PREPARATION OF HIGHLY ACTIVE Co-Mo/Al$_2$O$_3$ HDS CATALYSTS WITH CITRIC ACID ADDITION BY THE POST-TREATMENT METHOD

Nino Rinaldi

*Research Center for Chemistry, Indonesian Institute of Sciences,
Kawasan PUSPIPTEK, Serpong 15314, Tangerang*

ABSTRACT

A study of the influence of citric acid (CA) addition by a post-treatment method during the preparation of a series of Mo/Al$_2$O$_3$ catalysts on the thiophene HDS activity was conducted. The Mo/Al$_2$O$_3$ catalysts were also prepared by a chemical vapor deposition (CVD) technique using Co(CO)$_3$NO to introduce Co atom and characterized by means of NO adsorption, XRD, Mo K-edge EXAFS and XRF. With 8.7 wt% Mo, citric acid was not affected very much for the Co-Mo/Al$_2$O$_3$ catalysts. On the other hand, an outstanding result was shown that the HDS activity was drastically enhanced by 5 times up to Mo content around of 25 wt% Mo. It is suggested that the post treatment increased the dispersion of MoS$_2$ particles, in particular at a high Mo loading. This was also supported by the amount of NO adsorption and amount of Co anchored by the CVD results, which enhanced as the increasing Mo loading up to 25 wt% Mo. Moreover, Mo–CA complex species were observed on the post-treatment method and CVD technique was one of advanced method to prepare Co-Mo-S phases selectively.

INTRODUCTION

Development of highly active hydrodesulfurization (HDS) catalysts is still needed not only for obtaining zero sulfur emission and zero sulfur fuel in the future, but also to efficiently utilize limited natural resources. Supported nickel- or cobalt-molybdenum sulfide catalysts are widely used in the industrial HDS process [1]. It is now well recognized that the active sites of the HDS catalysts are the so-called Co(Ni)-Mo-S phase, in which Co(Ni) decorates the edge sites of highly dispersed MoS$_2$ particles [1]. Therefore, many improvements of HDS catalysts preparation have been proposed in order to get a greater amount of active sites, Co-Mo-S phases, as well as better knowledge of the structure of catalytically active phase, support-active phase interaction and new activation procedure. One simple and effective method to boost catalytic activity is with the use of chelating agent in the catalysts preparation [2], for instance citric acid (CA).

In the catalyst preparations, chelating agents are usually added by the simultaneous impregnation method, including citric acid. It has been reportedly that with using citric acid with the simultaneous-impregnation method, better performance of the HDS catalytic activity is obtained [2]. Moreover, the dispersion of MoS$_2$ particles and the degree of sulfidation of Mo oxide precursors are also improving [2-3]. Similar result is also observed on our previous result when citric acid was

added by the simultaneous impregnation method in the catalyst preparation [4]. However, information about the detail roles of citric acid is still unclear. In the present study, other preparation method of addition of citric acid was conducted. Citric acid was impregnated on the calcined Co-Mo/Al$_2$O$_3$ catalysts, as called a post-treatment method here. We studied the influence of citric acid to the performance on the HDS reaction of thiophene related with a series content of Mo and CA, and characterized them by a variety of physicochemical techniques. A chemical vapor deposition (CVD) technique with Co(CO)$_3$NO as the probe molecule was used to introduce Co atom on the sulfide Mo/Al$_2$O$_3$. By CVD, all of the Co atoms were preferentially anchored on vacant MoS$_2$ edge sites, resulting in the full occupation of the edges of the MoS$_2$ particles with Co atoms [5-7]. Hence, the maximum potential activity of Co-Mo catalysts can be estimated [6-7].

EXPERIMENTAL SECTION

Materials

The commercial standard of γ-Al$_2$O$_3$ (JRC-ALO-7) was supplied by the catalysis society of Japan. Ammonium heptamolybdate (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, citric acid (C$_6$H$_8$O$_7$), thiophene (C$_4$H$_4$S) and cobalt carbonyl (Co(CO)$_3$NO) were used in here as analytical grade.

