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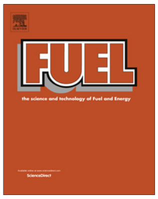

Full Length Article

Characterization and HDS activity of sulfided Co—Mo—W/SBA-16 catalysts: Effects of P addition and Mo/(Mo + W) ratio

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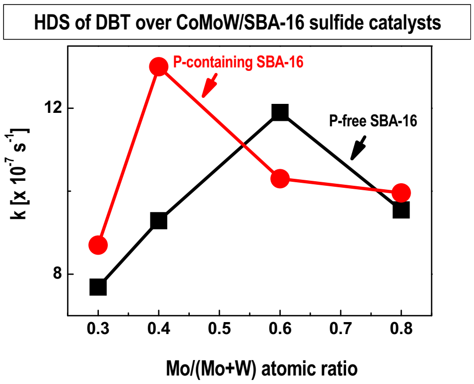
HIGHLIGHTS

- HDS activity of CoMoW/SBA-16 sulfide catalysts depends strongly on the Mo/(Mo + W) atomic ratio.
- CoMoW catalyst prepared with Mo/(Mo + W) atomic ratio of 0.4 and supported on SBA-16 modified with P was the most active.
- The most active catalyst exhibited the highest surface exposure and sulfidation degree of W species.

GRAPHICAL ABSTRACT



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ABSTRACT

Two series of SBA-16-supported Co—Mo—W ternary sulfide catalysts with atomic ratio r = Mo/(Mo + W) ranging from 0.3 to 0.7 were prepared by the simultaneous impregnation of SBA-16 and phosphated-SBA-16 substrates with metal precursors. The samples were characterized by a variety of techniques (chemical analysis, N_2 physisorption, SEM, XRD, DRS UV–vis, TPR, TPD-NH_3, Raman spectroscopy, HRTEM, XPS and coke burning). The catalytic performance was evaluated in the hydrodesulphurization (HDS) of dibenzothiophene (DBT), carried out in a batch reactor at 350 °C and 3.1 MPa of total H_2 pressure. The maximum activity at the same atomic ratio $r = 0.4$ was observed for the catalysts supported on SBA-16 modified with phosphorous (r = 0.4(P)). HRTEM evidenced that this was because different MoS_2 crystalline structures were formed: the P-free sample prepared with Mo/(Mo + W) atomic ratio of 0.6 ($r = 0.6$) exhibited the MoS_2-2H crystalline structure whereas the P-containing samples prepared with Mo/(Mo + W) atomic ratio of 0.4 (r = 0.4(P)) exhibited the interplanar distance corresponding to (003) planes of MoS_2-3R crystalline structure. Additionally, the best activity of the r = 0.4(P) sulfide catalyst was linked with the enhancement of the WS_2 species surface exposure accompanied with a larger sulfidation degree of W species (from XPS).

1. Introduction

Typically, the catalysts employed in refineries for hydrodesulphurization (HDS) of gasoline and diesel fuels are based on the

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Mo and/or W sulfides supported on γ-alumina [1]. However, those catalysts exhibit the thermodynamic limitations for deep HDS at high temperature [2]. In this sense, recent advances in technology for production of ultra-low sulfur transport fuels are based on a BRIM™ hydroprocessing technology [3]. Indeed, the catalysts based on this technology exhibit superior HDS activity and excellent stability due to formation of a large amount of so-called "brim sites", which are fully sulfur-coordinated sites [4,5]. The brim sites demonstrated possessing metallic character, which is an important feature for reactant adsorption, C—S bond scission and hydrogenation [3]. As a consequence, the catalyst possessing optimized amount of the metallic "brim sites" exhibited larger hydrogenation (HYD) functionality and enhanced rate of the direct desulfurization (DDS) reaction pathway.

It is known that the intrinsic properties of the edge Mo(W) sites depends strongly on the Mo(W) loading. Taking into account that the intrinsic properties of the edge Mo(W) sites depends strongly on the Mo(W) loading, one might expect that the Mo/(Mo + W) atomic ratio should be also important for catalyst design. The promotional effect of tungsten in the CoMo/γ—Al_2O_3 HDS catalysts with variable W loadings was investigated by Lee et al. [6]. The maximum promotion of HDS activity was found to occur at a low W content, corresponding to W/(W + Mo) = 0.025 (atomic ratio). The catalyst activity initially increased with an incease of W loading but then dropped at higher W loadings [6]. Recently, the effect of different Ni/(Ni + W) atomic ratio on the evolution of crystalline phases in unsupported Ni—W sulfide catalysts was studied by Olivas et al. [7]. From HRTEM, it was concluded that WS_2 layers start to be coated with NiS when the amount of Ni was increased. On the other hand, Bocarando et al. [8] observed that the variation of nickel concentration leads to an increase of the specific surface area. By changing the quantity of tungsten and minimization of nickel content, the catalyst exhibited preference for the HYD pathway and a slight preference for the DDS route.

