EVALUATION OF Co-Mo/Al$_2$O$_3$ CATALYSTS FOR HYDRODESULFURIZATION PREPARED BY THE CHEMICAL VAPOR DEPOSITION TECHNIQUE AND CITRIC ACID ADDITION

Nino Rinaldi

Research Center for Chemistry (PP Kimia) - LIPI
Kawasan Puspiptek, Serpong 15314, Tangerang
e-mail: nino_rinaldi@yahoo.com

ABSTRACT

EVALUATION OF Co-Mo/Al$_2$O$_3$ CATALYSTS FOR HYDRODESULFURIZATION PREPARED BY THE CHEMICAL VAPOR DEPOSITION TECHNIQUE AND CITRIC ACID ADDITION. Sulfided Co-Mo or Ni-Mo based catalysts still have been extensively used in refinery for Hydrodesulfurization (HDS) reaction, which is so-called Co-Mo-S phase as active sites. It is proposed that to obtain near zero sulfur content of fuels in the future is by improving the performance of Co-Mo catalysts. It could be approached with enhancing the amounts of active sites, Co-Mo-S phases, for instance with a sophisticated HDS catalysts preparation such as by a Chemical Vapor Deposition (CVD) technique using Co(CO)$_3$NO as a precursor of Co and by the citric acid addition. It is demonstrated that if MoS$_2$/Al$_2$O$_3$ is exposed to Co(CO)$_3$NO vapor and subsequently sulfided, Co-Mo-S phases form selectively when the Mo content exceeds monolayer loading. The maximum potential HDS activity of Co-Mo/Al$_2$O$_3$ catalysts also can be obtained by the CVD technique. With the conventional Co-Mo/Al$_2$O$_3$ catalysts, the edges of MoS$_2$ particles are completely occupied by Co atoms around of 4 wt% Co, thus more addition of Co caused blocking of the active sites by overlayers of Co sulfide clusters. However, with the citric acid addition, not only the amount coverage of Co atoms is increased, but also a high content of Mo could be also well dispersed (Mo > 20 wt%) on the surface support forms monolayer. In addition, the amount of Co forming Co-Mo-S phases was estimated from the correlation between NO/Mo and Co/Mo ratio by the CVD technique.

Key words: Hydrodesulfurization, Preparation, Co-Mo catalysts, Chemical Vapor Deposition, Citric acid

ABSTRAK

EVALUASI KATALIS HIDRODESULFIRISASI Co-Mo/Al$_2$O$_3$ YANG DIPREPARASI DENGAN TEKNIK *CHEMICAL VAPOR DEPOSITION* SERTA PENAMBAHAN ASAM SITRAT. Katalis sulfidasi Co-Mo atau Ni-Mo masih sering digunakan di kilang untuk reaksi Hidrodesulfirisasi (HDS), dengan fasa Co-Mo-S sebagai sisi aktif dari katalis. Diketahui bahwa untuk mendapatkan kandungan sulfur yang mendekati nol pada bahan bakar dapat dilakukan melalui pengembangan katalis Co-Mo. Hal ini bisa dicapai dengan meningkatkan jumlah sisi aktif katalis, fase Co-Mo-S, salah satunya adalah katalis dipreprasi menggunakan teknik *Chemical Vapor Deposition* (*CVD*) dengan Co(CO)$_3$NO sebagai prekusor Co serta penambahan asam sitrat. Jika katalis MoS$_2$/Al$_2$O$_3$ diuapkan pada uap Co(CO)$_3$NO dan selanjutnya disulfidasi, fase Co-Mo-S terbentuk secara selektif pada jumlah Mo diatas pembentukan monolayer. Maksimum pontensial *HDS* aktivitas katalis Co-Mo/Al$_2$O$_3$ juga bisa diperoleh dengan teknik *CVD*. Pada katalis Co-Mo/Al$_2$O$_3$ konvensional, semua tepi partikel MoS$_2$ diisi oleh atom Co pada konsentrasi Co sekitar 4 wt%, seterusnya jika jumlah Co ditambah akan mengakibatkan bloking pada sisi aktif akibat pembentukan klaster Sulfida Co. Namun, dengan penambahan asam sitrat, bukan saja jumlah atom Co yang mengisi tepi partikel MoS$_2$ meningkat, jumlah konsentrasi logam Mo yang terdispersi secara merata pada permukaan juga meningkat (Mo > 20 wt%) membentuk monolayer. Lebih lanjut, jumlah atom Co yang membentuk fase Co-Mo-S dapat dihitung melalui rasio antara NO/Mo dan Co/Mo dari teknik *CVD*.

Kata kunci : Hidrodesulfirisasi, Preparasi, Katalis Co-Mo, *Chemical Vapor Deposition*, Asam sitrat

INTRODUCTION

Supported nickel- or cobalt-molybdenum sulfide catalysts are widely used in the industrial HDS process. 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 [1-4]. With the increasing demand for obtaining zero sulfur emission and zero sulfur fuel in the future, 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. It is reportedly that with a Chemical Vapor Deposition (CVD) technique, using $Co(CO)_3NO$ as a precursor, was one of effective method to increase Co coverage on the MoS_2 catalyst [5-8]. Okamoto *et al.* show that the amount of Co accommodated on the Mo sulfide catalyst is proportional to the amount of NO adsorption, indicating that all Co sulfide species are selectively interacted with the edges sites of MoS_2 particles without the formation of inactive Co sulfide clusters, Co_9S_8 [8]. Hence, the maximum potential activity and the intrinsic activity of the Co-Mo catalyst can be evaluated.

During the development of HDS catalysts, chelating agents have been used as additives of Co-Mo catalysts [9-21]. It is well established that the addition of chelating agents in the catalyst preparation is very effective not only to improve the dispersion of Mo, but also increasing the coverage of Co on the edges of MoS_2 particles, thus improves the HDS activity. Recently, citric acid has also been used as a chelating agent. Fujikawa and co-workers, [22-24] in their developments of ultradeep Co-Mo HDS catalysts, used citric acid as a chelating agent combined with phosphoric acid. They showed that the addition of citric acid improves the Co coverage on the edges of MoS_2 particles, because citric acid forms a complex with Co. Mo dispersion is kept high throughout the preparation process, resulting in an increase in the HDS activity through use of citric acid in the impregnation solution [25]. XPS to show that the sulfidation degree of Mo improved upon addition of citric acid [26].