* Corresponding author. Tel/Fax : +62-21-7560090
Email address : ninorinaldi_77@yahoo.com

Moreover, all gases (He, H_2, 10% NO/He and 10% H_2S/H_2) were used as a high purity quality.

Instrumentation

On-line gas chromatography (GC), X-ray fluorescence (XRF), X-ray diffraction (XRD), and Mo K-edge X-ray Absorption Fine Structure (XAFS) were apparatus that used in the present study.

Procedure

Catalysts Preparation

A series of MoO_3/Al_2O_3 was prepared by an impregnation technique. γ-Al_2O_3 (SSA: 180 m^2g^{-1}) was impregnated with an $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (AHM) aqueous solution, followed by calcination at 773 K for 5 h. The Mo content of Mo/Al was 8.7-35 wt% Mo. Then, the calcined Mo/Al was impregnated with a citric acid (CA) aqueous solution (CA/Mo mole ratio = 2); this step was followed by just drying at 383 K for 16 h (without calcination). This catalyst preparation technique is denoted here as a post-treatment method. Another series, the CA/Mo mole ratio was varied up to 2 with 8.7 and 20 wt% Mo/Al_2O_3 catalysts were also prepared by the post-treatment method. The pH of the impregnation solution was not adjusted in the present study.

The prepared catalysts were sulfided in a 10% H_2S/H_2 flow at 673 K for 1.5 h. The sulfidation procedures have been described previously [4]. A chemical vapor deposition (CVD) technique using $Co(CO)_3NO$ as a precursor was applied to introduce Co into the sulfided Mo/Al_2O_3 catalyst [4-7]. 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 $Co(CO)_3NO$ kept at 273 K. 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 Co-Mo/Al_2O_3. The amount of Co incorporated by the CVD technique was determined for the sulfided catalysts by means of XRF analysis (Shimadzu, EDX-700HS). The accuracy of the Co content was within ± 5%.

Reaction Procedure

The initial activity of the freshly prepared catalyst was evaluated on the HDS reaction under mild conditions using a circulation system made of glass (batch system). 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 H_2 pressure of 20 kPa. The thiophene pressure was kept constant (2.6 kPa) during the reaction [4-5]. The reaction products were analyzed by on-line gas chromatography. The products were mainly C_4 compounds such as *n*-butane, 1-butene, and *cis-/trans-*2-butene and a corresponding amount of H_2S. The output products were periodically monitored during the reaction. The HDS activity was calculated on the basis of the accumulated amount of H_2S evolved after 1 h reaction divided by the catalyst weight. The amounts of H_2S evolved from the sulfided catalysts were estimated by blank experiments without introduction of thiophene vapor into the reactor, showing that they were negligibly small [less than $(5-10) \times 10^{-5}$ mol h^{-1} g^{-1}] compared with the amount of H_2S formed by the HDS reaction. The reproducibility of the HDS activity test was better than ± 4%.

Characterizations

The amount of NO adsorption on the sulfide Mo/Al_2O_3 catalyst prepared by citric acid addition was measured by a pulse technique. After cooling in the H_2S/H_2 stream, the sulfided catalyst (0.1 g) was flushed at room temperature with a high purity He stream (20 cm^3 min^{-1}). A pulse of 5.0 cm^3 of 10% NO/He (purity of NO > 99%, atmospheric pressure) was repeatedly injected every 8 min to the He stream by using a six-way stopcock until no adsorption was detected (pulse size; 20 μmol NO/pulse, 10–15 pulses). The effluent gas was analyzed by a gas chromatograph equipped with a thermal conductivity detector to measure the amount of NO. The amount of NO adsorption was calculated from the cumulative amount of NO adsorption. The reproducibility was usually within ± 5% of the total amount of NO adsorption [5,8].

