

Short communication

## Redispersion effects of citric acid on CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> hydrodesulfurization catalysts



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### ABSTRACT

Calcined CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were modified by citric acid (CA) with different CA/Co ratios and the corresponding structure evolutions were systematically characterized. Then combined with HDS activity results, potential redispersion effects of CA were suggested: (i) weaken the MoO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> interaction via competitive interacting with the OH groups of alumina surface to realize the redispersion of Mo oxides; (ii) transform tetrahedral MoO<sub>4</sub><sup>2-</sup> or  $\beta$ -CoMoO<sub>4</sub> into octahedral polymolybdate species and promote bulk MoO<sub>3</sub> to form well-dispersed MoO<sub>3</sub>; (iii) remove the CoAl<sub>2</sub>O<sub>4</sub>-like species. These effects probably together promote the resulting sulfided catalysts with more type II CoMoS active sites, thus enhancing the HDS activity.

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### 1. Introduction

With the quality standard of automobile diesel becoming stricter and the hydrodesulfurization (HDS) technologies facing constant challenges, developing catalysts has become the most economic strategy to realize an ultra-deep HDS efficiency [1–3]. So far, Co(Ni)-promoted Mo/Al<sub>2</sub>O<sub>3</sub> catalysts are still the most extensively used catalytic systems for HDS in the refining industry, and the so-called Co(Ni)-Mo-S phases has been generally considered as the active phases [4].

In the conventional impregnation method, the sulfided active phases are generally yielded through sulfurizing the oxidic precursors which have been in advance prepared through three steps, i.e., impregnation, drying and calcination. The calcination step could contribute to the high dispersion of the active species, however, just due to the often excessive high temperature to be used, it could induce the formation of strong Mo-O-Al bonds, resulting in the generation of type I CoMoS active phases with a low activity [5]. To overcome it, a chelating agents-assisted impregnation (CAI) method without the calcination step was thereupon developed, and in present it has attained extensive industrial application. However, some other unavoidable problems appear again, such as the undesired cycle life originating from the aggregation tendency of the active species in the running process due to the excessive weak metal-support interaction. Thereafter, a post-treatment method in which the chelating agents are added into the calcined oxidic catalysts was developed [6,7], and in fact, due to its resulted catalysts probably hold more suitable metal-support interaction and higher dispersion for metal species [8], it has been more used to regenerate

the runned catalysts [9–11]. Recently, Bui et al. regenerated industrial CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts using maleic acid (MA) as the redispersant and found MA could not only redisperse Anderson molybdenum salt species, but also promote the undesired Co species, e.g. CoMoO<sub>4</sub> to form Co-MA complex to delay their sulfidation process, thus favoring the formation of more CoMoS active species [12].

As one of the most important chelating agents used in CAI method, Citric acid (CA) has been widely considered to play two potential roles [13,14]: (i) delay the sulfuration of Co species later than Mo species, to form more Co-Mo-S phases [15]; (ii) act as the ligands of Mo anions to form Mo-CA complex, thus weakening the metal-support interaction and generating more type II CoMoS active phases [14,16]. These two roles apparently originate from the interaction between CA and metal ions in the impregnation solution and are thus unsuitable to be adapted to explain the roles of CA in the post-treatment method, in which CA functions nothing but through influencing the dispersion or chemical states of the oxidic Mo or Co species. However, to the best of our knowledge, the redispersion effects of CA on the calcined CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts have not been systematically studied. In this paper, calcined CoMo/Al<sub>2</sub>O<sub>3</sub> HDS catalysts were modified by CA with different CA/Co ratios and the potential redispersion effects of CA were finally suggested.

### 2. Experimental

#### 2.1. Preparation of CA-modified catalysts

The CA-modified catalysts were prepared by the following procedures: first the calcined CoMo/Al catalyst was prepared through impregnating Al<sub>2</sub>O<sub>3</sub> with an aqueous solution containing molybdenum trioxide, basic cobaltous carbonate and phosphoric acid, followed by

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drying at 393 K for 3 h and calcination at 673 K for 3 h under an air atmosphere. The loadings of MoO<sub>3</sub>, CoO and P<sub>2</sub>O<sub>5</sub> measured by X-ray fluorescence spectroscopy (XRF) were 25.0 wt.%, 5.6 wt.% and 3.0 wt.%, respectively. Then the CA-modified catalysts were prepared by impregnating the calcined CoMo/Al catalyst with CA solutions, followed by drying at 393 K for 3 h. The resulting catalysts are denoted as CA<sub>x</sub>/CoMo/Al, where x means the CA/Co molar ratio. For comparison purpose, CA/Al, Mo/Al and CA/Mo/Al were meanwhile prepared by the same method using CA and/or (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O as the precursor(s) and the MoO<sub>3</sub> loadings in Mo/Al and CA/Mo/Al catalysts were controlled the same with the above CoMo/Al catalysts.

