



The effect of organic additives and phosphoric acid on sulfidation and activity of (Co)Mo/Al₂O₃ hydrodesulfurization catalysts



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ABSTRACT

Organic additives and phosphoric acid are often reported to enhance the catalytic activity of MoS₂-based hydrodesulfurization (HDS) catalysts, although the origin of their effect is not well understood. We did a systematic study on the effect of chelating and non-chelating additives on catalyst activation (1 bar and 20 bar H₂/H₂S) and on structure and activity of sulfided Mo/Al₂O₃ and CoMo/Al₂O₃ catalysts. Phosphoric acid (PA) lowers the activity of Mo/Al₂O₃ catalysts but does increase the activity of CoMo/Al₂O₃ catalysts due to reduced Co₉S₈ formation and improved promotion by cobalt. Organic additives enhance the activity of promoted catalysts more than those of unpromoted ones, indicating that their main role is to improve Co–Mo interaction. Catalysts prepared with α -hydroxycarboxylic acids (citric acid and related compounds) are more active than those prepared with aminopolycarboxylic acids (NTA, EDTA). The α -hydroxycarboxylic acids improve sulfidation of molybdenum and cobalt by forming weak complexes that can be readily sulfided, yielding catalysts with optimal Co–Mo interaction. It is proposed that promoted sites in alumina-supported catalysts are in centrosymmetric sulfur coordination with a Co–S CN > 4, which excludes tetrahedral Co–Mo–S sites.

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1. Introduction

Increasingly stringent transportation fuel specifications and the processing of heavier crudes require development of more active hydrodesulfurization (HDS) catalysts [1]. Most HDS catalysts are composed of cobalt or nickel-promoted MoS₂ nanoparticles dispersed on γ -alumina [2]. The promoter is believed to be located at the edges of the MoS₂ particles as described in the CoMoS model [3,4] and serves as active sites during HDS reactions.

HDS catalysts can be composed of type I or type II CoMoS sites as proposed by Candia et al. [5]. The less-active type I structure is not fully sulfided and is typically thought to have strong interactions with the alumina support via Mo–O–Al linkages. Type II catalysts, which are about twice as active as the type I samples, are fully sulfided, have less or no support interaction and are thought to have a higher intrinsic activity. Support interaction and sulfidation degree can be modified by high temperature sulfidation [5] (although this is at the expense of dispersion), by changing the

support (e.g., to carbon or silica) [6,7] or by additives [8–10]. In particular, organic chelating agents have been successfully used to prepare highly active HDS catalysts.

Chelating agents are usually applied in a one-step co-impregnation procedure in the preparation of the catalyst precursor. The most widely used chelating agents are aminopolycarboxylic acids (APAs), such as nitrilotriacetic acid (NTA) [8,11–15] and ethylenediaminetetraacetic acid (EDTA) [12,16]. Deprotonated APAs preferentially bind to cobalt (or nickel) cations in solution and the resulting complexes remain intact after impregnation and subsequent drying steps [13]. In this way, the metal cations are shielded from direct interaction with the support [16,17]. In the following activation step, which comprises conversion of the precursor to the active sulfided state by heating in H₂/H₂S, chelation can delay sulfidation of cobalt to temperatures where MoS₂ is formed (~250 °C) as observed by QEXAFS [9] and XPS [12]. The higher temperature of cobalt sulfidation, compared to a catalyst without chelating agent, was proposed to minimize formation of the catalytically undesirable Co₉S₈ phase and facilitate formation of promoted sites (CoMoS) [9,12,17], which may explain the beneficial effect of chelating ligands on catalytic activity.

Another class of chelating agents found to enhance HDS activity is α -hydroxycarboxylic acids (AHAs), such as citric acid (CA)

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[18–23] and tartaric acid (TA) [24]. CA is reported to increase the sulfidation temperature of cobalt, leading to more CoMoS sites [19], enhanced reducibility of molybdates [21], improved cobalt and/or molybdenum dispersion [25,26] and modify interaction between metals and support [24,27,28]. We recently published that sulfidation of catalysts prepared with CA depends strongly on H₂/H₂S pressure. Activation in 20 bar H₂/H₂S resulted in more active catalysts in dibenzothiophene HDS despite a substantially lowered sulfidation temperature with respect to activation in 1 bar H₂/H₂S [29]. We therefore proposed that the temperature at which cobalt converts into the sulfide state is not related to the formation of CoMoS sites. Other more weakly interacting organic additives, such as polyethyleneglycol (PEG) [30] and ethylenediamine [31], were also found to increase HDS activity despite lowering the sulfidation temperature of the promoter.

To summarize, no general consensus has been reached on the role of (chelating) organic additives in the formulation of highly active HDS catalysts. One complicating factor is that additives do affect not only the chemical state and sulfidation rate of the promoter, but also that of molybdenum [31]. This is evidenced by studies concluding that chelating agents do also enhance the HDS activity of unpromoted MoS₂/Al₂O₃ catalysts [27,32]. However, so far a systematic study of additives, with varying propensity to chelate the metal ions in solution, on unpromoted or promoted HDS catalysts has been lacking.

Here, we study the effect of APAs (NTA and EDTA), AHAs (CA, TA and gluconic acid (GA)), tetraethyleneglycol (PEG) and phosphoric acid (PA) on sulfidation, catalyst composition and activity of (Co) Mo/Al₂O₃ catalysts. We also compare activation at 1 bar and 20 bar H₂/H₂S to gain understanding of the role of additives under activation conditions closer to those applied in industry, and obtain insight into the stability of metal chelates in H₂/H₂S. Catalysts are characterized by UV–visible diffuse reflectance spectroscopy (UV–Vis DRS), X-ray absorption spectroscopy (EXAFS and XANES), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) and their activity is evaluated in the HDS of thiophene and dibenzothiophene (DBT).