Moreover, X-ray diffraction (XRD) measurements were carried out on a Miniflex II Desktop X-ray Diffraction apparatus (Rigaku) with 30 kV and 15 mA, equipped with an automatic divergence slit. The radiation source was Cu $K_{\alpha1,2}$ (λ = 1.541841 Å) with a Ni filter. Mo K-edge X-ray Absorption Fine Structure (XAFS) spectra were measured for oxidic Mo/Al_2O_3 with or without the citric acid addition and for reference compounds 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 No. 2006G331, 2008G200). The synchrotron radiation was monochromatized by a Si (311) double crystal monochromator. The EXAFS data were analyzed by assuming a spherical wave approximation and a single scattering model. The EXAFS data were Fourier-transformed from *k*-space (40-150 nm^{-1}) to *R*-space. The empirical backscattering amplitude and phase shift for Mo-Mo pairs were extracted from EXAFS data for polycrystalline MoS_2.
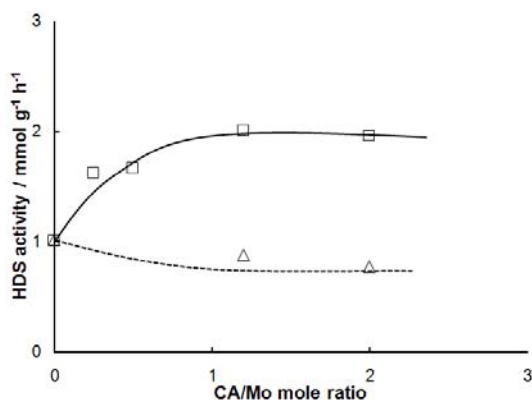
Fig 1. HDS activity of Mo/Al$_2$O$_3$ catalysts as a function of CA/Mo mole ratio by the post-treatment method. (Δ) 8.7 wt% Mo and ($\square$) 20 wt% Mo
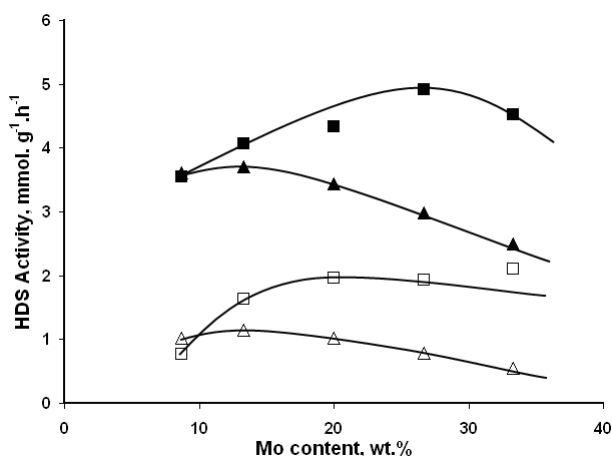
Fig 2. HDS activity of Co-Mo/Al$_2$O$_3$ prepared by CA addition as a function of Mo loading (CA/Mo = 2.0). (Δ) Mo/Al$_2$O$_3$-calcined, ($\square$) Mo/Al$_2$O$_3$-post-treated, (▲) Co-Mo/Al$_2$O$_3$-calcined, and (■) Co-Mo/Al$_2$O$_3$- post-treated

RESULT AND DISCUSSION

Catalytic Activity

Fig. 1 shows the catalytic activity of the Mo/Al$_2$O$_3$ catalysts for the HDS of thiophene as a function of CA/Mo mole ratio. The HDS activity of the 8.7 wt% Mo/Al$_2$O$_3$ catalysts was slightly decreased by the addition of citric acid using post-treatment method up to CA/Mo mole ratio = 1 and was leveled off by a further addition of citric acid. With the 20 wt% Mo/Al$_2$O$_3$ catalysts, the HDS activity was significantly increased when citric acid was added by the post-treatment method up to a CA/Mo mole ratio around 1 and became constant at CA/Mo > 1. It is noteworthy in Fig. 1 that the effect of citric acid addition strongly depends on the Mo loading and that the HDS activity of 20 wt% Mo/Al$_2$O$_3$ is

significantly increased by the post-treatment with citric acid at CA/Mo mole ratio > 1.