## 2.2. Characterizations

N<sub>2</sub> physical adsorption-desorption measurements were operated on an Autosorb-6B instrument. Temperature programmed reduction (TPR) characterizations were conducted on an AutochemII2920. Fourier transformed reduction spectra (FTIR) were carried out on a Nicolet 870 spectrometer. Thermogravimetric-mass spectrometric (TG-MS) analysis was performed on a Netzsch STA409 PC thermal analyzer. Raman spectra (RS) were recorded on a LabRAM Microscope. X-ray diffraction (XRD) analysis was carried out on a Bruker D5005 X-ray diffractometer. DRS UV-vis spectra were recorded on a Lambda 35 spectrophotometer. X-Ray photoelectron spectroscopy (XPS) analysis was operated on a Thermo Fisher-VG Escalab250 spectrometer. High-resolution transmission electron microscopy (HRTEM) images were obtained on a Philips Tecnai G2 F20 microscope.

## 2.3. Activity assessment

The HDS activity was assessed on a fixed-bed micro-reactor. Before the test, the catalysts were pre-sulfided with a sulfiding feed of cyclohexane solution containing 5 wt.% CS<sub>2</sub> for 4 h, under 6.4 MPa and 633 K. Then the HDS activity was tested using a decane solution containing 0.45 wt.% 4,6-dimethyldibenzothiophene (4,6-DMDBT) as the reactant, under the conditions of 6.4 MPa, liquid hourly space velocity 58.4 h<sup>-1</sup>, H<sub>2</sub>/feed volumetric ratio 500 and different temperatures 533 K, 553 K and 573 K. Then the products were analyzed with Agilent 7890A gas chromatograph. Details about the activity analysis methods see Supplementary information.

## 3. Results and discussion

### 3.1. Characterization results of the oxidic catalysts

The textural properties of Al<sub>2</sub>O<sub>3</sub> and CA/CoMo/Al catalysts are listed in Table S1, which clearly shows that with CA/Co ratio increasing, the surface area increases, while the pore volume and pore diameter decrease, indicating CA has been successfully introduced into the pores of the catalysts to fully interact with the active species [8].

The TPR profiles of the series CA/CoMo/Al catalysts were shown in Fig. 1. With the CA/Co ratio increasing, the peaks at low and high temperature zones both shifts to the left significantly, implying CA effectively decreases the MoO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> interaction and thereby facilitating the reduction of the oxides to generate sulfided active phases [17], as proved by the following XPS analysis results about the sulfidation degree of the Mo oxides. To explain this phenomenon, FTIR spectra of Al<sub>2</sub>O<sub>3</sub> and CA/Al were obtained (Fig. S1). Apparently, the addition of CA significantly decreased the amount of the hydroxyl groups of Al<sub>2</sub>O<sub>3</sub> [18]. Combining with the TPR results, it is reasonable to conclude that through competitive reacting with hydroxyl groups of Al<sub>2</sub>O<sub>3</sub>, CA can weaken the MoO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> interaction and thereby favor the redispersion of Mo species.

TG-MS measurement results (Figs. S2 and S3) confirm a strong interaction indeed exists between CA and the Mo or/and Co species, implying CA may probably redisperse the Mo and Co species through directly

