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Influence of the acidity of nanostructured CoMo/P/Ti-HMS catalysts on the HDS of 4,6-DMDBT reaction pathways

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Abstract

The influence of catalyst acidity on the reaction mechanism of the 4,6-dimethyldibenzothiophene (4,6-DMDBT) hydrodesulfurization (HDS) over CoMo hydrotreating catalysts was studied using a batch autoclave and fixed-bed reactor ($T = 598$ K and $P = 5.5$ MPa). P-free Ti-HMS and P-containing P/Ti-HMS mesoporous siliceous materials were synthesized and used as supports. The effect of the catalyst preparation method (successive vs. simultaneous impregnation) and phosphorous addition on catalyst acidity was studied by TPD-NH_3 and DRIFT-NH_3 techniques. For all synthesized catalysts, the reaction proceeds *via* dealkylation (DA) and isomerization (ISO) pathways, with the later being the main reaction route. Incorporation of Co and Mo phases by simultaneous impregnation was found to be the best method for catalyst preparation, whereas P-addition promote the isomerization route of 4,6-DMDBT transformation to a greater extent than the dealkylation route. On the contrary, the reaction on a CoMoP/γ-Al_2O_3 reference catalyst proceeds *via* HYD and DDS reaction pathways, the later being the main reaction route. The catalyst acidity–activity correlation indicates that both activity and selectivity depend largely on the presence of Brønsted acid sites as well as on the total amount of Brønsted and Lewis acid sites. By correlating HRTEM-activity data, the enhancement of activity and isomerization observed with the catalyst prepared by simultaneous impregnation and modified with P was related to the cumulative effects of the lower size of MoS_2 slabs and their higher surface density.

Keywords: HDS; DBT; 4,6-DMDBT; CoMo catalysts; Mesoporous silica; Phosphorous; Brønsted acidity

1. Introduction

The removal of sulfur from heavy diesel fractions is receiving increasing interest due to new environmental legislation requiring the further reduction of sulfur content. In 2009, the sulfur content from diesel fractions needs to be lower than 10 ppm [1]. In order to meet these specifications, there is a need for more efficient processes and more active catalysts. Traditional hydrodesulfurization (HDS) catalysts are Mo or W supported on alumina promoted by Ni or Co in sulfided state [2–5]. However, these catalysts are unable to achieve the deep HDS of alkyl-substituted dibenzothiophenes (DBT). Thus, new effective HDS catalysts are based on the totally different concept of bulk-like materials. For example, the unsupported NEBULA catalysts developed jointly by Akzo Nobel, Nippon Ketjen and Exxon Mobil and commercialized in 2001 are effective for deep HDS [6]. However, this new generation of catalysts is more expensive than the supported ones. Thus, the challenge is to design novel cost-effective supported catalysts.

The difficulty in converting alkyl-substituted DBTs over classical Co(Ni)-Mo/γ-Al_2O_3 catalysts is commonly ascribed to the steric hindrance of the alkyl groups, especially when both are in the 4- and 6-positions, which hinder the adequate interaction of the S-atom with the catalytic active site. Thus, the challenge is to engineer new catalysts (metals as well as supports) which can eliminate the planar configuration of alkyl-substituted DBT. Such destruction of the planar configuration of those compounds could be achieved through the hydrogenation of their aromatic rings, dealkylation, isomerization or C–C bond scission reactions [7–10].

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[2] http://www.ccmc.unam.mx/investiga/cat/menu_i_cat.html.

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In order to promote the migration of methyl groups in the aromatic ring structure, attempts were made to change the acid properties of support by use of the hybrid materials, e.g. HY-Al_2O_3 [10,11], HY-SiO_2 [11,12], ZSM-5/Al_2O_3 [10], SiO_2–Al_2O_3 [12] or Al_2O_3–TiO_2 [13]. In this sense, the higher hydrogenation/hydrogenolysis ratio was reported by Robinson et al. [7] for the HDS of 4E6MDBT over CoMo catalysts supported on Al_2O_3–SiO_2. The activity enhancement over the acid support was ascribed to the C–C bond scission in the thiophenic ring either before or after the desulphurization step [8]. For the HDS of 4,6-DMDBT, the effect of Al_2O_3-support modification by HY addition on the activity of CoMo catalysts was reported by Landau et al. [10] and Isoda et al. [11]. It was found that steric hindrance was diminished by the migration of methyl groups in the aromatic ring, but the reactants were cracked simultaneously due to the acidic nature of the catalysts [10,11]. For CoMo/Al_2O_3 catalysts tested in the HDS of 4,6-DMDBT, the effect of the modification of alumina acidity by P-loading was studied by Kwak et al. [14]. They found that the P_2O_5 content in the catalyst up to 0.5 wt% enhances catalytic activity due to the modification of molybdenum dispersion and Brønsted acidity by acid treatment. The authors proposed that an increase in Brønsted acidity allows the migration of the methyl groups in 4,6-DMDBT, thereby reducing steric hindrance in the adsorption of this compound on the catalyst surface [14]. Manoli et al. [15] observed that the addition of P increased both the number of Lewis sites and Mo^{4+} abundance in P-doped monometallic Mo carbide catalysts supported on alumina. Thus, a linear correlation was found between the intensity of the band at 1608 cm^{-1} (from pyridine IR spectra), which is characteristic of coordination sites, and Mo^{4+} abundance derived from XPS analysis.