Fig. 2 depicts the HDS activity of a series of Mo/Al$_2$O$_3$ catalyst as a function of Mo loading with/out the citric acid addition. The HDS activity of calcined Mo/Al$_2$O$_3$ catalysts was gradually decrease as the Mo loading was increased, suggesting that the dispersion area of MoS$_2$ particles was not enough on the Al$_2$O$_3$ surface (3-3.2 Mo nm^{-2}) and the bulky MoO$_3$ crystalline became created, in agreement with our previous result [6]. However, on the post-treated Mo/Al$_2$O$_3$ catalysts, the HDS activity was enhance 2 times even at higher Mo loading (Mo ≤ 25 wt%). It seems that the dispersion of MoS$_2$ particles was enhanced with the addition of citric acid. It is suggested that together with citric acid, perhaps, MoO$_3$ crystalline rendered the Mo-CA complex structures and become well dispersed on the support.

Moreover, the CVD technique was applied to get deeper insight into the different behaviors of these catalysts in Fig. 2 [7]. The HDS activity of calcined Co-Mo/Al$_2$O$_3$ catalysts was sharply decrease with increasing Mo loading, explaining that the dispersion of MoS$_2$ particles become decreased as a high Mo loading. Surprisingly, Fig.2 shows that the HDS activity was drastically increase even at higher Mo loading (up to 25 wt% Mo) which almost reach 5 times compare with the calcined catalysts before the CVD. It means that a great amount of active sites, Co-Mo-S phases, was formed because of the formation of highly dispersed of MoS$_2$ particles on the support when citric acid was added by the post-treatment. It is noteworthy that a post-treatment method with citric acid is effective to improve the performance activity of HDS catalyst.

Dispersion of Mo prepared by citric acid

The amount of Co anchored by the CVD process was evaluated by XRF analysis. The amounts of Co in Co-Mo/Al$_2$O$_3$ with/out the citric acid addition are depicted in Fig.3 as a function of Mo content. Obviously, the amount of Co on the calcined Co-Mo/Al$_2$O$_3$ was decreased as the Mo content was increased, indicating that the edge dispersion of MoS$_2$ particles become decreased with the increasing of Mo content. On the other hand, the amount of Co on the post-treated Co-Mo/Al$_2$O$_3$ catalysts significantly increased up to Mo content around of 25 wt% Mo. It seems that the MoS$_2$ particles are still highly dispersed on the support Al$_2$O$_3$ even at a high Mo loading by the post-treatment with citric acid.

Similar trend result is also observed on the NO adsorption capacity shown in Fig. 4. With the post-treatment, the NO adsorption capacity is still increased even at a high Mo loading (Mo ≤ 25 wt%), while it is not
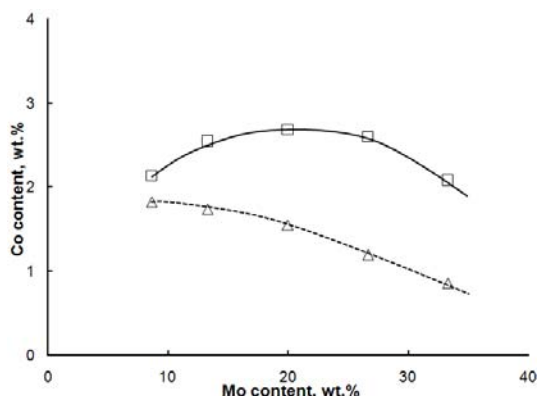
Fig 3. The amount of Co anchored by the CVD for Co-Mo/Al$_2$O$_3$ (CA/Mo mole ratio = 2) as a function of Mo loading. (Δ) calcined and (□) post-treatment
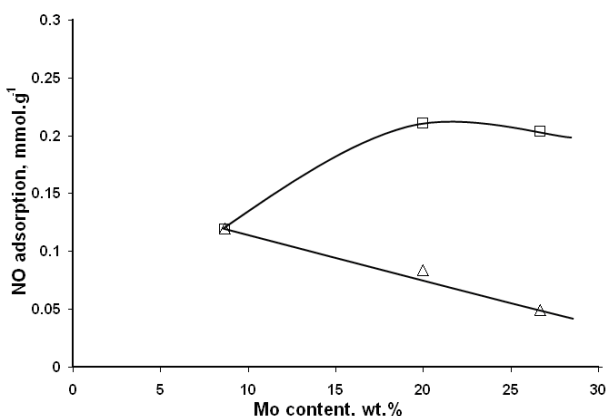

