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Efficient hydrodesulfurization catalysts based on Keggin polyoxometalates

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ABSTRACT

Bulk and supported hydrodesulfurization catalysts based on Mo and W and containing Co or Ni as promoters and phosphorus as a modifier are prepared through the polyoxometalate route using Keggin type phosphomolybdates and phosphotungstates and tested in the HDS of thiophene at 350–400 °C and 1 bar pressure. The corresponding oxidic pre-catalysts retain intact Keggin structure of the parent polyoxometalates and possess Brønsted and Lewis acidity. In the course of sulfidation, the oxidic pre-catalysts transform into an active sulfidic phase with the loss of Keggin structure and catalyst acidity. Catalyst activity increases in the order of supports: $SiO_2 < TiO_2 < \gamma\text{-}Al_2O_3$. $CoMoP/\gamma\text{-}Al_2O_3$ catalyst prepared through the polyoxometalate route shows higher HDS activity and butene selectivity than industrial catalyst of comparable composition. The results indicate that polyoxometalate catalyst preparation route can be considered a performance enhancement methodology for HDS catalysis.

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1. Introduction

Hydrodesulfurization (HDS) driven by ever stringent environmental legislation is one of the most important processes of the petroleum industry. It removes sulfur from oil fractions by catalytic hydrotreatment to upgrade the quality of fuels [1,2]. Present day HDS technology largely employs sulfided $Co(Ni)Mo/\gamma\text{-}Al_2O_3$ catalysts [1–3]. These catalysts, although durable, are not sufficiently active and selective to achieve the required very low sulfur content in transportation fuels. Consequently, research into improvement of HDS catalysts continues all over the world. Recent developments include new methods of preparation of Co(Ni)Mo catalysts such as chemical vapor deposition improving the dispersion of active phases [4], addition of phosphorus [4] and citric acid [5], new active phases for HDS catalysts, e.g., noble metals [6], transition metal carbides [7], nitrides [8] and phosphides [9,10].

The $Co(Ni)Mo/Al_2O_3$ HDS catalysts are obtained by in-situ sulfidation of an oxidic precursor (pre-catalyst), which is usually prepared by impregnation of γ-alumina support with appropriate

Mo and Co(Ni) compounds from aqueous solution, most typically using ammonium heptamolybdate and adding Co(II) or Ni(II) nitrate as a promoter, often with addition of phosphoric acid as a modifier [1–3]. Depending on the pH and P and Mo concentrations, such impregnation solutions contain P–Mo heteropoly anions such as $P_2Mo_5O_{23}{}^{6-}$, $PMo_9O_{31}(OH)_3{}^{6-}$, $PMo_{11}O_{39}{}^{7-}$, $PMo_{12}O_{40}{}^{3-}$ and $P_2Mo_{18}O_{62}{}^{6-}$ [2]. On the other hand, heteropoly compounds, especially molybdophosphates incorporating Co(II) and/or Ni(II) promoters as counter cations or addenda atoms, can be used directly for the preparation of oxidic precursors for HDS catalysts [11–23]. In the past decades, heteropoly compounds, also known as polyoxometalates (POM) [24], have attracted much interest as catalysts of various reactions and as such found application in several large-scale industrial processes [25–27]. Various types of heteropoly compounds have been used for the preparation of HDS pre-catalysts, the common Keggin type heteropoly compounds comprising heteropoly anions of the composition $[XM_{12}O_{40}]^{n-}$ ($M = Mo^{6+}$, W^{6+}; $X = P^{5+}$, Si^{4+}) most frequently applied. Catalyst preparation methodology through the polyoxometalate route has important advantages such as (i) incorporation of all the elements required for HDS catalyst within heteropoly compound thus allowing the preparation of oxidic precursor in a single impregnation step, (ii) close interaction between the key elements in the pre-

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catalyst and sulfided catalyst and (iii) extraneous counter ions can be excluded from the impregnation solution to reduce waste [16,17].