In the present study, investigating the effect of citric acid addition on the HDS activity of Co-Mo/Al_2O_3 catalysts was conducted on laboratory. Series of Mo/Al_2O_3 and Co-Mo/Al_2O_3 catalysts are prepared with the citric acid addition by a simultaneous impregnation method or by a post-treatment method. The prepared catalysts were characterized by several means of physicochemical techniques, and were tested for the HDS of thiophene. A CVD technique using $Co(CO)_3NO$ as a probe molecule was used in order to estimate the maximum potential activity and characterization of the catalyst [6–8].

EXPERIMENTAL METHOD

Catalyst Preparation

A series of MoO_3/Al_2O_3 was prepared by an impregnation technique. γ-Al_2O_3 (JRC-ALO-7: 180 $m^2 g^{-1}$) was impregnated with an $(NH4)_6Mo_7O_{24}.4H_2O$ (AHM) aqueous solution, followed by calcination at 773 K for 5 h (denoted as Mo/Al-C). The Mo content of Mo/Al-C was 8.7-35 wt% Mo. Then, the calcined Mo/Al-C was impregnated with a Citric Acid (CA) aqueous solution; this step was followed by just drying at 383 K for 16 hours (without calcination). The CA/Mo mole ratio was fixed of 2.0 as a function of Mo loading. The pH of the impregnation solution was not adjusted in the present study. This catalyst preparation technique is denoted here as a post treatment method. The catalysts thus prepared are designated as CA/Mo/Al here in after. Another series of Mo/Al catalysts (Mo-CA/Al) was prepared by simultaneous impregnation of AHM and CA, followed by drying at 383 K for 16 hours (without calcination).

A series of CoMo/Al catalysts (0-10 wt % Co, 8.7 wt % Mo) with varying Co contents was prepared by a double impregnation method (Mo first and then Co). An aliquot of the catalyst was calcined at 773 K for 5 h after each step. Then, the CoMo/Al catalysts were impregnated with citric acid (CA/Mo mole ratio = 2.0) and just dried at 373 K for 16 h (without calcination) to prepare CA/CoMo/Al. The pH of the impregnation solution was not adjusted in the present study. Another series of CoMo/Al catalysts (CoMo-CA/Al) was prepared by simultaneous impregnation of Co, AHM and CA, followed by just drying at 383 K for 16 hours.

The catalyst was sulfided in a 10% H_2S/H_2 flow at 673 K for 1.5 h. A CVD technique was employed to introduce Co into the sulfided catalyst [6]. Briefly, the sulfided catalyst was first evacuated at 673 K for 1 hours and subsequently exposed for 5 minutes at room temperature to a vapor of $Co(CO)_3NO$ kept at 273 K (CVD technique). After evacuation at room temperature, the catalysts were sulfided again at 673 K for 1.5 hours. The catalyst thus prepared is denoted, for example, CVD-Co/CA/Mo/Al and CVD-Co/CA/CoMo/Al, when CA/Mo/Al and CA/CoMo/Al were 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). The accuracy of the Co content was within ± 5 %.

Activity Test

The initial activity of the freshly prepared catalyst was evaluated on the HDS 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 hour 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 [6,7]. The reaction products were analyzed by on-line gas chromatography. The products were mainly C_4 compounds and a corresponding amount of H_2S. The amount of H_2S formation was 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 %.

Characterization

Laser Raman spectra of the prepared catalysts in the presence and absence of citric acid addition at several pH values of the impregnation solution 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 Ar$^+$ laser was used for excitation at an intensity of 20 mW at the source. Diffuse Reflectance Spectra (DRS) UV-Visible characterization of CoMo/Al with the citric acid addition at several pH value of the impregnation solution was carried out in air on a UV-2500PC spectrometer (Shimadzu) in a wavelength range of 240-850 nm, using $BaSO_4$ powder as a reference.

The amounts of NO adsorption on sulfided CA/Mo/Al were measured at room temperature by a pulse technique [6,27]. After cooling in the H_2S/H_2 stream, the sulfided catalyst was flushed with a high-purity He stream, then a pulse of 10 % NO/He was introduced periodically until no adsorption was detected. The reproducibility was usually better than $\pm$ 5 % of the total amount of NO adsorption.

Mo K-edge XAFS spectra for CoMo/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 No. 2006G331, 2008G200). The synchrotron radiation was monochromatized by a Si (311) 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 (40-150 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 MoS_2.

RESULTS AND DISCUSSION

Catalytic Activity of Mo/Al Catalysts

Figure 1 shows the thiophene HDS activity of the Mo/Al catalysts prepared by the addition of citric acid (CA/Mo = 2) as a function of Mo content. The HDS activity of the Mo/Al-C catalysts slightly increased up to Mo content around 13 wt% Mo and became lower with a further increase of Mo content. It is suggested that Mo is rather well dispersed on the support up to 13 wt% of Mo in the present study [2,7,28]. With Mo-CA/Al, a similar trend of the HDS activity was observed. However, the HDS activity of Mo-CA/Al was slightly lower than that of Mo/Al-C, implying that the dispersion of Mo particles is slightly decreased at <20 wt% Mo by the simultaneous impregnation of citric acid.

The great significance result as shown in Figure 1 is an extremely increased high HDS activity of CA/Mo/Al post-treatment catalysts. The HDS activity of the calcined Mo/Al catalysts was drastically increased by the post-treatment method, in particular, at a high Mo content (>20 wt% Mo). CA/Mo/Al was twice as active as the calcined catalysts at 20 wt% Mo. In contrast, Figure 1 shows that the HDS activity of CA/Mo/Al at 8.7 wt% Mo is the same as that of the simultaneous impregnation catalyst (Mo-CA/Al) but slightly lower than that of the calcined catalyst. Thus, the effect of the citric acid addition strongly depends on the Mo content of Mo/Al catalysts and on the addition method.