Fig 4. The amount of NO adsorption capacity of Mo/Al$_2$O$_3$ prepared by CA addition as a function of Mo loading (CA/Mo mole ratio = 2.0). The symbols are the same as those in Fig.3.
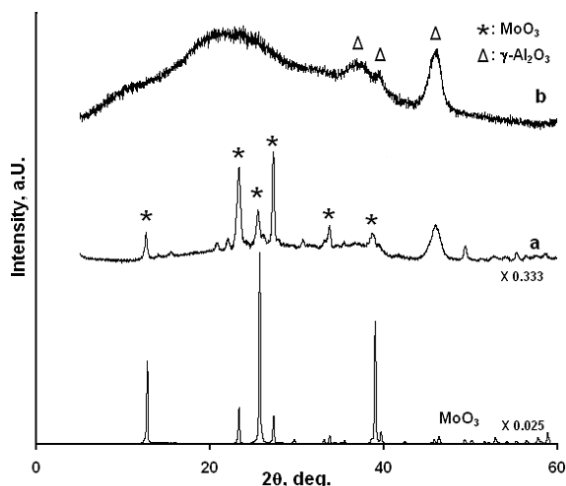

Fig 5. XRD patterns of the 20 wt% Mo/Al$_2$O$_3$ catalysts prepared by the addition of citric acid (CA/Mo = 2). (a) calcined and (b) post-treatment. The XRD pattern of MoO$_3$ is also shown as a reference

observed on the calcined Mo/Al$_2$O$_3$ catalysts. The amounts of NO adsorption (Fig. 4) and Co incorporation (Fig. 3) clearly show that the post-treatment of the calcined Mo/Al catalysts with citric acid greatly increases the dispersion of MoS$_2$ particles and, correspondingly, the amount of active sites, Co-Mo-S. Moreover, interesting point is shown at the 8.7 wt% Mo content in Fig. 4. The amount of NO adsorption was not changed after the citric acid was added. It considers that Mo has already well dispersed forming monolayer on the surface support [6], in consistent with the result in Fig. 2.

Fig. 5 shows that MoO$_3$ diffraction peaks were clearly observed for the calcined 20 wt% Mo/Al catalyst together with the peaks due to γ-Al$_2$O$_3$. The diffraction peaks due to crystalline MoO$_3$ were removed when citric acid was used by the post-treatment (Fig. 5-b) and become boarded peaks. It is considered that citric acid consumes the crystalline MoO$_3$ particles to form Mo-CA complexes and Mo becomes well-dispersed or in an amorphous form on the surface Al$_2$O$_3$. Meanwhile, the XRD patterns of the calcined Mo/Al catalyst with 8.7 wt% Mo showed no MoO$_3$ diffraction peaks with or without the addition of citric acid by the post-treatment, indicating that Mo is already well-dispersed on the support forming monolayer at 8.7 wt% Mo [6].

Mo K-edge XAFS measurements were conducted in order to get information on the local structure of Mo species. Fig. 6 shows the Mo K-edge XAFS Fourier transforms (FT) for oxidic Mo/Al$_2$O$_3$ prepared by the post-treatment method using citric acid (CA/Mo = 1.2). This present study only used the Mo-Mo region to discriminate these Mo species due to the Mo-O region 0.08–0.20 nm is not well resolved for differentiation of Mo species. And thus, only the Mo-Mo region 0.23–0.40 nm was analyzed to characterize Mo species in the Mo/Al$_2$O$_3$ catalysts. The Mo-Mo structural parameters, as derived from the XAFS analyses for the oxide catalysts, are listed in Table 1. As shown in Table 1, the Mo-Mo atomic distance for the 8.7 wt% Mo/Al$_2$O$_3$ catalysts was 0.33 nm after calcination, indicating that molybdenum is present mainly as polymolybdate-like species (Fig. 6A). The Mo-Mo atomic distance was increased to 0.34 nm and became close to that for the Mo-CA complex, when citric acid was added by the post-treatment method, showing that Mo-CA complexes are formed even at a CA/Mo mole ratio of 1.2, in consistent with Fig.1. However, the Mo-Mo coordination number of the catalysts was lower than that for the reference compound as listed in Table 1, suggesting a structural disorder of Mo-CA complexes due to the interaction with the support surface and/or a partial formation of the complexes. Nevertheless, the

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Table 1. Structural parameters[a] derived from Mo K-edge EXAFS for Mo/Al oxide catalysts prepared by using citric acid (CA/Mo mole ratio = 1.2).

