



# Comparison of citric acid and glycol effects on the state of active phase species and catalytic properties of CoPMo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalysts



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## ABSTRACT

CoPMo/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared using H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> and Co complexes with citric acid (CA) or non-complexing organic additives such as ethylene glycol (EG), diethylene glycol, triethylene glycol (TEG), glycerol, and a mixture of EG and CA. The catalysts were characterized by low-temperature N<sub>2</sub> adsorption, Raman spectroscopy, thermogravimetric analysis, temperature-programmed reduction, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy. The prepared samples were tested in hydrodesulfurization (HDS) of dibenzothiophene (DBT). The addition of either CA or glycols led to several beneficial effects such as weakening of the slab-support interaction at enhancing the promotion degree, dispersion and stacking number of the CoMoS species. It has been shown that the promotion degree of CoMoS edges increased with a pore volume gain by the additive-impregnated catalysts after their sulfidation. Catalysts with CA, TEG or the EG-CA mixture demonstrated higher activity in DBT HDS. Probable reasons for the found relationships are discussed.

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## 1. Introduction

Manufacture of clean fuels has been so far one of the most challenging issues in a modern oil refinery. Varying feedstock quality and unconventional hydrocarbon resources involved in hydroprocessing call for more active hydrotreating (HDT) catalysts to enhance optimization and energy efficiency of hydroprocessing. Hydrodesulfurization (HDS) of petroleum feedstock is generally performed with Co(Ni)Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, in which the Co(Ni)MoS active phase consists of nanosized MoS<sub>2</sub> slabs decorated with Co(Ni) atoms [1]. Active catalysts are obtained by sulfidation of a supported oxidic precursor. The latter is typically prepared by the incipient wetness impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with an aqueous solution containing Co and Mo, followed by a drying and a calcination step [2,3]. The catalyst preparation is a key step to reach high activities and to avoid any loss of cobalt atoms to inactive species like CoAl<sub>2</sub>O<sub>4</sub> and bulk CoS<sub>x</sub>.

During the last decade, many improvements have been made to increase the active phase portion in Co(Ni)Mo/Al<sub>2</sub>O<sub>3</sub> catalysts.

Heteropolyanions (HPAs) as precursors offer new opportunities for improving catalysts' activity [4]. Various types of HPAs with Keggin [XM<sub>12</sub>O<sub>40</sub>]<sup>n-</sup> and lacunary Keggin [XM<sub>9-11</sub>O<sub>34-39</sub>]<sup>n-</sup> [5–15], Anderson [XM<sub>6</sub>O<sub>24</sub>H<sub>6</sub>]<sup>n-</sup> [16–31], Strandberg [X<sub>2</sub>M<sub>5</sub>O<sub>23</sub>]<sup>n-</sup> or Waugh [Ni<sub>9</sub>MoO<sub>32</sub>]<sup>6-</sup> structures [32,33] (where M(M') is a metallic cation and X a non-metallic one) have been reported. These generally let afford better catalytic performance than their counterparts based on conventional precursors due to improved sulfidation allowed by a better dispersion of the oxidic precursor even at high metallic loadings [4]. Cobalt salt of the dimer of Anderson-type HPA Co<sub>2</sub>Mo<sub>10</sub>O<sub>39</sub>H<sub>4</sub><sup>6-</sup> is an interesting starting material to introduce both metals into the same entity, without foreign counterions and with a Co/Mo ratio equal to 0.5 corresponding to the optimum Co/Mo ratio for conventional HDT catalysts [16,23,34,35]. The association of Co and Mo at the molecular level in the same HPA preserved after drying of the catalyst ensured efficiency for the promoting effect with a larger CoMoS active phase. This HPA-based system was further improved by a simultaneous use of Co<sub>2</sub>Mo<sub>10</sub>HPA and chelating agents [36–38]. Also, the simultaneous use of Keggin HPA and Co(Ni)-chelates for preparation of HDT catalysts was investigated in a few other works [39–42]. The CoMoS active phase species were formed more selectively when Co<sub>2</sub>Mo<sub>10</sub>HPA and Co-chelate complexes simultaneously used for

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**Table 1**  
Composition and textural properties of prepared Co-Add-PMo catalysts in oxide and sulfided states.