To evaluate the maximum potential activity [6], the sulfided Mo/Al, Mo-CA/Al and CA/Mo/Al were subjected to the CVD of Co(CO)$_3$NO. It has proposed that fully promoted Co-Mo catalysts without active site blockings by catalytically inactive Co sulfide clusters can be prepared by the CVD technique [6]. The HDS
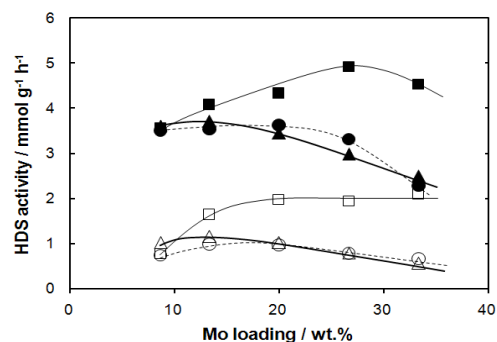

Figure 1. HDS activity of the Mo/Al catalysts prepared by the addition of citric acid (CA/Mo mole ratio = 2) as a function of Mo loading. (open symbols) : Mo/Al and (closed symbols) : CVD-Co/Mo/Al. (O,●) calcined, (△,▲) simultaneous impregnation and (□,■) post-treatment
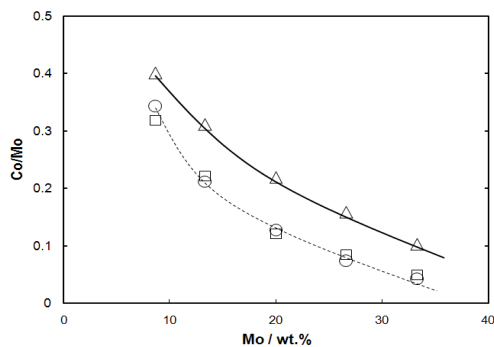
Figure 2. Correlation between the Co/Mo weight ratio for the Mo/Al catalysts prepared by the addition of citric acid (CA/Mo mole ratio = 2) as a function of Mo loading. (O) calcined, (□) simultaneous impregnation and (Δ) post-treatment

Figure 3. Correlation between the Co/Mo weight ratio for the NO/Mo mole ratio for Mo/Al catalysts prepared by the addition of citric acid (CA/Mo mole ratio = 2). (O) calcined, (□) simultaneous impregnation and (Δ) post-treatment

activities of the catalysts are depicted in Figure 1 (closed symbols) as a function of Mo loading. The addition of Co by the CVD technique enhanced the HDS activity. The HDS activity of CVD-Co/Mo/Al-C remained unchanged up to Mo content of 13 wt% Mo and then gradually decreased with a further increase of Mo content, in agreement with our previous study [26]. The HDS activity of CVD-Co/Mo-CA/Al was almost the same as that of the calcined catalysts. This is in conformity with the observation that the HDS activities of the unpromoted Mo/Al–C and of the Mo-CA/Al catalysts are almost the same (Figure 1, opened symbols). On the other hand, the HDS activity of CVD-Co/CA/Mo/Al was considerably increased up to Mo content around 27 wt% Mo and then decreased with a further increase of Mo content. The HDS activity of CVD-Co/Mo/Al was about 70 % increased at 27 wt% Mo by the post-treatment of the calcined Mo/Al with citric acid.

The CVD technique can also be used for characterization of the surface structure of the catalysts [6-8], thus the amount of Co anchored after the CVD process was evaluated in order to estimate the dispersion of MoS_2 particles. The amounts of Co in CVD-Co/Mo/Al are depicted in Figure 2 as a function of Mo content. Obviously, the amount of Co was decreased as the Mo content was increased. CVD-Co/Mo/Al-C and CVD-Co/Mo-CA/Al catalysts showed a similar amount of Co after the CVD, suggesting that the dispersion of MoS_2 particles in these catalysts is not very different. Moreover, the same HDS activity of CVD-Co/Mo/Al-C and CVD-Co/Mo-CA/Al catalysts (Figure 1) is also ascribed to the intrinsic activity of Co-Mo-S being almost the same in these catalysts. On the other hand, with the CVD-Co/CA/Mo/Al catalysts the amount of Co was increased compare to the simultaneous-impregnation catalysts. It is 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 Co-Mo-S. This information is also supported from the NO adsorption capacity shown in Figure 3 that the dispersion of MoS_2
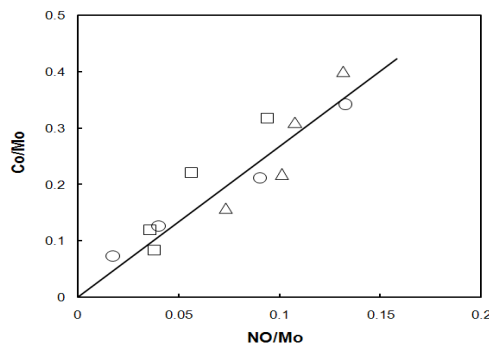
particles is significantly increased by the post-treatment method as well the active phase Co-Mo-S.

Moreover, Figure 3 shows the correlation between the amount of Co by the CVD and the NO adsorption capacity of Mo/Al catalysts with the addition of citric acid. It is already known that the amount of NO adsorption capacity describes the edges sites of MoS_2 particles [2,29-32]. A good proportional correlation in Figure 3 for these catalysts suggests that with the CVD, Co is selectively anchored only on the edges of MoS_2 particles to form the active sites, Co-Mo-S, after sulfidation.

Catalytic Activity of CoMo/Al Catalysts

The HDS activity of CoMo/Al is depicted in Figure 4 as a function of Co loading. With the calcined CoMo/Al catalyst (CA/Mo = 0) in Figure 4, the HDS activity is gradually enhanced up to a Co content of 4 wt% and is slightly decreased upon further addition of Co, suggesting that the active sites are masked by the catalytically inactive cobalt sulfide clusters, particularly at >4 wt% Co [8]. Similar trend result of HDS activity was shown when citric acid was added even by the post-treatment of by the simultaneous impregnation method. However, the HDS activity of CoMo-CA/Al and CA/CoMo/Al is slightly higher than that of the calcined CoMo/Al catalysts although the increase of the HDS activity of CoMo/Al upon post-treatment is not very large (12%). It is suggested that due to improving the Co coverage on the edges of MoS_2 particles, because citric acid forms a complex with Co [22-24].

CoMo/Al was subjected to CVD for characterization of the surface structure of the catalysts. The HDS activity of the catalysts is depicted in Figure 4. The HDS activity of CoMo/Al is considerably increased by the addition of Co using CVD at a low loading of Co. The HDS activity of CVD-Co/CoMo/Al gradually decreases as the original amount of Co increases up to 4 wt% and becomes identical with that of CoMo/Al at >4 wt% Co. It is suggested that the edges of MoS_2
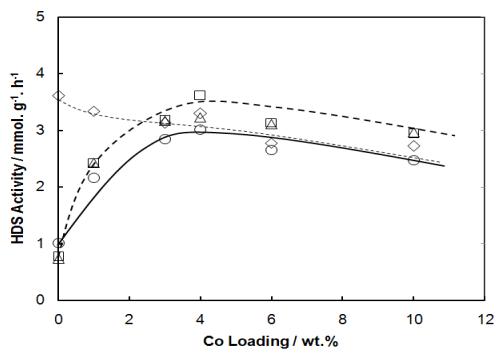
Figure 4. HDS activity of CoMo/Al2O3 catalysts as a function of Co loading (CA/Mo mole ratio = 2). (O) CoMo/Al, (◇) CVD-Co/CoMo/Al, (△) CoMo-CA/Al and (□) CA/CoMo/Al

particles are partially decorated by Co at <4 wt% Co [8]. On the other hand, at a higher Co content (Co > 4 wt%), the HDS activity of the catalyst is identical to that of the calcined CoMo/Al, indicating that the MoS_2 edge sites are already fully covered by Co at >4 wt% Co.