In this work, which follows up our recent study on polyoxometalate NiMo/SiO$_2$ HDS catalysts [23], we prepared bulk and supported Co and Ni phosphomolybdate and phosphotungstate catalysts via the POM route from Co(II) and Ni(II) salts of phosphomolybdic H$_3$[PMo$_{12}$O$_{40}$] and phosphotungstic H$_3$[PW$_{12}$O$_{40}$] heteropoly acids (HPA) and tested for their activity in the HDS of thiophene, which is relevant to the hydrotreating of FCC naphtha [1,2]. Our aim was to investigate the effect of POM composition and catalyst support on the catalytic activity, the role of Brønsted and Lewis acidity of the pre-catalyst and to follow the evolution of pre-catalyst in the course of HDS reaction. It is demonstrated that CoMo/Al$_2$O$_3$ catalyst prepared through the POM route has the potential of reducing hydrogen consumption in HDS process and the loss of high octane alkenes in the final gasoline pool. Therefore, the POM catalyst preparation route can be considered a performance enhancement methodology for HDS catalysis.

2. Materials and methods

2.1. Chemicals and materials

Phosphomolybdic and phosphotungstic acid hydrates (H$_3$[PMo$_{12}$O$_{40}$]·12H$_2$O and H$_3$[PW$_{12}$O$_{40}$]·28H$_2$O), Ni(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O and thiophene (99%) were from Sigma–Aldrich. Catalyst supports Aerosil 300 silica (S_{BET} = 300 m2 g−1), P25 titania (anatase/rutile = 3:1, S_{BET} = 51 m^2 g^{-1}) and Aluminiumoxid C γ-alumina (S_{BET} = 120 m^2 g^{-1}) were from Degussa.

2.2. Preparation of HDS pre-catalysts

Bulk Ni(II) and Co(II) salts of H$_3$[PMo$_{12}$O$_{40}$] and H$_3$[PW$_{12}$O$_{40}$] with M(II)/HPA molar ratios of 1:1 and 1.5:1 (i.e., M(II)/Mo(VI) or M(II)/W(VI) ratio of 1:12 and 1:8) were prepared by dissolving the HPA in a minimum amount of deionized water at room temperature followed by addition of the required amount of the corresponding metal nitrate (Co(NO$_3$)$_2$ or Ni(NO$_3$)$_2$) with stirring. Excess water was distilled off using a rotary evaporator and the resulting residue oven dried at 100 °C overnight. The solids were calcined in air at 350 °C for 2 h with a heating rate of 10 °C min^{-1} and finally ground into a powder of 45–180 μm particle size.

Supported H$_3$[PMo$_{12}$O$_{40}$] and H$_3$[PW$_{12}$O$_{40}$] pre-catalysts with 30 wt% HPA loading based on anhydrous HPA were prepared by wet impregnation of support (γ-Al$_2$O$_3$, SiO$_2$ or TiO$_2$) with an aqueous solution of HPA at room temperature with stirring for 2 h. Solid residues were isolated by rotary evaporation, oven dried at 100 °C and air calcined at 350 °C for 2 h at a heating rate of 10 °C min^{-1}. The pre-catalysts were then ground into a powder with a particle size of 45–180 μm. γ-Al$_2$O$_3$-supported Ni(II) and Co(II) phosphomolybdate and phosphotungstate pre-catalysts with M(II)/HPA molar ratios of 1:1 and 1.5:1 and 30 wt% POM loading were prepared similarly by impregnation of γ-Al$_2$O$_3$ with HPA and Ni(NO$_3$)$_2$ or Co(NO$_3$)$_2$ in required quantities from aqueous solution. The slurry was stirred for 2 h at room temperature followed by rotary evaporation to remove water. The residue was dried overnight at 100 °C and air calcined at 350 °C for 2 h resulting in lightly colored powders, which were ground into 45–180 μm particle size.