Catalyst	Atomic ratio Co/Mo	Content in the catalyst (wt.%)			Textural characteristics of oxide (sulfided) samples			Pore volume distribution for oxide (sulfided) samples (%)			
		Mo	Co	Carbon	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (Å)	<40 Å	40–80 Å	80–170 Å	>170 Å
Alumina	–	–	–	–	187	0.57	80	0	54	44	3
Co-PMo	0.50	12.0	3.7	0.2	149 (127)	0.25 (0.32)	104 (64)	4 (6)	29 (51)	64 (35)	3 (8)
Co-CA-PMo	0.49	12	3.6	1.8	132 (277)	0.14 (0.30)	102 (38)	6 (24)	27 (32)	61 (35)	6 (9)
Co-EG-PMo	0.50	12	3.7	0.6	74 (156)	0.23 (0.26)	104 (64)	0 (7)	31 (45)	66 (39)	3 (8)
Co-DEG-PMo	0.49	12	3.7	1.1	78 (171)	0.24 (0.33)	102 (64)	0 (9)	35 (38)	60 (44)	4 (9)
Co-TEG-PMo	0.50	12	3.6	1.4	56 (203)	0.18 (0.34)	102 (48)	5 (15)	32 (50)	58 (28)	4 (7)
Co-Gly-PMo	0.51	12	3.7	0.9	57 (214)	0.19 (0.33)	102 (64)	0 (8)	29 (40)	67 (45)	4 (8)
Co-EG-CA-PMo	0.51	12	3.7	2.5	25 (276)	0.09 (0.28)	104 (38)	0 (31)	22 (33)	70 (30)	7 (6)

catalyst preparation [37]. It was attributed to delaying sulfidation of promoter atoms at low temperature due to formation of stable complexes with chelating agents. However, the Co-chelate addition significantly changed the active phase morphology due to different interactions between precursors and support surfaces in each catalyst. Citric acid (CA)- and tartaric acid-containing catalysts showed higher activity than the nitrilotriacetic acid- and ethylenediaminetetraacetic acid-containing counterparts. It was shown that high catalytic performance was more directly related to the (Co/Mo) ratio at the edge of MoS<sub>2</sub> slabs. More recently, we reported [38] that loading of Co and Mo from Co<sub>2</sub>Mo<sub>10</sub>HPA and Ni from nickel-citrate led to formation of ternary NiCoMoS/Al<sub>2</sub>O<sub>3</sub> catalysts with enhanced performance as compared to CoMoS/Al<sub>2</sub>O<sub>3</sub> analogs. It was achieved due to the co-promotion effect of both metals and probably due to sequential sulfidation of Co<sub>2</sub>Mo<sub>10</sub>HPA and Ni-citrate precursors with formation of the NiCoMoS phase having CoMoS and NiMoS active sites or mixed NiCoMoS sites that are readily accessible by the reactants.

Not long ago, Costa et al. [36] investigated the use of additive-impregnated dried catalysts on a series of various CoMo/Al<sub>2</sub>O<sub>3</sub> solids prepared by the conventional route, Co<sub>2</sub>Mo<sub>10</sub>Co, and a solution containing P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub><sup>6-</sup> and Co<sup>2+</sup> (Co/Mo = 4). The additive impregnation step was performed on the dried solid by the incipient wetness impregnation with an aqueous solution of triethylene glycol (TEG) with a TEG/Mo molar ratio close to 0.75. It was reported that formation of the “CoMoS” phase was needed but not sufficient to explain catalytic performance of all studied catalysts. Catalytic activity in toluene hydrogenation of additive-free dried, additive-impregnated dried and calcined catalysts directly correlates with the number of mixed Co–Mo sites present at the MoS<sub>2</sub> edges. Using TEM, XPS and DFT calculations the authors concluded that the organic additive was used to produce a higher number of mixed Co–Mo sites rather than to create different active sites.

