



## Impact of preparation method and support modification on the activity of mesoporous hydrotreating CoMo catalysts

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### ABSTRACT

This work seeks to optimize CoMo/HMS-Ti catalysts for the hydrodesulphurization (HDS) of dibenzothiophene (DBT) by support modification with phosphorous, as well as select a suitable catalyst preparation method. The Ti-loaded hexagonal mesoporous silica ((HMS)-Ti material prepared with Si/Ti molar ratio of 40) was modified varying the phosphorus amount (0.2–1.0 wt%) and used as support to deposit oxide Co and Mo precursors by simultaneous and successive impregnation methods. Structural features of the pure supports and oxide CoMo-loaded materials have been revealed by different techniques including specific surface area ( $S_{\text{BET}}$ ), X-ray diffraction, temperature-programmed reduction (TPR), UV–vis diffuse reflectance spectroscopy (DRS UV–vis) and micro-Raman spectroscopy. Activity–structure correlations showed that the number of irregular oxide Mo<sup>6+</sup> particles, as determined by Raman spectroscopy, influenced the final catalytic response of sulphided systems. All catalysts prepared by simultaneous impregnation showed larger HDS activity than their counterparts prepared by successive impregnation, and this was linked, in part, to a higher specific surface area of the former systems. All P-containing catalysts recorded greater activity than their P-free counterparts because the presence of phosphorus on the support surface forced the formation of octahedral Co<sup>2+</sup> species and irregular oxide Mo<sup>6+</sup> particles. From the activity–structure correlation, the optimum P-loading was archived at 0.64% of P<sub>2</sub>O<sub>5</sub>. © 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Due to the strict environmental regulations imposed in many countries, the limit for sulphur content in diesel is expected to move from the currently accepted ultra-low sulphur diesel (ULSD, S < 50 ppm) to the proposed S-free diesel fuel (SFD, S < 10 ppm) by 2011 [1]. The alumina-supported Mo or W catalysts promoted by Ni or Co are traditional hydrodesulphurization (HDS) systems [2–4]. The new generations of catalysts, such as NEBULA<sup>®</sup>, which are based on the totally different concept of bulk-like materials [5] are more expensive than alumina-supported ones. Thus, the challenge is to design novel cost-effective supported catalysts.

Considering the Co(Ni)Mo(W) formulation, two approaches are mainly used in the design of new supported hydrotreating catalysts: (i) the substitution of  $\gamma$ -alumina by new supports and/or (ii) the modification of alumina by additives such as boron, fluorine or phosphorous, etc. (Refs. [6,7] and references within). Concerning the phosphorous doping of alumina, the beneficial

effect of the phosphorous addition to commercial catalysts has been recognized in many patents [8–11]. However, it was found that a large amount of phosphorous decreased HDS activity [6,7]. This is linked to a weakening of the interaction of the Mo phase with the altered support resulting in lower dispersion of the Mo phase [6,7]. A review published by Iwamoto and Grimblot [7] covers all aspects of phosphorous incorporation into the alumina-supported catalysts. Briefly, irrespectively of the support, literature reports suggest that the phosphorous effect depends on its content, nature of phosphorous precursor, method of phosphorous introduction and pH of preparative solution [7]. All these factors might affect the following aspects of the final catalyst: (i) its structural and textural properties ( $S_{\text{BET}}$ ), (ii) its thermal stability, (iii) the distribution between the different Co and Mo structures in the oxide precursors and/or (iv) the morphology and orientation of MoS<sub>2</sub> phases formed after precursor sulphidation [2,7].

