



# Preparation of Co–Mo/B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrodesulfurization: Effect of citric acid addition

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## ABSTRACT

The effect of citric acid (CA) addition was studied on the HDS of thiophene over Co–Mo/(B)/Al<sub>2</sub>O<sub>3</sub> catalysts. The catalysts were characterized by means of LRS, Mo K-edge EXAFS, NO adsorption capacity measurements, and UV–vis spectra. The catalysts were subjected to a chemical vapor deposition (CVD) technique using Co(CO)<sub>3</sub>NO as a precursor of Co in order to get deeper insights into the effect of citric acid addition. It was shown that the HDS activity was enhanced by the citric acid addition up to the CA/Mo mole ratio of around 1 and leveled off with further addition. The amount of Co anchored by the CVD was increased by the addition of citric acid, suggesting an increase in the dispersion of MoS<sub>2</sub> particles on the catalyst by the simultaneous presence of Co, Mo and citric acid, in conformity with the increase in the NO adsorption capacity. In contrast to Co–Mo catalysts, the edge dispersion of MoS<sub>2</sub> particles in Mo/B/Al<sub>2</sub>O<sub>3</sub> was not affected by the addition of citric acid. The LRS, UV–vis spectra and Mo K-edge EXAFS showed that Co–CA and Mo–CA surface complexes are formed by the addition of citric acid. The Co–CA surface complex is more preferentially formed on CoMo/Al than on CoMo/B/Al, in agreement with a greater promoting effect of citric acid at a lower CA/Mo mole ratio for CoMo/Al than for CoMo/B/Al.

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## 1. Introduction

Recent increasing demands for transportation fuels with lower contents of sulfur and nitrogen have become a strong incentive to develop more active catalytic systems for the hydrotreatment, in particular, for the hydrodesulfurization (HDS) processes. Co(Ni)–Mo sulfide catalysts have been very widely used for industrial HDS [1,2]. The active phase in these catalysts is generally accepted to consist of MoS<sub>2</sub> slabs with the promoter (Co, Ni) atoms decorating their edges, the so-called Co–Mo–S or Ni–Mo–S phase [1]. Many attempts have been made to increase the number of active sites on the catalysts [1–4]. The use of a chelating agent in the preparation of HDS catalysts [5–17] has been found very effective in increasing the number of Co(Ni)MoS by increasing the coverage of Co(Ni) on the edges of MoS<sub>2</sub> particles.

It has been reported that the preparation of HDS catalysts using citric acid as a chelating agent significantly improves their catalytic activity [18–22]. Fujikawa et al. suggested that the activity improvement is due to an increase in the Co coverage on the edges of MoS<sub>2</sub> particles, since citric acid forms a complex with Co [18–20].

They employed citric acid as a chelating agent combined with phosphoric acid in their development of ultra-deep Co–Mo HDS catalysts. Bergwerff et al. [21] showed an increased Mo dispersion and enhanced HDS activity by the addition of citric acid in the impregnation solution. In addition, Funamoto and Segawa [22] reported by XPS that the sulfidation degree of Mo is improved by the addition of citric acid. However, the detailed roles of citric acid in improving the performance of HDS catalysts still remain unveiled.

In the present study, we investigated the effect of citric acid addition on the catalytic performance of CoMo/B/Al<sub>2</sub>O<sub>3</sub> catalysts and characterized the catalysts by means of a variety of physicochemical techniques in order to get better insights into exact roles of the chelating agent, citric acid. In addition, a chemical vapor deposition (CVD) technique with Co(CO)<sub>3</sub>NO as a probe molecule was used for the characterization of the catalysts. By the CVD, all the Co atoms are preferentially anchored on vacant MoS<sub>2</sub> edge sites, resulting in a full occupation of the edges of the MoS<sub>2</sub> particles with the Co atoms [23–25]. Hence, the intrinsic activity of the Co–Mo–S phase and the surface structure of Co–Mo catalysts can be estimated.