Of great importance in Figure 4 is at the amount of Co of 4 wt%. With the post-treatment, the HDS activity of 4 wt% CA/CoMo/Al is equal to the calcined CVD-Co/Mo/Al (Co = 0) as a maximum potential activity, while it is not shown on the simultaneous impregnation catalysts. It should be note that, with 4 wt% Co, all Co is fully attached on the MoS_2 particles without the formation of Co sulfide clusters, Co_9S_8, when citric acid was added, in particular by the post-treatment, thus reaches the maximum potential activity. It is proposed that the addition of citric acid by the post-treatment is one of promising method to prepare highly active HDS catalyst.

Laser Raman Spectroscopy

The Raman spectra of Mo/Al catalysts are presented in Figure 5(A) as with and without the addition of citric acid. The dried Mo/Al catalyst (CA/Mo = 0, uncalcined, Figure 5(A(a)) clearly shows a strong band at 950 cm^{-1}, a sharp band at 900 cm^{-1} and weak bands at 577 and 363 cm^{-1}. These bands indicate the presence of an Anderson-type heteropolyanion $[Al(OH)_6Mo_6O_{18}]^{3-}$ species [20,33]. The formation of hexamolybdoaluminate involves molybdenum-assisted dissolution of the alumina support: alumina cations in solution react with molybdate to form $[Al(OH)_6Mo_6O_{18}]^{3-}$ [20]. The calcined 8.7 wt% Mo/Al catalyst on Figure 5(A(b)) showed a strong band at 960 cm^{-1}, which is assigned to a v_s (Mo=O) stretching vibration mode due to polymolybdatespecies [33–35].

After citric acid (CA/Mo=2) has been added to dried Mo/Al, the peak intensity due to the $AlMo_6$ Anderson-type anion was completely removed, where a broad band at 950 cm^{-1} predominated for Mo-CA/Al on Figure 5(A(c)). Apparently, the band at 950 cm^{-1} is not fully assigned to the $AlMo_6$ species, since the bands
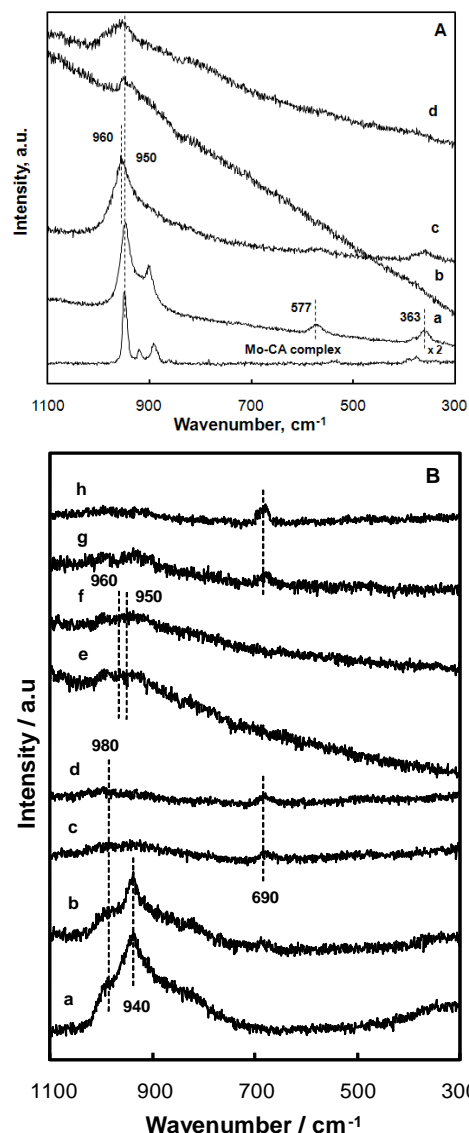
Figure 5. Raman spectra of the Co-Mo/Al catalysts prepared by the citric acid addition (CA/Mo = 2). (A) Mo/Al and (B) CoMo/Al: (a) dried, (b) calcined, (c) simultaneous impregnation and (d) post-treatment. The LRS of Mo-CA complex is also shown as a reference

at 900 cm^{-1} (sharp band), 577 and 363 cm^{-1}, characteristic of the $AlMo_6$ Anderson-type species, are completely removed, while the band at 950 cm^{-1} remains unaffected. In order to assign the band at 950 cm^{-1}, a reference compound $K_4[(MoO_2)_2O(Hcit)_2].4H_2O$ (H_4cit = citric acid) was synthesized [36]. Figure 5(A) depicts the LRS of the reference compound, showing a strong band at 950 cm^{-1} and weak bands at 921, 892, 538 and 385 cm^{-1}. Moreover, when citric acid was added on the calcined Mo/Al, the band of 960 cm^{-1} was also shifted to a broad band at 950 cm^{-1} as shown in Figure 5(A(d)) (CA/Mo/Al). This spectra is similar to in Figure 5(A(c)). Although this study could not detect the rest of the bands because of strong fluorescence, the band at 950 cm^{-1} should be assigned to a Mo–CA surface complex. A Mo–CA surface complex is formed of Mo/Al catalysts after citric acid is added,

even by the post-treatment pr by the simultaneous-impregnation method.