Contrary to alumina-supported catalysts [7], there are only a handful of studies on the effect of phosphorous modification of hexagonal mesoporous silica (HMS) materials and their use as supports for the preparation of hydrotreating catalysts [12–15]. After P-modification, the important factors to be considered are: surface area, pore size distribution, acidity and stability during

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on-stream reaction. Owing to their textural properties, hexagonal mesoporous silicas and SBA-15 materials are very interesting because of their large specific surface areas (above  $1000 \text{ m}^2 \text{ g}^{-1}$ ), uniform-sized pores (about 4 nm), thick framework walls, small crystallite size of primary particles and complementary textural porosity [16,17]. Thus, their wide pore openings are expected to minimize the mass transfer problems of bulky reactants and products, which may be encountered in other materials such as zeolites [17]. Unfortunately, the drawback of these materials is their low stability during on-stream conditions. In order to enhance the acidity and stability of mesoporous silicas, the substitution of  $\text{Si}^{4+}$  atoms by  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$  or  $\text{Al}^{3+}$  ions in the pore walls has been intensively studied [16–22]. Similarly, the cycle-aging tests performed by Kang et al. [23] over  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalysts modified with a third additive (Si, Ti or P) showed that the addition of Ti led to the enhancement of activity and stability for hydrodesulphurization and hydrodemetallization (HDM) reactions. Their Ti-containing catalysts showed the highest coke tolerance, as deduced from the maintenance of surface activity.

For technological and economic reasons, the impregnation method is the one most frequently used for preparing heterogeneous catalysts with a high surface area in order to improve the accessibility of the active phases. However, in general, the phosphorous effect was found to be different when catalysts are prepared by sequential impregnation and simultaneous impregnation. In this sense, the thiophene HDS activity of  $\text{MoP}/\text{Al}_2\text{O}_3$  catalysts prepared by simultaneous impregnation method was reported to reach a maximum for a loading of 4 wt%  $\text{P}_2\text{O}_5$ , whereas the activity of the catalysts prepared by sequential impregnation was nearly independent of phosphate content. Nava et al. [12] recently reported that the dibenzothiophene (DBT) HDS activity of  $\text{CoMo}/\text{HMS-P}$  catalysts was clearly higher when the catalysts were prepared by simultaneous impregnation of the P/HMS supports with metal salt precursors with respect to those of sequential impregnation (with Mo being introduced first). In the former case, the optimized phosphate content on the HMS support was found to be about 1.5 wt% and the enhancement of HDS activity was linked to the larger surface exposure of both Co and Mo sulphide species [12]. Our previous study on the effect of P addition on the  $\text{CoMo}/\text{HMS-Ti}$  [22] showed that HDS activity increases up to a P-content of 0.64 wt% and then decreases. Besides this, a linear correlation was observed between the amount of molybdenum oxide species with irregular structure and the HDS activity of sulphided catalysts [22]. Such correlation might indicate that irregular  $\text{MoO}_3$  species with  $\text{Mo}=\text{O}_T$  bond could be precursors of the irregular  $\text{MoS}_2$  species active in HDS reaction [24]. The interesting question is whether the amount of such species depends on the impregnation method employed.

In order to clarify our previous results [22] and the results reported by Nava et al. [12], two series of  $\text{CoMo}$  catalysts have been prepared by co-impregnation and simultaneous impregnation methods in order to obtain catalysts with varying morphology. The synthesized  $\text{HMS-Ti}$  ( $\text{Si}/\text{Ti} = 40$ ) material was used as support and its morphology has been varied by incorporating varying amounts of phosphorous. The calcined catalysts have been characterized by XRD,  $S_{\text{BET}}$ , temperature-programmed reduction (TPR), UV–vis diffuse reflectance spectroscopy (DRS) spectroscopy and micro-Raman spectroscopy techniques, whereas the sulphided catalysts have been tested in the HDS of dibenzothiophene performed in a batch reactor at 598 K and total pressure of 5.5 MPa. DBT was selected as a model molecule, as this is a typical sulphur-containing hydrocarbon present in the petroleum fraction of high-boiling oil or coal derived liquids.

