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Effect of ethyleneglycol addition on the properties of P-doped NiMo/Al_2O_3 HDS catalysts: Part I. Materials preparation and characterization

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ABSTRACT

Phosphorous-doped NiMo/Al_2O_3 hydrodesulfurization (HDS) catalysts (nominal Mo, Ni and P loadings of 12, 3, and 1.6 wt%, respectively) were prepared using ethyleneglycol (EG) as additive. The organic agent was diluted in aqueous impregnating solutions obtained by MoO_3 digestion in presence of H_3PO_4, followed by $2NiCO_3{\cdot}3Ni(OH)_2{\cdot}4H_2O$ addition. EG/Ni molar ratio was varied (1, 2.5 and 7) to determine the influence of this parameter on the surface and structural properties of synthesized materials. As determined by temperature-programmed reduction, ethyleneglycol addition during impregnation resulted in decreased interaction between deposited phases (Mo and Ni) and the alumina carrier. Dispersion and sulfidability (as observed by X-ray photoelectron microscopy) of molybdenum and nickel showed opposite trends when incremental amounts of the organic were added during catalysts preparation. Meanwhile Mo sulfidation was progressively decreased by augmenting EG concentration in the impregnating solution, more dispersed sulfidic nickel was evidenced in materials synthesized at higher EG/Ni ratios. Also, enhanced formation of the so-called "NiMoS phase" was registered by increasing the amount of added ethyleneglycol during simultaneous Ni–Mo–P–EG deposition over the alumina carrier. That fact was reflected in enhanced activity in liquid-phase dibenzothiophene HDS (batch reactor, $T = 320\,^{\circ}\mathrm{C}$, $P = 70\ \mathrm{kg/cm^2}$) and straight-run gas oil desulfurization (steady-state flow reactor), the latter test carried out at conditions similar to those used in industrial hydrotreaters for the production of ultra-low sulfur diesel ($T = 350\,^{\circ}\mathrm{C}$, $P = 70\ \mathrm{kg/cm^2}$, LHSV = 1.5 $\mathrm{h^{-1}}$ and H_2/oil = 2500 $\mathrm{ft^3/bbl}$).

1. Introduction

Fulfilment of very stringent regulations regarding S content (i.e., ~10–15 ppm for diesel) in fuels obtained from oil-derived middle distillates hydrotreatment requires improved processes and more active hydrodesulfurization (HDS) catalysts [1]. In this context, the use of various types of organic additives during catalyst preparation has resulted in materials of enhanced S removal activity. For example, different beneficial effects have been related to chelators addition due to their strong interaction with the promoter metals (Ni and Co) to deposit [2]. It has been determined [2,3] that those organic compounds delay promoter sulfidation to temperatures high enough to permit efficient integration of sulfidic Co or Ni species to then already formed MoS_2 (or WS_2), thus optimizing promoted phases ("NiMoS" or "CoMoS") formation. It could be stated that the origin of the enhanced HDS activity of catalysts prepared in presence of chelating ligands is rather well-established [4].

Regarding the effect of glycols as HDS catalysts additive the scenario is different. It could be said that, so far, there is no general agreement about the origin of their beneficial influence on the hydrodesulfurizating properties of otherwise conventional CoMo or NiMo alumina-supported materials. Although utilization of those organic additives in improving hydrotreating catalysts has been previously patented [5,6] just a few reports related to their use in improving those formulations are available in the open literature. Prins and co-workers [7] synthesized Al_2O_3-supported CoMo catalysts (doped with phosphate) in

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presence of tri-ethyleneglycol, ethyleneglycol and tri-ethyleneglycol dimethyl ether, the resulting materials being tested in thiophene HDS. The catalysts containing either ethyleneglycol or tri-ethyleneglycol and phosphorous (simultaneously impregnated with Mo and Co) showed a ~70% increase in activity, as compared to the material with no additives. Even more, a synergistic effect of simultaneous glycols and P addition was observed, the influence of both agents on effectively promote HDS activity being higher when added together. It was proposed that the organic compound interacts with both basic OH groups and coordinatively unsaturated Al^{3+} sites on the alumina surface preventing decomposition of Co diphosphopentamolybdate complexes (present in the impregnating solution) during their deposition on the carrier. Thus, close proximity of Co and Mo in those impregnated complexes could result in enhanced formation of the so-called ‘‘CoMoS phase’’ during sulfiding. The aforementioned authors also registered increased molybdenum sulfidability in $CoMo/Al_2O_3$ material impregnated in presence of tri-ethyleneglycol [8]. Other authors [9] have also proposed optimized promoter integration to MoS_2 phase in HDS catalysts prepared in presence of glycols as origin of important improvements in catalytic activity (in tetraline hydrogenation and 4,6-dimethyldibenzothiophene HDS), as to that of conventional formulations with no organic additive. In this case, the di-ethyleneglycolbutylether added (at Mo/organic additive = 0.75) seemed to slow-down Mo and Co sulfidation at temperatures up to 200 °C, its influence (differently to that observed for chelating ligands) being more important on the former. Interestingly, those authors deposited the organic additive on a previously impregnated industrial alumina-supported Co–Mo–P formulation. Then, the role of glycols must have been different to that they exerted when simultaneously impregnated with Mo, Co and P [7,8]. Other group reported [10] that toluene hydrogenation was more strongly enhanced over $CoMo/Al_2O_3$ formulations (with or without phosphorous) when the additive (tri-ethyleneglycol) was impregnated on dried impregnated precursors, instead of on the corresponding calcined materials. Iwamoto et al. [11] also determined a beneficial effect of simultaneously impregnating polyethylene glycol (PEG), Mo and Co on alumina carrier. The prepared materials had higher activity (in thiophene, dibenzothiophene and light gas oil HDS) than a reference conventional sulfided catalyst of similar composition prepared with no organic agent. After characterizing the solids by various instrumental techniques the authors concluded that polyethylene glycol addition promoted better sulfided phases dispersion by hindering their sintering. In the opposite to that carried out during the other aforementioned investigations, Iwamoto et al. [11] submitted the impregnated solids (modified by PEG addition) to calcining (at 550 °C) precluding any effect of the organic additive (which was thus decomposed by combustion) during the sulfiding of either cobalt or molybdenum. Considering that reported in the pertinent literature, it could be concluded that the magnitude of the effect of glycols on HDS properties depends on the preparation step where they are added. Also, it must not be discarded that the positive influence of those organic species on the HDS activity of corresponding catalysts could be related to several independent phenomena.