Industrial CoMo/Al$_2$O$_3$ pre-catalyst (ICI Catalyst 41–6, Co/Mo = 0.62 mol/mol), containing CoO (4.0%), MoO$_3$ (12.0%), SiO$_2$ (1.0%) and γ-Al$_2$O$_3$ (balance) [3], was crushed and sieved to a powder with a particle size of 45–180 μm. It had a surface area of 220 m^2 g^{-1} and a pore volume of 0.6 cm^3 g^{-1} [3]. For comparison with the industrial ICI 41–6 catalyst, 15%Co$_{1.5}$[PMo$_{12}$O$_{40}$]/Al$_2$O$_3$

pre-catalyst containing similar Mo loading (13% MoO$_3$) but a lower Co/Mo molar ratio of 0.125 was prepared by grinding 30%Co$_{1.5}$[PMo$_{12}$O$_{40}$]/Al$_2$O$_3$ with equal quantity of γ-Al$_2$O$_3$ support. The powder was pressed into a pellet then crushed to a 45–180 μm catalyst powder.

2.3. Techniques

Catalyst surface area, pore volume and pore size were determined on a Micromeritics ASAP 2010 instrument by measuring nitrogen adsorption at −196 °C. Before measurement the catalysts were pre-treated at 240 °C in vacuum. Powder X-ray diffractograms were collected on a PANalytical Xpert diffractometer using Cu Kα radiation (λ = 0.1542 nm). ICP-AES analysis of sulfur was carried out on a Spectro Ciros emission spectrometer. Fourier transform infrared (FTIR) spectra of pre-catalysts and spent catalysts were recorded on a Nicolet Nexus FTIR spectrometer using powdered catalyst mixtures with KBr. In FTIR spectra of γ-Al$_2$O$_3$-supported catalysts, the absorption of support was subtracted using a γ-Al$_2$O$_3$-KBr mixture as the background. DRIFT (diffuse reflectance infrared Fourier transform) spectra of adsorbed pyridine were taken on the same spectrometer. Catalyst samples were ground with KBr (1–10 wt% in KBr) and pre-treated at 150 °C/10^{-3} kPa for 1 h. The samples were then exposed to pyridine vapor at room temperature for 1 h, followed by pumping out at 150 °C/10^{-3} kPa for 1 h to remove physisorbed pyridine. The DRIFT spectra of adsorbed pyridine were recorded at room temperature at a 4 cm^{-1} resolution. Temperature programmed reduction (H$_2$-TPR) of catalysts was carried out on a Micromeritics TPD/TPR 2900 apparatus equipped with a thermal conductivity detector. Catalyst samples (20–30 mg) were heated up to 950 °C at a rate of 10 °C min^{-1} in a H$_2$–N$_2$ (5:95) gas flow (60 mL min^{-1}).

2.4. Catalyst testing

The HDS of thiophene was carried out in flowing H$_2$ at 350–400 °C under atmospheric pressure in a down-flow quartz fixed-bed reactor (9 mm i.d.) with online GC analysis (Varian 3800 instrument with a 30 m × 0.25 mm × 0.5 μm HP-INNOWAX capillary column and a flame ionization detector) (Supplementary material, Fig. S1). For more accurate offline GC analysis of C$_1$–C$_4$ hydrocarbon products, a 60 m × 0.32 mm GS-GasPro capillary column was used, which allowed for complete separation of these hydrocarbons. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. Thiophene was fed by passing hydrogen flow controlled by a Brooks mass flow controller through a stainless steel saturator which held liquid thiophene at 0 °C to keep the chosen thiophene partial pressure of 2.63 kPa in hydrogen flow [28]. The reactor was packed with 0.2–0.4 g of pre-catalyst powder of 45–180 μm particle size. The gas feed entered the reactor at the top at a flow rate of 10–20 mL min^{-1} (space time W/F = 152 608 g h mol^{-1}, where W (g) is the catalyst weight and F (mol h^{-1}) is the molar flow rate of thiophene). Prior to reaction monitoring, the pre-catalysts were sulfided in situ in the feed flow containing thiophene (2.63 kPa) in H$_2$ for 1 h at the reaction temperature. The downstream flow was analyzed by the on-line GC to continuously monitor thiophene conversion. Product selectivity was determined at selected times on stream by offline GC analysis using the GS-GasPro capillary column. The selectivity was defined as the percentage of thiophene converted into a particular product and quoted in mol.%. The mean absolute percentage error in conversion and selectivity was ≤5% and the carbon balance was maintained within 95%.