## 2. Experimental

### 2.1. Catalyst preparation

B<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> (B/Al) materials were prepared by an impregnation technique [26,27].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-7: 180 m<sup>2</sup> g<sup>-1</sup>, a reference

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catalyst provided by the Catalysis Society of Japan) was impregnated with an aqueous solution of  $\text{H}_3\text{BO}_3$ , followed by calcination at 773 K for 5 h. Then, the B/Al materials were simultaneously impregnated with  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (AHM), citric acid (CA), and  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , followed by drying at 383 K for 16 h (without calcination). The catalyst thus prepared is denoted as CoMo-CA/B/Al hereinafter. The Mo, Co, and B contents were fixed at 8.7 wt% Mo, 3 wt% Co, and 1.2 wt% B, respectively, while the CA content was varied between 0 and 2.2 CA/Mo mole ratios. The pH of the impregnation solution was not adjusted in the present study. CoMo-CA/Al catalysts were also prepared for comparison by a simultaneous impregnation method in the same way.

A series of Mo-CA/B/Al catalysts (8.7 wt% Mo, CA/Mo mole ratio = 2.0) with a varying boron content (0–4.7 wt% B) was also prepared by a simultaneous impregnation of B/Al with AHM and citric acid, followed by drying at 383 K for 16 h (without calcination).

The prepared catalysts were sulfided in a 10%  $\text{H}_2\text{S}/\text{H}_2$  flow at 673 K for 1.5 h. The sulfidation procedures have been described previously [26]. A CVD technique using  $\text{Co}(\text{CO})_3\text{NO}$  as a precursor was applied to introduce Co into the sulfided catalyst [23–26]. Briefly, the sulfided catalyst was first evacuated at 673 K for 1 h and subsequently exposed for 5 min at room temperature to a vapor of  $\text{Co}(\text{CO})_3\text{NO}$  kept at 273 K (CVD technique). After 10 min evacuation at room temperature, the sample was sulfided again at 673 K for 1.5 h. The catalyst thus prepared is denoted as, for example, CVD-Co/CoMo-CA/B/Al, when CoMo-CA/B/Al was subjected to the CVD technique. The amount of Co incorporated by the CVD technique was determined for the sulfided catalysts by means of XRF (Shimadzu, EDX-700HS).

## 2.2. Reaction procedure

In order to evaluate the initial activity of the freshly prepared catalyst, we conducted the reaction under mild conditions using a circulation system made of glass. The catalyst (about 0.1 g) sulfided in situ was evacuated at 673 K for 1 h before the catalytic reaction. The HDS of thiophene was carried out at 623 K and the initial  $\text{H}_2$  pressure of 20 kPa. The thiophene pressure was kept constant (2.6 kPa) during the reaction [23]. The reaction products were analyzed by on-line gas chromatography. The products were mainly  $\text{C}_4$  compounds and a corresponding amount of  $\text{H}_2\text{S}$ . The amount of  $\text{H}_2\text{S}$  formed was periodically monitored during the reaction. The HDS activity was calculated on the basis of the accumulated amount of  $\text{H}_2\text{S}$  evolved after 1 h reaction per catalyst weight. The amounts of  $\text{H}_2\text{S}$  evolution from the sulfided catalysts were estimated by blank experiments without the introduction of thiophene vapor into the reactor, showing that they were negligibly small ( $<5\text{--}10 \times 10^{-5} \text{ mol h}^{-1} \text{ g}^{-1}$ ) compared with the amount of  $\text{H}_2\text{S}$  formed by the HDS reaction. The reproducibility of the HDS activity test was better than  $\pm 4\%$ .

## 2.3. Characterization

### 2.3.1. LRS measurements

Laser Raman spectra of CoMo/B/Al with and without the citric acid addition were obtained at room temperature in air on an NRS-2100 spectrometer (JASCO) equipped with a CCD detector. The 514.5 nm line of an  $\text{Ar}^+$  laser was used for excitation at an intensity of 10 mW at the source.

### 2.3.2. NO adsorption

The amount of NO adsorption on sulfided CoMo-CA/B/Al was measured by a pulse technique. After cooling in the  $\text{H}_2\text{S}/\text{H}_2$  stream, the sulfided catalyst was flushed with a high purity He stream at room temperature. The detailed procedures have been described elsewhere [23,28].

