, XRD, TPD–NH₃, TGA, FT-IR of NO adsorption, HRTEM, XPS). Textural data of the oxide catalysts confirm that sequential impregnation with Mo, Co salt solutions followed by calcination does not destroy the mesoporous structure of these materials. There is only a minimal blocking of the host pore systems by the widely-dispersed metal oxides located inside them. XPS analysis of the sulfided catalysts revealed that Co₃Mo₁₀/HMS catalyst shows lower Mo exposure than on its Co₃Mo₁₀/SBA-15 counterpart. Notwithstanding the catalytic response of HMS- and SBA-15-supported catalysts in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) was similar. It was also observed that the Co₃Mo₁₀/P/HMS sample show a drop in activity with respect to Co₃Mo₁₀/HMS sample due to the strong decrease in the specific surface area and a large surface concentration of unsulfided Co²⁺ species on the former sample. The increase of total metal content from 15 to 19.5 wt.% (Co_{4.5}Mo₁₅/P/HMS) led to catalyst, which behaves a little better in DBT conversion than a commercial CoMoP/Al₂O₃ catalyst in the target reaction.

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1. Introduction

In recent years, the synthesis of hexagonal mesoporous silicas MCM-41, HMS and SBA-15 by cooperative assembly of silica and surfactants have attracted a great interest with regard to their technical applications as catalysts and catalyst supports [1–3]. This is because they usually display very high surface areas of 1000 m² g⁻¹ or more, they are thermally stable in dry atmosphere at temperatures up to 1073 K, and have ordered wide pores, which might provide better transport for reactants and products [3]. The perspectives on the catalytic applications of mesostructured materials have been reviewed by Trong On et al. [2].

The ordered mesoporous silicate named M41S was first synthesized at the Mobil Corporation [4]. Among those materials, MCM-41 was the one most extensively studied [5]. This material shows a large specific area, a hexagonal array and uniform pore channels, yet its practical application is limited due to its poor hydrothermal stability. Subsequently, the synthesis of other hexagonal mesopor-

ous sieves such as HMS was reported [6,7]. However, the more remarkable advance in the synthesis of mesoporous materials was performed by Zhao et al. [8], who synthesized hydrothermally stable SBA-15 silica molecular sieves using triblock copolymer surfactants for templation of this material. The SBA-15 possesses a high specific area (600–1000 m²/g), being formed by a hexagonal array of uniform tubular channels with pore diameters (ranging from 5 to 30 nm), which are significantly larger than those of HMS and MCM-41. Moreover, the SBA-15 material is more hydrothermally stable than HMS. This is due to their thicker walls and ability to form stable crystal nuclei of the constitutive oxide within the walls. Our previous study on CoMo/Ti-SBA-15 [9] and CoMo/Ti-HMS [10–12] catalysts showed that both SBA-15 and HMS materials modified with Ti are good supports for CoMo catalysts. This is, in part, because the framework of those materials may control the metal oxide particle size limiting the growth of the clusters introduced into the confined space of the channels. Thus, the aim of this work is the comparison of the catalytic response of both CoMo/HMS and CoMo/SBA-15 systems under the same HDS reaction conditions. To our best knowledge, such comparison is not yet reported in literature.

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Among the many elements used as additives for hydrotreating catalysts, phosphorus is most often used as a third element. Indeed, in past, for the hydroprocessing of feedstocks the commercial Co(Ni)Mo/Al₂O₃ catalysts were often modified by phosphorus [13]. However, when employing model compounds such as thiophene, dibenzothiophene (DBT) and that of its alkyl derivatives, the effect of P incorporation into Co(Ni)Mo/Al₂O₃ catalysts was contradictory [14–27]. Concerning the catalyst structure, it was reported that: (i) phosphorus acts as a second promoter [27]; (ii) phosphorus decreases metal-support interaction [28]; (iii) the solubility of molybdate during catalyst preparation is enhanced by the formation of phosphomolybdate complexes [17,29]; (iv) phosphorous modified not only the acidity but also the physical properties of alumina [30]; (v) the dispersion of the active phase is improved [16,17,31,32]; (vi) the formation of inactive Co/Ni species is inhibited [21,33]; (vii) stacked layers are formed that are easier to sulfide [18]; (viii) catalyst deactivation during on-stream operation is minimized [33] and (ix) the AlPO₄ phase is formed on the alumina surface [34,35].

Compared with alumina-supported catalysts, the modification of silica with phosphorus was much less studied [36–40]. Our previous study showed that HMS material containing optimized amount of phosphorus on surface (1.5 wt.% as P₂O₅) is effective support for CoMo phases [37]. However, phosphate species located on the support surface might act as physical barrier for Co and Mo species inhibiting the formation of a mixed Co-Mo phase. Considering a remote control model proposed by Delmon [41], even in this case the synergy between Co and Mo species might occur through migration of hydrogen spillover on the support surface. Recently, the synergy between Mo/SiO₂ and Co/SiO₂ beds separated by 5 mm of SiO₂ in the HDS of gas oil was reported in literature [42–45] and interpreted in terms of the remote control effect.