To try to contribute in elucidating the effect of ethyleneglycol (EG) addition on HDS catalyst properties, in this work we prepared P-doped $NiMo/Al_2O_3$ materials using that additive at various amounts (EG/Ni molar ratios of 1, 2.5 and 7). Materials characterization included N_2 physisorption, X-ray diffraction, thermal analysis (TG and DTA), Fourier transformed infrared spectroscopy (FTIR) and temperature-programmed reduction. Sulfided catalysts were studied by high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. Catalytic activity of selected samples was tested in both model compound (dibenzotiophene) HDS and real feedstock (straight-run gas oil) desulfurization.

2. Experimental

2.1. Catalysts synthesis

High surface area alumina was obtained from calcining a commercial boehmite (Versal 200 from Euro Support) at 500 °C (5 h). The textural properties (as determined by N_2 physisorption) of the final Al_2O_3 carrier were surface area (S_g) = 307 m^2/g, pore volume (V_p) = 0.9 cm^3/g and average pore diameter (from $4 \times V_p/S_g$) ~12 nm. Texture of this support seemed to be especially suitable for its application as carrier of catalysts for the hydrotreatment of middle distillates [12]. Previously to impregnation, the support was dried at 120 °C (2 h) to eliminate physisorbed water. Pore-filling simultaneous impregnation was carried out by using an aqueous solution (pH ~ 1.4) prepared from digestion (at ~80 °C under vigorous stirring) of MoO_3 99.5 wt% (PQM) in presence of H_3PO_4 85.3 wt% (Tecsiquim). After 2 h, a yellow transparent solution was observed. $2NiCO_3{\cdot}3Ni(OH)_2{\cdot}4H_2O$ (Sigma–Aldrich) was then added, heating being maintained for 2 h. Ni concentration corresponded to Ni/(Ni + Mo) = 0.29 whereas the ratio $P_2O_5/(NiO + MoO_3)$ = 0.1 (mass ratio) was fulfilled [13]. Molar concentrations of Mo, Ni and P in impregnating solutions corresponded to 1.67, 0.68 and 0.69, respectively. A transparent emerald green solution was thus obtained. Ethyleneglycol (EG, J.T. Baker) at various EG/Ni molar ratio (EG/Ni = 1, 2.5 and 7) was added to the final impregnating solution which pH was essentially not altered after this step (final pH ~1.6). Nominal Mo, Ni and P loadings corresponded to 12, 3 and 1.6 wt% in final catalyst, respectively. After impregnation materials were dried at 120 °C (2 h). Calcining was avoided to preserve organic additive integrity. Samples were identified by using the NMP(*x*) key where ‘‘*x*’’ represented the EG/Ni ratio. A reference material with no organic additive, sample NMP(0), was also synthesized. This solid was dried at 120 °C (2 h), calcining being avoided. Sulfided catalysts were obtained by submitting impregnated precursors to treatment at 400 °C (heating rate 6 °C/min) under H_2/H_2S (Praxair) at 50 ml/min/6 ml/min during 2 h.

2.2. Materials characterization

Textural properties of various materials were determined by N_2 physisorption (at −196 °C), in a Micromeritics ASAP 2000 apparatus. Surface area and pore size distribution of the alumina support were determined by BET and BJH (N_2 adsorption branch data) protocols, respectively. Structural order was studied by powder X-ray diffraction (Siemens D-500 Kristalloflex, Cu Kα radiation, λ = 0.15406 nm, 35 kV, 25 mA). Thermal analyses were carried out with a Netzch Thermische Analize, STA 409 EP apparatus under static air atmosphere. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of various materials was performed by using a Bruker TENSOR 27 instrument. Samples (in KBr) were placed in a cup inside a diffuse reflectance unit. Spectra were averaged over 40 scans in the 210–4000 cm^{-1} range to a nominal 4 cm^{-1} resolution. Spectra taken are presented in the Kubelka–Munk format. Temperature-programmed reduction (TPR) experiments were conducted by using an Altamira 2000 equipment. Samples of as-made (dried) Ni–Mo–P/Al_2O_3 impregnated precursors, either with or without glycol, were put in a quartz reactor. Circa 50 mg of materials ground at particle size that passed through U.S. Mesh 80 (180 μm) were heated from 30 to