### 2.3.3. XAFS measurements

Mo K-edge XAFS spectra for Mo/B/Al with and without the citric acid addition and for reference compounds were measured in a transmission mode at room temperature at NW-10A in the PF-AR (Photon Factory-Advanced Ring for pulse X-Rays) of the Institute of Material Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF-AR) with 6.5 GeV ring energy and 100–50 mA stored current (proposal Nos. 2006G331 and 2008G200). The synchrotron radiation was monochromatized by a Si (3 1 1) channel-cut monochromator. The EXAFS data were analyzed assuming a spherical wave approximation and a single scattering model. The EXAFS data were Fourier-transformed from  $k$ -space ( $40\text{--}150 \text{ nm}^{-1}$ ) to  $R$ -space. The empirical backscattering amplitude and phase shift for Mo-S and Mo-Mo pairs were extracted from EXAFS data for polycrystalline  $\text{MoS}_2$ .

### 2.3.4. UV-vis spectra

DRS UV-vis spectra of CoMo-CA/B/Al and CoMo-CA/Al were collected in air on a UV-2500PC spectrophotometer (Shimadzu) in a wavelength range of 240–850 nm using  $\text{BaSO}_4$  powder as a reference.

## 3. Results

### 3.1. HDS activity

The catalytic activity of the simultaneously impregnated Co-Mo catalysts for the HDS of thiophene is depicted in Fig. 1 as a function of CA/Mo mole ratio. The HDS activity of CoMo-CA/Al was gradually increased by the addition of citric acid up to CA/Mo mole ratio = 1 and leveled off for further additions of citric acid. On the other hand, the HDS activity of CoMo-CA/B/Al remained unchanged by the citric acid addition up to CA/Mo = 0.4, and then was increased at the CA/Mo mole ratio between 0.6 and 1.2, followed by a constant activity with a further addition of citric acid up to CA/Mo = 2.2. The HDS activity values for these catalyst systems were increased 20% by the citric acid addition (CA/Mo > 1).

These catalysts were subjected to the CVD of  $\text{Co}(\text{CO})_3\text{NO}$ . The HDS activity of CVD-Co/CoMo-CA/(B)/Al is also shown in Fig. 1. The HDS activity of CoMo-CA/Al was not changed by the addition of Co using the CVD, suggesting that the edges of the  $\text{MoS}_2$  particles are already fully promoted by Co [25]. On the other hand, below CA/

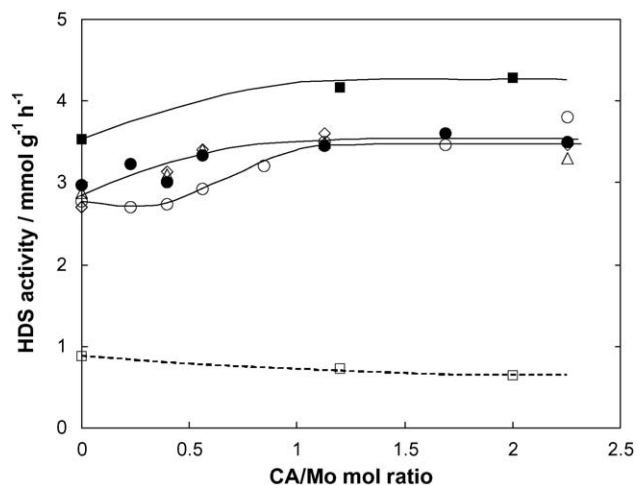


Fig. 1. HDS activities of Co-Mo catalysts as a function of the CA/Mo mole ratio. ( $\Delta$ ) CoMo-CA/Al, ( $\circ$ ) CoMo-CA/B/Al (1.2 wt% B), ( $\diamond$ ) CVD-Co/CoMo-CA/Al, ( $\bullet$ ) CVD-Co/CoMo-CA/B/Al (1.2 wt% B), ( $\square$ ) Mo-CA/B/Al, and ( $\blacksquare$ ) CVD-Co/CoMo-CA/B/Al (1.2 wt% B).

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