2. Experimental

2.1. Catalyst preparation

A suite of Mo/Al₂O₃ and CoMo/Al₂O₃ catalysts with various additives (Table 1) was prepared by impregnating a 75–125 μm sieve fraction crushed γ-Al₂O₃ extrudates (BET surface area 300 m²/g, pore volume 0.80 cm³/g, average pore diameter 8.5 nm) with an aqueous solution containing respective metal salts and organic additives. Chemicals were purchased from Sigma-Aldrich with ≥98% purity grade. Catalysts without additives were

prepared by co-impregnation of an aqueous solution containing ammonium heptamolybdate tetrahydrate (AHM) and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O). Catalysts with H₃PO₄ (85%), GA, TA, CA, AHM or NTA as additive were prepared by first dissolving the additive and then adding solutions of AHM and Co(NO₃)₂·6H₂O. Samples containing PEG were prepared by adding PEG last to the H₃PO₄, AHM and Co(NO₃)₂·6H₂O solution to avoid precipitation of the metal salts. Due to the low solubility of EDTA in water, (Co)Mo-EDTA was prepared in a two-step impregnation. In the first step, an aqueous solution of AHM and Co(NO₃)₂·6H₂O was impregnated on the carrier and the product was dried at 80 °C. Then, an ammoniacal solution of EDTA was prepared and impregnated on the carrier (0.4 mL g⁻¹).

Catalysts with organic additives were dried at 110 °C, but not calcined in order to preserve the organic molecule. All other precursors were dried at 110 °C and subsequently calcined at 450 °C for 2 h in flowing air as indicated in Table 1. The targeted final composition of the catalysts (after calcination) was 14.5 wt% molybdenum, which corresponds to one monolayer, a Co:Mo molar ratio of 0.4 and a P:Mo molar ratio of 0.45. The organic additives were applied in equimolar (NTA, EDTA, PEG) or in 6:5 M ratio (CA, GA, TA) with molybdenum. These ratios yield catalysts with high activity [14,30] and a composition comparable to commercial ones [33].

2.2. Characterization

XPS measurements were performed on a Kratos AXIS Ultra spectrometer, equipped with a monochromatic X-ray source (Al Kα = 1486.6 eV) and a delay line detector. Samples were sulfided at 1 or 20 bar H₂S(10%)H₂ (50 mL min⁻¹ STP) at 50 °C, 150 °C, 250 °C and 350 °C for 2 h, subsequently cooled in helium and transferred to the glove box without exposure to air. Samples were then ground, attached to double-sided carbon tape, and transferred to the XPS apparatus in N₂ atmosphere via an airtight transport vessel. The background pressure prior to analysis was 2 × 10⁻⁹ mbar. Survey scans were collected at constant pass energy of 160 eV, and region scans at 40 eV. The spectra were calibrated to the alumina support (Al 2p = 74.4 eV) and fitted with CasaXPS software using a Shirley background subtraction and Gaussian(65%)–Lorentzian(35%) curves. Mo 3d spectra were deconvoluted into Mo^{IV} (as in MoS₂), Mo^V (MoS_xO_y) and Mo^{VI} (as in MoO₃) doublets. The degree of sulfidation χ was calculated as $\chi(\text{MoS}_2) = [\text{Mo}^{\text{IV}}]/([\text{Mo}^{\text{IV}}] + [\text{Mo}^{\text{V}}] + [\text{Mo}^{\text{VI}}])$. HRTEM was done using a monochromated FEI Tecnai transmission electron microscope operated at an accelerating voltage of 200 keV. Samples sulfided in 20 bar H₂/H₂S(10%) at 350 °C for 2 h were transported to an argon-filled glove box (<1 ppm of O₂ and H₂O) in sealed glass ampoules. Then, a suspension was made in *n*-hexane and a few droplets were placed on a microgrid carbon film (Quantifoil) supported on a Cu TEM grid.

Table 1
List of samples and terminology.

Additive	Log K ₁ ^a	Treatment	Mo/Al ₂ O ₃ samples	CoMo/Al ₂ O ₃ samples
–		Dried	Mo ^{dr}	CoMo ^{dr}
–		Calcined	Mo ^{cal}	CoMo ^{cal}
Phosphoric acid		Dried	Mo-PA ^{dr}	CoMo-PA ^{dr}
Phosphoric acid		Calcined	Mo-PA ^{cal}	CoMo-PA ^{cal}
Polyethylene glycol		Dried	Mo-PEG	CoMo-PEG
Phosphoric acid + Polyethylene glycol		Dried	Mo-PA-PEG	CoMo-PA-PEG
Citric acid	4.4 ^b	Dried	Mo-CA	CoMo-CA
Gluconic acid	1.0 ^b	Dried	–	CoMo-GA
Tartaric acid	2.5 ^b	Dried	–	CoMo-TA
Nitrilotriacetic acid	10.6 ^b	Dried	Mo-NTA	CoMo-NTA
Ethylenediaminetetraacetic acid	16.2 ^b	Dried	Mo-EDTA	CoMo-EDTA

^a Stability constant K₁ of cobalt chelates in solution (K₁ = [Co²⁺L]/[Co²⁺][L] with L = ligand).

^b Data taken from [34–36].

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