## 2. Experimental

### 2.1. Synthesis of pure materials

The titanium-containing hexagonal mesoporous silica material ( $\text{HMS-Ti}$ ;  $\text{Si}/\text{Ti}$  molar ratio of 40) was synthesized at ambient temperature employing the electrically neutral ( $S^{010}$ ) assembly pathway proposed by Tanev and Pinnavaia [25,26] and following a recipe similar to that described by Gotier and Tuel [27]. Dodecylamine ( $\text{C}_{12}\text{H}_{25}\text{NH}_2$ , Aldrich 98%) was used as surfactant. The reaction mixture was slightly modified by the addition of an auxiliary structure director mesitylene ( $\text{C}_9\text{H}_{12}$ , Aldrich 98%), as first proposed by Kresge et al. [28], and appropriate amounts of titanium(IV) butoxide (97%, Aldrich) dissolved in tetraethyl orthosilicate (TEOS, 97% Aldrich). The reaction products were filtered, washed with distilled water and dried at room temperature for 24 h, followed by drying at 378 K for 2 h. Subsequently, the samples were calcined at 823 K for 3.5 h in air, with a heating rate of  $2.5 \text{ K min}^{-1}$ . The phosphorus-containing  $\text{HMS-Ti}$  materials (coded hereafter as  $\text{P}(x)/\text{HMS-Ti}$ ) were prepared by impregnation of the calcined  $\text{HMS-Ti}$  material with an aqueous solution of phosphoric acid ( $\text{H}_3\text{PO}_4$ , Fluka 85 wt% in water) using the pore-filling method. The concentration of phosphoric acid was adjusted to obtain the nominal P-content of 0.2, 0.42, 0.64, 0.86 and 1.0 wt%. The solids were dried at room temperature for 16 h and then at 378 K for 2 h, and finally calcined at 773 K for 4.5 h, reaching this temperature in 3.5 h.

### 2.2. Catalysts preparation

Two series of binary  $\text{CoMo}$  catalysts were prepared by successive (SUC) and simultaneous (SIM) impregnation of the corresponding support using the pore-filling method. The pH zero point charges (ZPC, determined by mass titration) of the  $\text{HMS-Ti}$  and  $\text{P}(x)/\text{HMS-Ti}$  materials were in the range 4.6–5.2. For the SUC series, the solids were impregnated firstly with an aqueous solution of ammonium heptamolybdate [ $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , Aldrich 99%; pH 4]. The impregnate samples were dried at room temperature for 18 h and then at 378 K for 2 h, followed by calcination at 773 K for 4.5 h, reaching this temperature within 3.5 h. Monometallic Mo samples were then impregnated with the solution of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2$ , Aldrich 98%; pH  $\approx$  6) followed by drying and calcination as above. Employing the simultaneous impregnation method, the support was impregnated with the aqueous solution containing both cobalt nitrate and ammonium heptamolybdate salts. Drying and calcination were performed as above for the samples prepared by successive impregnation. All  $\text{CoMo}$ -loaded samples were prepared with nominal contents of 3.0 and 9.0 wt% of Co and Mo, respectively ( $\text{Co}/(\text{Co} + \text{Mo})$  atomic ratio = 0.32). The chemical composition and labelling of the catalysts is given in Table 1.

### 2.3. Support/catalyst characterization

The X-ray patterns were recorded on a Rigaku 2100 diffractometer, using a monochromatic  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1541 \text{ nm}$ ) in the  $2\theta$  range of  $0.15\text{--}80^\circ$  at a step of  $0.02^\circ$ .

The textural properties of the sulphided catalysts were determined by  $\text{N}_2$  adsorption–desorption isotherms at 77 K with an ASAP 2000 Micromeritics device. Prior to the experiments, the supports and *ex situ* sulphided catalysts (10%  $\text{H}_2\text{S}/\text{H}_2$ , 673 K, 2 h) were degassed at 543 K in a vacuum for 5 h. The volume of adsorbed  $\text{N}_2$  was normalized to standard temperature and pressure. Specific surface area ( $S_{\text{BET}}$ ) was calculated by the BET equation applied to the range of relative pressures  $0.05 < P/P^0 < 0.30$ . Average pore

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