The Raman spectra of CoMo/Al oxidic catalysts as a function of Co loading is depicted in Figure 5(B). Obviously, the calcined CoMo/Al shows a set of bands at 940, 817, 370, and 335 cm^{-1}, which are assigned to $CoMoO_4$, an unfavorable phase for the formation of the Co-Mo-S-type structure [2,37]. A shoulder peak at 980 cm^{-1} shows the presence of polymolybdate species. Calcined 4 wt% CoMo/Al exhibits essentially the same spectrum as the 3 wt % Co catalyst. However, a band at 940 cm^{-1} is not observed for the calcined CoMo/Al at 6 wt % Co, and only a band due to Co_3O_4 is observed at 690 cm^{-1} in Figure 5(B(c)). This might be partly due to the strong fluorescence background. The band at 690 cm^{-1} indicates the presence of Co_3O_4 species [33,34]. It is evident that, at high Co content, poorly dispersed Co_3O_4 is formed on the catalysts, which is in agreement with the results of other workers [2,18]. Figure 4 shows that the optimum content of Co for 8.7 wt % Mo catalysts is around 4 wt %. At higher Co content, Co_3O_4 species becomes more abundant, and catalytically inactive cobalt sulfide clusters predominate after sulfidation, accompanying extensive blocking of the active sites and thereby reducing the activity of the catalysts at high Co content [8] which is in agreement with Figure 4.

After citric acid has been added, a broad band appears around 950-960 cm^{-1} for CA/CoMo/Al catalysts having 3 and 4 wt % Co (Figure 5B-e and -f), at the expense of a set of bands due to $CoMoO_4$ and a band at 980 cm^{-1} assigned to polymolybdates. A band at 960 cm^{-1} can be assigned to a $_{Vs}$ (Mo=O) stretching vibration mode of polymolybdate species [33-35], while the band at 950 cm^{-1} may be ascribed to Mo-CA complex formation, in accordance with the reference compound of Mo-CA complexes [36]. However, because the bands around 950-960 cm^{-1} are broad and not well resolved, it seems difficult to assign them to specific Mo species, but it is evident that surface $CoMoO_4$ and polymolybdate species react with citric acid to form Mo-CA surface complexes. For the catalysts at high Co contents (6 and 10 wt % Co), the band around 950-960 cm^{-1} is not clear because of strong fluorescence, but a band 690 cm^{-1} is observed, indicating that the Co_3O_4 species remains intact after the addition of citric acid. It seems difficult to redisperse Co_3O_4 even after citric acid has been added (CA/Mo = 2).

Mo K-Edge EXAFS

In order to obtain further information on the local structure of Mo species, Mo K-edge EXAFS measurements were obtained for Mo/Al. The Mo K-edge EXAFS Fourier transforms (FT) for oxidic Mo/Al is depicted in Figure 6 with and without the addition of citric acid. The FT peaks in the Mo–Mo region ranging 0.23-0.4 nm are characteristic to each reference

Table 1. Structural parametersa derived from Mo K-edge EXAFS for Mo/Al oxide catalysts prepared by citric acid addition

Catalyst precursor	Absorber-scatterer pair	R (nm)	CN	E_0 (eV)	σ (10^{-3} nm)	R_f (%)
8.7wt% Mo/Al						
Dried (un-calcined)*	Mo-Mo	0.333	0.9	-2	6.9	11.7
Calcined*	Mo-Mo	0.333	0.7	-4.9	7.8	11.7
Simultaneous-impregnation	Mo-Mo	0.341	0.8	-2.9	6.8	2.6
Post-treatment	Mo-Mo	0.342	0.6	-1.1	8.3	3.4
20wt% Mo/Al						
Dried (un-calcined)*	Mo-Mo	0.330	1.2	-9.0	7.5	7.5
Calcined*	Mo-Mo	0.374	0.9	-5.6	7.4	7.4
Simultaneous-impregnation	Mo-Mo	0.342	0.3	-0.4	7.5	9.6
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	
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Mo-Mo	0.325	1.8	-1.8	7.3	5
	Mo-Mo	0.343	2.0	-1.6	7.3	
$K_4[(MoO_2)_2O(Hcit)_2] \cdot 4H_2O$	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

compound, while theMo-O region 0.08-0.20 nm is very complicated and not well resolved. Accordingly, the Mo-Mo region is used to discriminate these Mo species in the present study. The Mo-Mo structural parameters as derived from the EXAFS analysis are listed in Table 1.

As shown in Table 1, the Mo-Mo atomic distance for the 8.7 wt% Mo/Al catalysts was 0.33 nm after drying and after calcination, indicating that molybdenum is present mainly as polymolybdate-like species in these catalysts, in agreement with the LRS spectra in Figure 5(A). 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 or by the simultaneous impregnation method, showing that Mo-CA complexes are formed regardless the addition method. However, the Mo-Mo coordination number of the catalysts was lower than that for the reference compound as listed in Table 1; 0.8 for the simultaneous impregnation catalyst and 0.6 for the post-treatment catalyst, 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 presence of a Mo-CA monomeric complex is not excluded for these catalysts.

The Mo-Mo local structure for 20 wt% Mo is shown in Figure 6(B). The Mo-Mo atomic distance for the dried catalyst was about 0.33 nm, suggesting that the local structure of Mo for the dried catalyst is described as polymolybdate-like species. On the other hand, 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
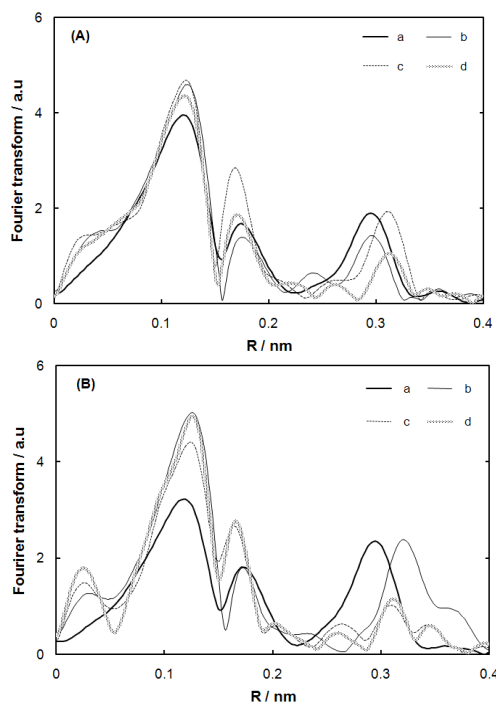
Figure 6. Fourier transforms of k3-weighted Mo K-edge EXAFS for Mo/Al prepared by the citric acid addition. (A). 8.7 wt% Mo and (B). 20 wt% Mo: (a). dried, (b). calcined, (c). simultaneous impregnation and (d). post-treatment

Figure 7. UV-Visible spectra of 3 wt.% Co-Mo catalysts with the addition of citric acid (CA/Mo mole ratio = 2). (a). Dried (CA/Mo = 0), (b). Calcined (CA/Mo = 0), (c). Simultaneous-impregnated and (d). post-treated. The UV-Vis spectrum of β-CoMoO₄ is shown for comparison

catalyst in Figure 6(B(b)). When citric acid was used in the preparation, the Mo–Mo atomic distance became 0.34 nm regardless of the addition procedure. The local structure of Mo in 20 wt% Mo-CA/Al and CA/Mo/Al 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 (Table1), suggesting that the Mo-CA complexes on 20 wt% Mo/Al catalysts are in structural disorder and/or are partially formed because of simultaneous formation of polymolybdate-like species in Figure 6(B) after citric acid is added. We conclude from the characterizations EXAFS 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, thus significantly improves the HDS activity of 20 wt% Mo/Al (Figure 1). It is worthy to be note that by the post-treatment with citric acid is one of promising way to prepare highly active HDS catalyst, in particular for a high Mo loading (>20 wt% Mo).