Catalyst precursor	Absorber-scatterer pair	R (nm)	CN	E_0 (eV)	σ (10^{-3} nm)	R_f (%)
8.7wt% Mo/Al						
calcined*	Mo-Mo	0.333	0.7	-4.9	7.8	11.7
post-treatment	Mo-Mo	0.342	0.6	-1.1	8.3	3.4
20wt% Mo/Al						
calcined*	Mo-Mo	0.374	0.9	-5.6	7.4	7.4
post-treatment	Mo-Mo	0.342	0.3	0.1	7.7	9.3
Reference compound						
MoO_3	Mo-Mo	0.345	2.1	0.4	6.2	9.7
	Mo-Mo	0.378	2.1	-0.9	6.0	
$(NH_4)_6Mo_7O_{24} \bullet 4H_2O$	Mo-Mo	0.325	1.8	-1.8	7.3	5
	Mo-Mo	0.343	2.0	-1.6	7.3	
$K_4[(MoO_2)_2O(Hcit)_2] \bullet 4H_2O$	Mo-Mo	0.339	1.5	-6.5	6.4	4.5

[a] R, distance; CN, coordination number E_0, inner potential σ, Debye-Waller-like factor; R_f, R factor defined as $R_f = \{\sum[\chi_{obs}(k) - \chi_{cal}(k)]^2 / \sum\chi_{obs}(k)^2\}^{1/2}$
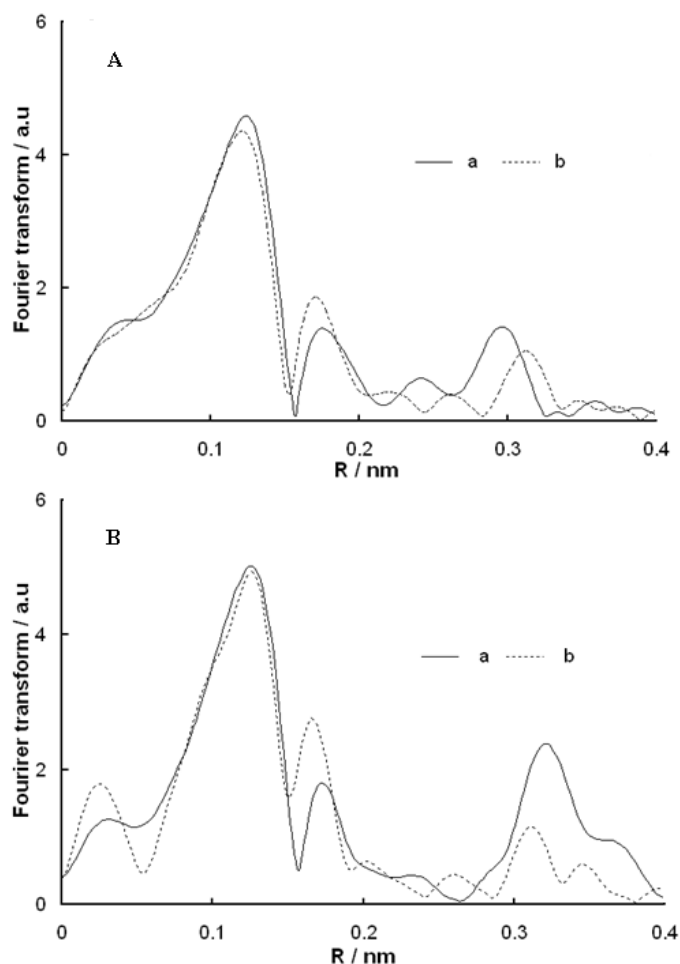* CA/Mo mole ratio = 0

Fig 6. Fourier transforms of k^3-weighted Mo K-edge EXAFS for Mo/Al$_2$O$_3$ prepared by CA addition (CA/Mo mole ratio = 1.2). (A) 8.7 wt% Mo and (B) 20 wt% Mo: (a) calcined and (b) post-treatment

presence of a Mo-CA monomeric complex is not excluded for these catalysts.