It is known that the presence of support can substantially modify the intrinsic properties of the edge Mo(W) sites [9]. Among different supports, alumina is still most frequently employed as support because of its outstanding textural and mechanical properties and relatively low cost [10]. However, the alumina-supported catalysts exhibit undesirable strong metal-support interaction (SMSI) [11]. To overcome this problem, the modification of alumina surface by its phosphatation was frequently employed [11]. Explanation of the beneficial effect of phosphate loading on the support surface include: (i) decrease the metal-support interaction [12]; (ii) easier solubility of molybdate by formation of phosphomolybdate complexes [13], (iii) acting of P as a second promoter [13]; (iv) inhibition of the formation of the inactive $CoAl_2O_4$ or $NiAl_2O_4$ species [12], and (v) improved formation of Type-II Co(Ni)—Mo—S structures [1]. For alumina-supported catalysts, it was observed that phosphate anion promotes HDS activity by hydrogen activation and it acts as structural promoter of γ-Al_2O_3 by enhancing its thermal stability [14]. Interestingly, it was found that, at similar catalyst acidity, the porosity defined the catalytic response of sulfided $NiMo/Al_2O_3$ catalysts in the hydrotreating of Maya crude [15]. Conversely, at similar porosity, the catalyst acidity was the main factor influencing on the HDS activity of those catalysts [15].

As compared to alumina-supported catalysts, the modification of mesoporous siliceous materials (MSM) with phosphorus was much less studied [16–25]. The influence of P-loading and the catalyst preparation method (sequential and successive impregnation) was investigated for CoMo catalysts supported on HMS [17] and HMS-Ti [18,19]. Contrary to the catalysts prepared by successive impregnation, their counterparts prepared by co-impregnation exhibited P promotional effect. This was linked with a larger surface exposure of both Co and Mo sulfides on the catalyst surface, as demonstrated by XPS analyses [17], and a larger specific surface area of the samples prepared by the co-impregnation [18,19]. HRTEM images revealed the formation of smaller crystallites and larger stacking number of MoS_2 layers in the best catalyst prepared by co-impregnation [17]. Interestingly, the most active CoMo/P/HMS-Ti catalyst was prepared with much lower P content than that needed for the best Ti-free CoMo/P/HMS sample (0.64 vs. 1.5 wt.% of P_2O_5) [17–19].

Among different MSM materials [16–27], the effect of P loading was scarcely investigated for the SBA-15 [18,19,24] and SBA-16 systems [25–27]. The advantages of mesoporous siliceous substrates include high surface-to-volume ratio, variable framework compositions and high thermal stability. In particular, the SBA-16 exhibits a 3D cubic arrangement of mesopores ($Im3m$ space group symmetry) and each mesopore is connected with eight neighbors [26,27]. Thus, one might expect that the SBA-16 substrate, which was initially synthesized in the presence of triblock copolymer Pluronic F127 [28,29], could provide more favorable mass transfer than the unidirectional pore system of other hexagonal mesoporous substrates such as SBA-15 or HMS. Additionally, the support modification with phosphorus might affect the following aspects of the final catalyst: (i) its structural and textural properties (S_{BET}); (ii) its thermal stability, (iii) the distribution between the different Co and Mo structures in the oxide precursors and/or (iv) the morphology of MoS_2 and "Co(Ni)—Mo—S" type structures generated upon precursor sulfidation [24,25]. Recently, the state-of-the art overview of the literature on the effect of phosphorus addition to zeolites was reviewed by van der Bij and Weckhuysen [30] whereas the effect of phosphorous addition to mesoporous siliceous materials was examined by Huirache-Acuña et al. [31]. The latter revision clearly showed that there is still some controversy in literature referring to effect of support modification with phosphorous.

Within this scenario, the aim of the present investigation was to study the role of Mo/(Mo + W) ratio and effect of SBA-16 support modification with phosphorous on the activity the CoMoW/SBA-16 sulfide catalysts in the hydrodesulphurization (HDS) of dibenzothiophene (DBT) carried out in a batch reactor a 350 °C and total H_2 pressure of 3.1 MPa. This reaction was selected because DBT is a typical S-containing molecule present in the petroleum fraction of high-boiling oil or coal derived liquids. Moreover, taking to account that DBT molecule covers surface area of 8.0×12.2 Ǻ^2, one might expect the absence of any diffusion limitation for DBT molecule to entry into the porous structure of the SBA-16-supported catalysts.

2. Experimental

2.1. Support preparation

The siliceous SBA-16 mesoporous systems were synthesized according to the procedure described by Flodström and Alfredsson [32]. Briefly, for the synthesis of SBA-16 material, 8 g of Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, BASF) triblock copolymer was used as the structure directing and the corresponding amount of water (60 mL) and HCl 2 M (240 mL) were mixed under stirring. After dissolution, 24 g of TEOS was added and allowed to react at room temperature for about 24 h. Then, the mixture was transferred into polypropylene bottles and heated at 80 °C for 48 h. The solid residue was filtered, washed and dried at room temperature and then at 110 °C for 24 h. Finally, the sample was calcined at 550 °C for 6 h.

The support modification with phosphate was performed by employing the post-synthesis method (grafting). Typically, the SBA-16 was impregnated with aqueous solutions of H_3PO_4 of appropriate concentrations to obtain substrates with P_2O_5 loadings

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