DRS UV-Vis Spectra

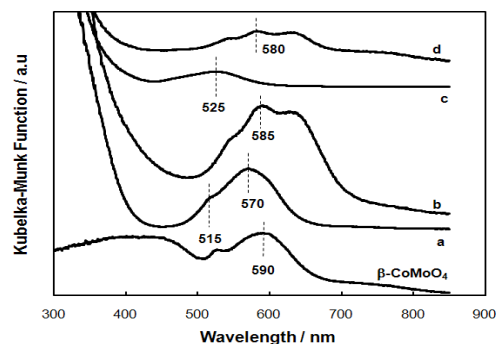The diffuse UV-Vis reflectance spectra of CoMo/Al catalysts are depicted in Figure 7 with and without the addition of citric acid (CA/Mo = 2). Two bands of reflectance at 570 and 515 nm were observed on the dried CoMo/Al catalyst (CA/Mo = 0, uncalcined, Figure 7(a)). The shoulder band at 515 nm is assigned to Co^{2+} ions in an octahedral coordination [38,39]. This band reveals the exchange of water ligands to support hydroxyl groups and the formation of surface Co species between $[Co(H_2O)_6]^{2+}$ and the Al_2O_3 surface [38,39]. The reflectance band at 570 nm is also characteristic of Co^{2+} ions in an octahedral coordination [39]. This band may be ascribed to the formation of inner-sphere surface Co^{2+} complexes by the exchange of one or more water ligands of $[Co(H_2O)_6]^{2+}$ ions with Al_xOH_y (x = 1, 2, or 3; y = 0 or 1) surface ligands [40,41]. This indicates that some of the Co^{2+} ions strongly interact with the support surface. When citric acid has been added by the simultaneous impregnation, only a single reflectance peak was observed at 525 nm on CoMo–CA/Al in Figure 7(c). This band indicates the formation of a Co^{2+} citric acid complex (Co-CA complex) such as $[Co(C_6H_5O_7)_2]^{4-}$, in agreement with Weckhuysen and coworkers [38]. It is proposed that citric acid modifies the interaction between Co and the Al_2O_3 surface, and thus the resultant Co-CA complexes are well dispersed on the surface.

Moreover, the calcined CoMo/Al shows a triplet band at 545, 585, and 630 nm in Figure 7(b), characteristic of Co^{2+} ions in a tetrahedral coordination ($CoAl_2O_4$-like species) as found in $CoAl_2O_4$ [39-42]. Taking into consideration the facts that the band at 590 nm due to $CoMoO_4$ overlaps with the bands due to $CoAl_2O_4$ and also that the Raman spectra for CoMo/Al catalysts in Figure 5B show the formation of $CoMoO_4$, it is likely that the $CoMoO_4$ spectrum considerably contributes to the triplet band. When citric acid has been added by the post-treatment (CA/CoMo/Al), the triplet band at 545, 580, and 630 nm is still observed in Figure 7(d). However, the position of the triplet band is slightly changed, particularly the center band. Therefore, in conjunction with the Raman results in Figure 5(B), it is suggested that the $CoAl_2O_4$-like species is not removed by the addition of citric acid and that the slight change in the

spectral feature of the triplet band is compatible with the removal of $CoMoO_4$ species by citric acid. It is concluded that citric acid easily removes the $CoMoO_4$ species and forms Co-CA and Mo-CA surface complexes.

Evaluation of Co-Mo/Al_2O_3 Catalyst by The Simultaneous Impregnation and by The Post-treatment Methods

It was found for the first time that the addition of citric acid by the post-treatment method significantly enhances the HDS activity of the catalysts compared to the addition by a conventional simultaneo us-impregnation method. Therefore, it is proposed that the post-treatment method with citric acid is one of the promising ways to prepare highly active Co-Mo HDS catalysts. The detailed roles of the citric acid addition on the supported Mo/Al and CoMo/Al catalysts prepared by the simultaneous-impregnation method and by the post-treatment method are illustrated in the schematic model below as Figure 8.

For Mo/Al catalysts system, Figure 1 clearly shows that the HDS activity of 8.7 wt% Mo/Al and CVD-Co/Mo/Al is not changed or even decreased by the addition of citric acid regardless the addition method. Figure 2 also shows that the amounts of Co anchored by the CVD is unchanged after citric acid is added, in particular by the simultaneous impregnation, demonstrating that the dispersion of MoS2 particles is also unchanged. Therefore, it is conclude that with the 8.7 wt% Mo/Al catalyst system the addition of citric acid does not affect the catalyst properties very much or is even detrimental, since in the present Mo/Al-C catalyst a monolayer dispersion of Mo is established and Mo oxides are extremely highly dispersed on the support at 8.7 wt% Mo [2,7,28,37]. Yet, LRS in Figure 5(A) and, in particular, Mo K-edge EXAFS in Figure 6 clearly show that Mo-CA complexes are formed by the addition of citric acid. It is considered 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.