With the 20 wt% Mo/Al$_2$O$_3$ catalysts shown in Fig. 6B, the Mo-Mo atomic distance for the calcined catalyst was 0.37 nm. It is clearly shown that molybdenum is present predominantly as MoO$_3$ species on the calcined catalyst, in conformity with the XRD results shown in Fig. 5. When citric acid was used in the preparation, the Mo-Mo atomic distance became 0.34 nm by the post-treatment. The local structure of Mo in 20 wt% Mo/Al$_2$O$_3$-post-treated shows the formation of Mo-CA surface complexes. However, the Mo-Mo coordination number of the Mo-CA surface complexes (0.3) was considerably lower than that of the reference compound (Table 1), suggesting that the Mo-CA complexes on 20 wt% Mo/Al$_2$O$_3$ catalysts are in structural disorder and/or are partially formed. We conclude from the characterizations by XRD and XAFS that citric acid consumes crystalline MoO$_3$ particles and, probably, coexisting well-dispersed Mo oxide clusters to form highly dispersed Mo-CA surface complexes and, in part, polymolybdate species by the post-treatment of calcined Mo/Al with citric acid. The Mo K-edge XANES spectra for these catalysts (not shown for brevity) are consistent with this conclusion.

Effect of post-treatment on Mo/Al$_2$O$_3$ catalyst

Fig. 2 clearly shows that the HDS activity of 8.7 wt% Mo/Al$_2$O$_3$ and Co-Mo/Al$_2$O$_3$ is not changed or even decreased with the addition of citric acid by the post-treatment method. The amounts of NO adsorption (Fig. 3) demonstrate that the dispersion of MoS$_2$ particles is unchanged or even decreased after citric acid was added. Therefore, we conclude that with the 8.7 wt% Mo/Al$_2$O$_3$ catalyst system the addition of citric acid does
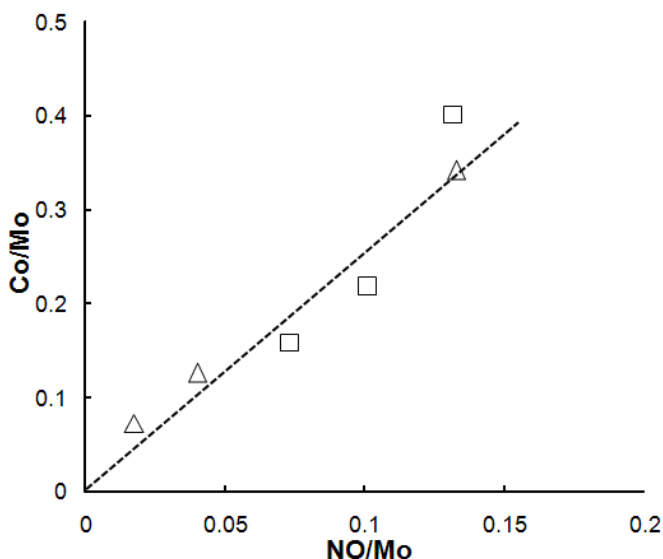
Fig 7. Correlation between the NO/Mo mole ratio for Mo/Al$_2$O$_3$ and the Co/Mo mole ratio for Co-Mo/Al$_2$O$_3$ by the CVD. (Δ) calcined and (□) post-treatment

not affect the catalyst properties very much or is even detrimental, since in the present Mo/Al$_2$O$_3$-calcined catalyst a monolayer dispersion of Mo is established and Mo oxides are extremely highly dispersed on the support at 8.7 wt% Mo [1,6,9]. Yet, Mo K-edge XAFS (Fig. 6A) clearly show that Mo-CA complexes are formed by the addition of citric acid. We consider that the Mo-CA complex formation weakens the support-Mo precursor interactions and thus results in a slight decrease of the dispersion of MoS$_2$ particles.