The influence of the catalyst preparation conditions on the surface of P-modified alumina-supported Mo catalysts has been studied by several authors [16–19]. In general, it was found that the co-impregnation was superior method of the catalyst preparation with respect to sequential impregnation [16–19]. However, in the case of Mo impregnation preceding Co impregnation, the better performance in HDS reaction was also reported [20]. Similarly to alumina-supported catalysts modified with P [14,15], our recent study on the CoMoP/HMS catalysts demonstrated that the morphology of the sulfided CoMo species depends on the method of catalyst preparation and on the P-concentration on the surface of HMS support, with the former factor being more important than the later [21]. The successive impregnation catalysts were less active in the HDS reaction of DBT than that prepared by simultaneous impregnation. We attributed the higher catalytic activity of the latter samples to the larger surface exposure of both Co and Mo sulfided species [21]. On the other hand, our previous study showed that Ti-loading into hexagonal mesoporous silica (HMS) material has a positive effect on the activity of supported CoMo catalysts in the HDS of DBT and 4E6MDBT [22]. Regarding this later reaction, we observed that after Ti-incorporation into HMS material, additional acid-catalyzed isomerization occurs. With respect to a conventional CoMoP/Al_2O_3 sample, the CoMo/Ti-HMS catalyst with Si/Ti = 40 showed greater selectivity toward isomerization route products.

Within the above scope, this work was undertaken to study the influence of both catalyst preparation method (successive vs. simultaneous impregnation) and catalyst acidity on the reaction mechanism of 4,6-DMDBT hydrodesulphurization over CoMo catalysts performed using a batch and fixed-bed reactors. The catalysts were supported on HMS modified by both Ti and P (P/Ti-HMS). The synthesized bare supports and CoMo catalysts were characterized by N_2 adsorption–desorption isotherms (S_{BET}), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), temperature-programmed desorption (TPD) of NH_3, and DRIFTS of adsorbed NH_3 in order to correlate catalytic activity with catalyst structure.

2. Experimental

2.1. Synthesis of the pure supports and catalysts

The Ti-HMS material (Si/Ti molar ratio of 40) was prepared following a procedure similar to that described by Gotier and Tuel [23] using dodecylamine ($C_{12}H_{25}NH_2$, Aldrich 98%) as surfactant. The procedure followed during preparation has been described elsewhere [22,24]. The P-containing material (P/Ti-HMS) was prepared by impregnation of the calcined Ti-HMS material (pore filling method) with the required amount of H_3PO_4 (Fluka; 85 wt% in water). 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 zero point charges (ZPC) of the Ti-HMS and P/Ti-HMS materials were 5.1 and 4.8, respectively.

The P-free and P-containing CoMo catalysts were prepared by successive (SUC) and simultaneous (SIM) impregnations using the pore filling method. The catalysts will be labeled hereafter as SUC, SUC-P, SIM and SIM-P. Regarding the successive impregnation method, the catalyst preparation procedure involved the first impregnation with aqueous solution of $NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich 99%; pH 4). Thereafter the solid was dried at room temperature for 18 h and then at 378 K for 2 h. After this, the calcination was performed at 773 K for 4.5 h, reaching this temperature within 3.5 h. Then the second impregnation was performed with an aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ (Aldrich 98%; pH 8) followed by drying and calcination as before was carried out. In the catalysts prepared by simultaneous impregnation method (SIM, SIM-P), the cobalt and molybdenum were added from an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich 99%) and $Co(NO_3)_2\cdot 6H_2O$ (Aldrich 98%; pH 8). The solid was dried at room temperature for 18 h and then at 378 K for 2 h. Finally, calcination was performed at 773 K for 4.5 h, reaching this temperature within 3.5 h. 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 = 0.32). Both P-containing catalysts show nominal P content of 0.64 wt%.