The aim of the research was to compare effects of CA as a chelating agent and of glycols as non-complexing organic additives on the state of active phase species and catalytic properties of CoPMo/Al<sub>2</sub>O<sub>3</sub> HDT catalysts prepared with Keggin-type H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> HPA frequently used as an alternative to classical ammonium heptamolybdate.

## 2. Experimental

### 2.1. Preparation of Co-Add-PMo catalysts

Co-Add-PMo catalysts were prepared by the incipient wetness technique via the impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Engelhard) of 0.25–0.5 mm with acidic aqueous solutions (pH  $\approx$  3–4) containing the required amounts of 12-molybdophosphoric heteropolyacid H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> × 3H<sub>2</sub>O, Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O or CoCO<sub>3</sub> (Aldrich) and organic additives with molar ratios Add/Mo = 1/1 and Co/Mo = 0.5. CA, ethylene glycol (denoted as EG), diethylene glycol (denoted

as DEG), TEG, glycerol (denoted as Gly), and the EG – CA mixture with the equal molar ratio were purchased in Aldrich and were used as organic additives for catalyst preparation. All impregnated solids were aged at room temperature overnight and subsequently air-dried at 110 °C for 10 h without calcination. The content of Mo and Co in the catalysts was measured using an EDX800HS analyzer (Table 1).

To analyze the catalysts in the active state, the obtained oxidic samples were sulfided. A mixture of dimethyldisulfide (DMDS, 2 wt% of sulfur) and decane at 3.5 MPa was utilized in a stepwise procedure conducted over 10 h at 240 °C and 8 h at 340 °C.

### 2.2. Characterization of the catalysts

#### 2.2.1. Textural characteristics

The textural characteristics of the prepared catalysts were measured by low-temperature N<sub>2</sub> adsorption on a Quantachrome Autosorb-1 porosimeter. Before the adsorption measurement, the sulfided samples were outgassed under vacuum (<10<sup>-1</sup> Pa) at 350 °C for 4 h. Specific surface area (SSA) was calculated using the BET method. The total pore volume and pore size distribution were found from a desorption branch of the isotherm using the BJH model.

#### 2.2.2. Raman spectroscopy

The Raman spectra of the samples were recorded using a Senterra (Bruker) laser Raman spectrometer ( $\lambda$  = 532 nm) at room temperature. The spectra were recorded from 100 to 3300 cm<sup>-1</sup> with an accuracy of 2 cm<sup>-1</sup>. However, due to the intense background signal of alumina supports, only the 200–1100 cm<sup>-1</sup> spectral range characteristic of the Mo–O stretching vibrational mode is presented.

#### 2.2.3. Thermogravimetric analysis

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the oxide Co-Add-PMo catalysts were carried out using a NETZSCH STA 4449 F3 Jupiter apparatus. TGA-DSC curves were recorded in flowing air in the range from room temperature to 600 °C (heating rate 10 °C/min). For analysis, 20 mg of a sample was loaded in a corundum crucible; calcined alumina was used as a reference sample.

#### 2.2.4. Temperature-programmed reduction (TPR)

The TPR analysis of the catalysts in oxide and sulfide states was carried out using a thermal conductivity detector (TCD). For analyzing the catalysts in oxide state, the samples were calcined at 400 °C for 4 h to remove Add and water, hindering TPR measurements. For analyzing the catalysts in sulfide state, the dried samples were sulfided in a quartz reactor at 400 °C for 4 h with a mixture of H<sub>2</sub>S and H<sub>2</sub> (10 vol.% of H<sub>2</sub>S), heating rate 5 °C/min, then cooled to room temperature and passed over to the TPR analysis without a contact

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