Accordingly, the main objective of this work is to study CoMo hydrotreating catalysts prepared by sequential impregnation with the aim to clarify the effect of support structure (HMS, P/HMS, SBA-15) and the influence of metal loading. Contrary to the P/HMS [37] system, the optimum P-loading in SBA-15 substrate was not established by us, both HMS and P/HMS systems were selected for investigation of the effect of metal loadings. Catalyst activity was studied in the HDS of DBT reaction, which is a widely used model reaction for the deep HDS of diesel fuels. The physicochemical properties of pure supports and CoMo catalysts have been evaluated by various techniques and their activity compared with those of a conventional CoMoP/Al₂O₃ catalyst.

2. Experimental

2.1. Synthesis of the supports and catalysts

Siliceous SBA-15 mesoporous material was synthesized according to the procedure described by Flodström and Alfredsson [45]. The pluronic triblock copolymer (BASF, EO₂₀-PO₇₀-EO₂₀, P123) was used as the structure-directing agent and tetraethylorthosilicate (TEOS, 98%, Aldrich) as a source of silica. In a typical synthesis, the triblock copolymer was dissolved in a solution of water and HCl under stirring, after which the required amount of TEOS was added to the solution at 308 K and kept under stirring conditions for 24 h. The mixture was subsequently transferred into polypropylene bottles and heated at 358 K for 24 h. After synthesis, the solid obtained was filtered, washed thoroughly with distilled water, dried at 373 K and finally calcined at 773 K for 6 h to remove the organic template.

The HMS molecular sieve was prepared following the method reported by Zhang et al. [46]. Tetraethylorthosilicate (TEOS, 98%, Aldrich) was used as the neutral silica precursor, dodecylamine

(DDA, 98%, Aldrich) was the neutral structure director and mesitylene (MES, 97%, Aldrich) was used as a swelling agent. In a typical synthesis, the surfactant (DDA) and water were vigorously stirred to obtain a homogeneous solution. MES was added to the surfactant solution and stirred for 15 min. TEOS was then added to the surfactant-auxiliary solution and the mixture was allowed to react under stirring at room temperature for about 20 h. After synthesis, the solid residue obtained was filtered, washed thoroughly with distilled water and dried in air. The sample was dried at 373 K in air for 24 h and finally calcined at 813 K in air for 6 h. Subsequently, the P-modified HMS material (nominal 1.5 wt.% of P₂O₅) was prepared by incipient wetness impregnation of calcined HMS material with aqueous solutions of H₃PO₄. After the evaporation of water at room temperature, the solids were dried at 383 K overnight and then calcined at 773 K for 3 h.

The CoMo hydrotreating catalysts were prepared by successive impregnation of different supports via incipient wetness method. The molybdenum salt (ammonium heptamolybdate tetrahydrate, Aldrich, ACS reagent) was introduced first. Then the Mo/support impregnates were dried overnight at 383 K in air and calcined at 773 K in air for 3 h. Finally, the Mo-loaded samples were impregnated with a cobalt salt (cobalt(II) nitrate hexahydrate, Aldrich, 98%). All catalysts recorded the same Co:Mo molar ratio of 1:3. Drying and calcinations were the same as above. The catalysts with a low metal loading (Mo = 10 wt.% and Co = 3 wt.%) will be referred to henceforth as Co₃Mo₁₀/support, whereas those with high metal loading (Mo = 15 wt.%, Co = 4.5 wt.%) are referred to as Co_{4.5}Mo₁₅/support.

2.2. Catalyst characterization

The textural properties of the calcined catalysts were determined from the adsorption isotherms of nitrogen at 77 K recorded with a Micromeritics TriStar 3000 apparatus. The samples were previously degassed at 423 K for 24 h under a vacuum (10⁻⁴ mbar) to ensure a clean surface, free of any loosely-bound adsorbed species. The specific areas of the samples were determined according to standard BET procedure from the nitrogen adsorption data collected in the relative equilibrium pressure interval of 0.03 < P/P₀ < 0.3. Pore size distributions were calculated from the adsorption and desorption branches of the corresponding nitrogen isotherm using the BJH method. The total pore volume (V_p) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.98, and the micropore volume (V_μ) and the micropore area (S_μ) were estimated using the *t*-plot method.

X-ray diffraction (XRD) patterns of the powdered oxide samples were recorded by scanning 2θ angles within the range of 0.5–6° (small-angle) and 6–80° (wide-angle) in scan mode (0.02° and 0.04°, respectively; 20 s) using an X'Pert PRO X-ray diffractometer (PANalytical).

The acidity of the bare supports was determined by temperature-programmed desorption (TPD) of ammonia using a Micromeritics 2900 apparatus provided with a TCD and interfaced to a data station. The procedure followed during TPD-NH₃ measurements has been described elsewhere [47]. Briefly, the samples of 50 mg were degassed in a He flow (Air Liquide, 99.996%) at 383 K for 1 h. Ammonia-saturation was then performed by flowing a 5% NH₃/He mixture at 400 K for 0.5 h. After equilibration in an argon flow for 1 h at 353 K, the samples were heated at 10 K/min up to 1200 K, and the TCD signal of ammonia desorption was recorded.

The reducibility of oxide catalysts was studied by thermogravimetry (TGA) combined with temperature-programmed reduction (TPR). The reduction was carried out in a H₂/N₂ atmosphere (5% H₂ v/v) in a Pyris 1 (Perkin Elmer) TGA instrument, in the 313–1323 K temperature interval with a heating rate of 5 K/min, and with results being presented as differential thermal analysis

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