On the other hand, the HDS activities of 20 wt% CA/Mo/Al and CVD-Co/CA/Mo/Al are significantly increased by the citric acid addition by the post-treatment method (Figure 1). Moreover, Figures 2 and 3 also clearly show that the dispersion of MoS_2 particles is greatly increased by the post-treatment at a high Mo content (20 wt% Mo). It is proposed 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 and, in part, polymolybdate species, in supporting by the Mo EXAFS measurement (Figure 6). However, the increase of the dispersion of MoS_2 particles was not observed for the simultaneous impregnation catalyst, in particular, at 20 wt% Mo
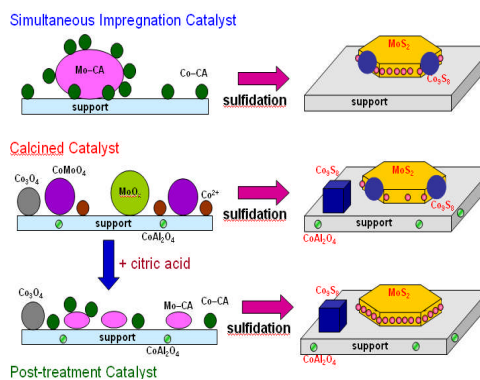

Figure 8. Schematic model of the Co-Mo catalysts with the addition of citric acid

(Figure 2). Although Mo-CA surface complexes and polymolybdate species are also formed after citric acid is added by the simultaneous impregnation (Figures 5 and 6), the dispersion of MoS_2 particles is even lower than or similar to that of the calcined catalysts (Figure 2). The different behaviors of 20 wt% Mo/Al between the post-treatment and the simultaneous impregnation methods may be explained in terms of the dispersion of Mo–CA surface complexes during the catalyst preparation. When AHM and citric acid are simultaneously present in the impregnation solution, citric acid reacts with AHM to form Mo-CA complexes, and then these complexes in the solution are precipitated and agglomerated on the outer surface of pores during the drying process, in particular, at a high Mo content, leading to a large size of MoS_2 particles on the support surface after sulfidation. While by the post-treatment method, citric acid consumes Mo oxide species including crystalline MoO_3 particles on the calcined Mo/Al catalyst to form Mo-CA complexes in situ. The resultant Mo-CA surface complexes are expected to be better dispersed inside the pores, since most of the Mo oxide species have already been well dispersed in the pores by a wetting process during the calcination [37,43,44], thus increased the edge dispersion of MoS_2 particles significantly, leading to the great improvements of the catalytic activity of the calcined catalyst.

For CoMo/Al catalysts system, with the simultaneous-impregnation method, AHM, Co nitrate, and citric acid are added simultaneously followed by the drying. According to the Mo K-edge XAFS and UV-Visible spectra measurements (Figures 6 and 7), citric acid not only interacts with Mo but also with Co to form Mo-CA and Co-CA complexes. Moreover, the HDS activity of the simultaneous-impregnation Co-Mo catalysts is slightly increased compared to the corresponding dried catalyst. The slight increase of the HDS activity for the simultaneous-impregnation Co-Mo catalysts is suggested to be due to the improvement of Co dispersion and to the increase in the sulfidation temperature of Co by the formation of Co-CA complexes, thus forming a considerably increased amount of

Co-Mo-S phase, although the formation of catalytically inactive Co sulfide clusters, Co_9S_8, is still observed on the simultaneous-impregnation Co-Mo catalysts in Figure 5(B).

It is well-known that the formations of MoO_x and $CoMoO_4$ species together with small amounts of Co_3O_4 and $CoAl_2O_3$-like species are mostly observed on calcined Co-Mo catalysts. These Co species will be transformed to catalytically inactive Co sulfide clusters after sulfidation and block the edge sites of MoS_2 particles, causing a decrease of HDS activity. In the present study, the formations of these ill-dispersed bulk phases are observed on calcined Co-Mo catalysts, in particular at a high Mo and Co content, as confirmed by LRS and UV-Visible measurements (Figures 5 and 7). However, it was found that some of these phases are favorable for the addition of citric acid by the post-treatment method, in particular MoO_3 and $CoMoO_4$ species, as observed by the Mo K-edges EXAFS and LRS measurements.

As shown from the schematic model shown above, when citric acid was added on calcined Co-Mo catalysts by the post-treatment method, citric acid consumes the MoO_x (MoO_3 particles) and $CoMoO_4$ species and redisperses those species to form Mo-CA and Co-CA complexes, as evidenced by LRS, Mo K-edge XAFS, and UV-visible measurements, resulting in significant increases of the dispersion of Mo and Co after sulfidation. Hence, the HDS activity of the post-treatment Co-Mo catalysts is drastically enhanced and becomes close to the maximum potential activity even without using the CVD, in particular at 4 wt% Co and 8.7 wt% Mo, while extensive active site blocking are observed to take place on the simultaneous impregnation Co-Mo catalysts. It is suggested that the post-treatment method increases the edge dispersion of MoS_2 particles and that the MoS_2 edges are also fully promoted by Co without the active site blockings by inactive Co sulfide clusters, thus considerably improving the catalytic performance of Co-Mo catalysts compared with the simultaneous-impregnation method.

CONCLUSION

This study demonstrates, for the first time, that the addition of citric acid by the post-treatment method to Co-Mo calcined catalysts (CA/CoMo/Al) improves the thiophene HDS activity more significantly than the addition of citric acid by the simultaneous-impregnation method (CoMo-CA/Al). The maximum potential activity is obtained by post-treatment using citric acid as a chelating agent. Citric acid consumes already dispersed $CoMoO_4$ and MoO_3 species and thus increases the dispersion of Co and Mo via Co-CA and Mo-CA complexes formation, resulting in a larger amount of Co-Mo-S after sulfidation, without active-site blocking by cobalt sulfide clusters. This study shows that with

the post-treatment, a large amount of Mo loading (>20 wt% Mo) could be prepared and well-dispersed on the support, thus improves the catalytic activity. Moreover, the maximum potential activity of CoMo/Al could be obtained by the post-treatment with citric acid addition without the CVD at 4 wt% Co. It is concluded that the addition of citric acid by the post-treatment method is one of the promising ways to prepare a highly active HDS catalysts for cleaner fuels.

ACKNOWLEDGMENT

REFERENCES

[1]. C. SONG, *Catal. Today,* **86** (2003) 211-263

[2]. H. TOPSØE, B. S. CLAUSEN, and F. E. MASSOTH, HYDROTREATING, *Catalysis*, Springer, Berlin, (1996)

[3]. D.D. WHITEHURST, T. ISODA, I. MOCHIDA, *Adv. Catal.*, **42** (1998) 345-471

[4]. T. KABE, A. ISHIHARA, W. QIAN, *Hydrodesulfurization and Hydrodenitrogenation*, Kodansha, Tokyo, (1999)

[5]. F. MAUGÉ, A. VALLET, J. BACHELIER, J.C. DUCHET, J.C. LAVALLEY, *J. Catal.*, **162** (1996) 88-95

[6]. Y. OKAMOTO, K. OCHIAI, M. KAWANO, K. KOBAYASHI, T. KUBOTA, *Appl. Catal.*, **A 226** (2002) 115-127

[7]. Y. OKAMOTO, S. ISHIHARA, M. KAWANO, M. SATOH, T. KUBOTA, *J. Catal.*, **217** (2003) 12-22

[8]. Y. OKAMOTO, K. OCHIAI, M. KAWANO, T. KUBOTA, *J. Catal.*, **222** (2004) 143-151

[9]. M. SUN, D. NICOSIA and R. PRINS, *Catal. Today,* **86** (2003) 173-189.