Moreover, the present study demonstrates that the HDS activities of 20 wt% Mo/Al$_2$O$_3$ and Co-Mo/Al$_2$O$_3$ are significantly increased after citric acid was added by the post-treatment method (Fig. 2). Figs. 3 and 4 clearly show that the dispersion of MoS$_2$ particles is greatly increased by the post-treatment at a high Mo content (up to 25 wt% Mo). It is revealed by XRD (Fig. 5) and the Mo K-edge XAFS (Fig. 6 and Table 1) that, in the case of the post-treatment, citric acid consumes crystalline MoO$_3$ particles and, probably, coexisting well-dispersed Mo oxide clusters to form well-dispersed Mo-CA surface complexes. The present study demonstrates that the addition of citric acid by the post-treatment is very effective to increase the edge dispersion of MoS$_2$ particles on the catalysts, in particular, at a high Mo content (up to 25 wt% Mo).

We also propose that other favorable effects of citric acid addition on the 20 wt% Co-Mo/Al$_2$O$_3$ catalysts causes weakened interactions between Mo and the support surface due to the formation of Mo-CA surface complexes as well as the increased dispersion of Mo precursors at the expense of crystalline MoO$_3$ particles. Therefore, facilitating easy sulfidation of Mo and thus

improving the sulfidation degree of Mo on the Mo/Al$_2$O$_3$ catalysts by the post-treatment method, in particular at high Mo loading (20 wt% Mo). This agrees with the observations by Funamoto and Segawa [3] and by Fujikawa et al. [10].

Moreover, in order to estimate the adsorption sites of Co(CO)$_3$NO on MoS$_2$, we made a correlation between the Co/Mo mole ratio for Co-Mo/Al$_2$O$_3$ by the CVD and the NO/Mo mole ratio for Mo/Al$_2$O$_3$ as depicted in Fig. 7. It is shown that a good proportional correlation in Fig. 7 for these catalysts, demonstrating that the Co atoms introduced to Mo/Al$_2$O$_3$ by the CVD was selectively decorated on the edge sites of MoS$_2$ particles to form active sites, Co-Mo-S phases, since it is well established [1] that NO molecules absorb on coordinatively unsaturated Mo sites on the edge sites of MoS$_2$ particles [5]. However, it is also shown in Fig. 7 that the Co/Mo ratio for the post-treatment catalysts at 8.7 wt% Mo was slightly higher than the value expected from the linier line, describing an excess amount of Co over that requires for full decoration on MoS$_2$ edges sites is anchored on 8.7 wt% Mo/Al$_2$O$_3$-post-treatment. It is suggested that Co atom was also adsorbed on the Al$_2$O$_3$. With 8.7 wt% Mo, a monolayer dispersion of MoS$_2$ particles (3-3.2 Mo nm^{-2}) was already formed on the support. Therefore, the addition of citric acid just modified the interaction between support and Mo precursor and the textural properties of Al$_2$O$_3$. Thus, some of Co atoms is also anchored with the surface Al$_2$O$_3$ together with citric acid. Moreover, it is worth to be noted that the CVD technique is one of advanced method for the HDS catalyst preparation to prepare active sites selectively, Co-Mo-S, without the formation of Co sulfide clusters, Co$_9$S$_8$ [5-7].

CONCLUSION

Based on the HDS activity and the physicochemical data, it is concluded that the HDS activity and the edge dispersion of MoS$_2$ particles are not modified very much by the post-treatment method with citric acid at 8.7 wt% Mo loading due to already monolayer dispersion. On the other hand, significantly improvement of the HDS activity and the edge dispersion of MoS$_2$ particles are observed at a high Mo content (up to 25 wt% Mo) by the post-treatment. It is indicated that citric acid consumes crystalline MoO$_3$ particles on the calcined MoO$_3$/Al$_2$O$_3$ by the post-treatment method to form well-dispersed Mo-CA surface complexes and thus improves the edge dispersion of MoS$_2$ particles on the catalyst surface after sulfidation. Moreover, it is suggested that the sulfidation degree of Mo for Mo/Al$_2$O$_3$catalysts is also increased with citric acid addition by the post-treatment in particular, at a high Mo content. A CVD technique is

one of advance method for the HDS catalysts preparation to form Co-Mo-S phases selectively without the formation of Co sulfide clusters.

ACKNOWLEDGEMENT

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