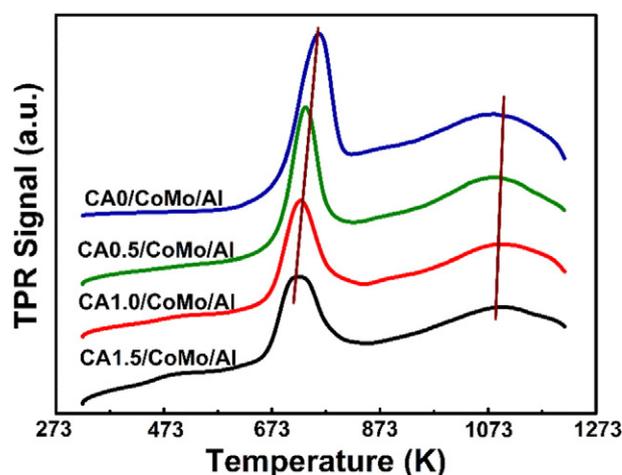


Fig. 1. TPR spectra of the CA/CoMo/Al catalysts.

reacting with them. To accurately understand its effects on the Mo species, RS analysis of CA/CoMo/Al catalysts was carried out (Fig. 2). The peaks at 340 cm<sup>-1</sup> and 839 cm<sup>-1</sup> were assigned to Mo-O vibration of MoO<sub>4</sub><sup>2-</sup>, while the peak at 940 cm<sup>-1</sup> was ascribed to the overlap of Mo-O vibration of polymolybdate (such as Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup>) and β-CoMoO<sub>4</sub> [14,19]. When CA was added, the intensities of the peaks at 340 cm<sup>-1</sup> and 839 cm<sup>-1</sup> were both decreased remarkably, indicating CA could effectively remove MoO<sub>4</sub><sup>2-</sup>. Besides, the intensity of the band at 940 cm<sup>-1</sup> decreased gradually with CA/Co ratio increasing, probably due to the CA-promoted decomposition of the polymeric Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> or/and β-CoMoO<sub>4</sub> [14]. To distinguish the potential effects of CA on MoO<sub>4</sub><sup>2-</sup>, polymolybdate and β-CoMoO<sub>4</sub>, sample Mo/Al and its CA-modified CA/Mo/Al were first characterized by RS (Fig. S4). The spectra of Mo/Al<sub>2</sub>O<sub>3</sub> exhibit a strong peak at 839 cm<sup>-1</sup> and a weak peak at 940 cm<sup>-1</sup>, however, very interestingly, just when CA was added the intensity of the peak at 839 cm<sup>-1</sup> decreased remarkably, while the peak at 940 cm<sup>-1</sup> increased greatly, fully suggesting CA facilitates the transformation of the MoO<sub>4</sub><sup>2-</sup> species into polymolybdate ones. Then its effect on β-CoMoO<sub>4</sub> was studied by comparing the XRD patterns of catalyst Co/Mo/Al containing amounts of β-CoMoO<sub>4</sub> species described in Supplementary information and its CA-modified counterpart CA/CoMo/Al together with card no. 21-868 of pure β-CoMoO<sub>4</sub> (Fig. 3A). The peaks at 37.2°, 45.6° and 66.9° are assigned to γ-Al<sub>2</sub>O<sub>3</sub> (PDF card no. 29-1486). Combined with XRD pattern of pure β-CoMoO<sub>4</sub>, that of Co/Mo/Al exhibits a typical peak of β-CoMoO<sub>4</sub> at 26.6°, whereas when CA was

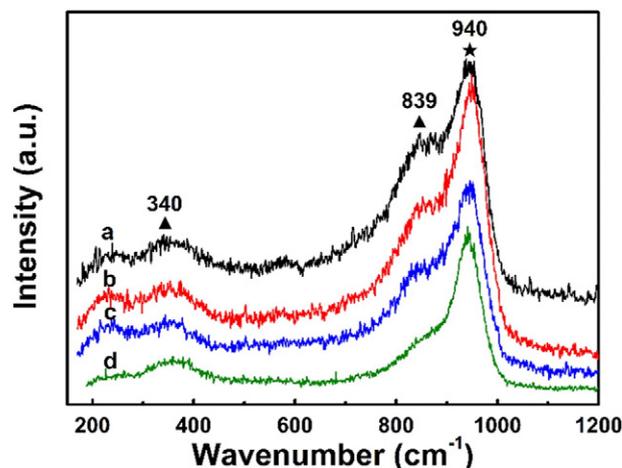


Fig. 2. RS spectra of the CA/CoMo/Al catalysts: (a) CA0/CoMo/Al, (b) CA0.5/CoMo/Al, (c) CA1.0/CoMo/Al and (d) CA1.5/CoMo/Al.

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