[10]. J.A.R. VAN VEEN, E. GERKEMA, A.M. VAN DER KRAAN, A. KNOESTER, *J. Chem. Soc., Chem. Commun.* (1987) 1684-1686

[11]. Y. OHTA, T. SHIMIZU, T. HONNA, M. YAMADA, *Stud. Surf. Sci. Catal.*, **127** (1999) 161-168

[12]. T. SHIMIZU, K. HIROSHIMA, T. HONNA, T. MOCHIZUKI, M. YAMADA, *Catal. Today*, **45** (1998) 271-276

[13]. K. INAMURA, K. UCHIKAWA, S. MATSUDA, Y. AKAI, *Appl. Surf. Sci.*, **121/122** (1997) 468-475

[14]. L. MEDICI, R. PRINS, *J. Catal.*, **163** (1996) 38-49

[15]. R. CATTANEO, T. SHIDO, R. PRINS, *J. Catal.*, **185** (1999) 199-212

[16]. L. COULIER, V.H.J. DE BEER, J.A.R. VAN VEEN, J.W. NIEMANTSVERDRIET, *J. Catal.*, **197** (2001) 26-33

[17]. T. KUBOTA, N. HOSOMI, K.K. BANDO, T. MATSUI, Y. OKAMOTO, *Phys. Chem. Chem. Phys*., **5** (2003) 4510-4515

[18]. P. MAZOYER, C. GEANTET, F. DIEHL, S. LORIDANT, M. LACROIX, *Catal. Today,* **130** (2008) 75-79

[19]. R. IWAMOTO, N. KAGAMI, A. IINO, *J. Jpn. Petrol. Inst*., **48** (2005) 237-242

[20]. N. FRIZI, P. BLANCHARD, E. PAYEN, P. BARANEK, M. REBEILLEAU, C. DUPUY, J.P. DATH, *Catal. Today,* **130** (2008) 272-282

[21]. V. COSTA, K. MARCHAND, M. DIGNE, C. GEANTET, *Catal. Today*, **130** (2008) 69-74

[22]. T. FUJIKAWA, *Catal. Surv. Asia*, **10** (2006) 89-97

[23]. T. FUJIKAWA, M. KATO, H. KIMURA, K. KIRIYAMA, M. HASHIMOTO, N. NAKAJIMA, *J. Jpn. Petrol. Inst*., **48** (2005) 106-113

[24]. T. FUJIKAWA, M. KATO, T. EBIHARA, K. HAGIWARA, T. KUBOTA, Y. OKAMOTO, *J. Jpn. Petrol. Inst*., **48** (2005) 114-120

[25]. J.A. BERGWERFF, M. JANSEN, B.R.G. LELIVELD, T. VISSER, K. P. DE JONG, B.M. WECKHUYSEN, *J. Catal*., **243** (2006) 292-302

[26]. T. FUNAMOTO, K. SEGAWA, *11ᵗʰ Korea-Japan Symp. Catal. Seoul*, **GO-37** (2007)

[27]. Y. OKAMOTO, M. KAWANO, T. KAWABATA, T. KUBOTA, I. HIROMITSU, *J. Phys. Chem*., **B109** (2005) 288-296

[28]. Y. OKAMOTO, T. IMANAKA, *J. Phys. Chem*., **92** (1988) 7102-7112

[29]. Y. OKAMOTO, Y. KATOH, Y. MORI, T. IMANAKA, S. TERANISHI, *J. Catal*., **70** (1981) 445-448

[30]. N.-Y. TOPSØE, H. TOPSØE, *J. Catal*., **77** (1982) 293-296

[31]. N.-Y. TOPSØE, H. TOPSØE, *J. Catal*., 84 (1983) 386-401

[32]. T. KUBOTA, K. SATO, A. KATO, USMAN, T. EBIHARA, T. FUJIKAWA, Y. ARAKI, K. ISHIDA, Y. OKAMOTO, *Appl. Catal*., **A 290** (2005) 17-24

[33]. H. JEZIOROWSKI, H. KNÖZINGER, P. GRANGE, P. GAJARDO, *J. Phys. Chem*., **84** (1980) 1825-1829

[34]. S.S. SALEEM, *Infrared Phys*., **27** (1987) 309-315

[35]. J. MEDEMA, C. VAN SANTEN, V.H.J. DE BEER, A.J.A. KONNINGS, D.C. KONNINGSBERGER, *J. Catal*., **53** (1978) 386-400

[36]. Z. ZHOU, H. WAN, K. TSAI, INORG. CHEM., **39** (2000) 59-64

[37]. S. EIJSBOUTS, *Appl. Catal*., **A 158** (1977) 53-92

[38]. J.A. BERGWERFF, A.A. LYSOVA, L.E. ALONSO, I.V. KOPTYUG, B.M. WECKHUYSEN, *Chem-Eur. J*., **14** (2008) 2363–2374

[39]. L.G.A. VAN DE WATER, G.L. BEZEMER, J.A. BERGWERFF, M. VERSLUIJS-HELDER, B.M. WECKHUYSEN, K.P. DE JONG, *J. Catal*., **242** (2006) 287–298

[40]. J. VAKROS, K. BOURIKAS, S. PERLEPES, C. KORDULIS, A. LYCOURGHIOTIS, *Langmuir*, **20** (2004) 10542–10550

[41]. T. ATALOGLOU, C. FOUNTZOULA, K. BOURIKAS, J. VAKROS, A. LYCOURGHIOTIS and C. KORDULIS, *Appl. Catal*., **A288** (2005)1-9

[42]. L.F. LIOTTA, G. PANTALEO, A. MACALUSO, G. DI CARLO and G. DEGANELLO, *Appl. Catal*., **A245** (2004)167–177

[43]. S. GÜNTHER, L. GREGORATTI, M. KISKINOVA, E. TAGLAUER, P. GROTZ, U.A. SCHUBERT, H. KNÖZINGER, *J. Chem. Phys.,* **112** (2000) 5440 -5446

[44]. T.I. KORÁNYI, Z. PAÁL, J. LEYRER and H. KNÖZINGER, *Appl. Catal*. **64** (1990) L5-L8.