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Catalysis Today 132 (2008) 9–17

CATALYSIS TODAY

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A novel preparation-characterization technique of hydrodesulfurization catalysts for cleaner fuels

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Abstract

In the present review of our study, it is shown that the CVD technique using $Co(CO)_3NO$ provides a novel characterization technique of hydrodesulfurization (HDS) catalysts combined with the catalyst preparation. The resultant CVD or designed catalysts are very appropriate for the determination of the CoMoS structure and reaction mechanism due to a selective formation of CoMoS. The CVD technique is also very effective to prepare highly active HDS catalysts, since full promotion of MoS_2 particles can be achieved. The CVD technique can be applied to estimate the surface structure of supported Co(Ni)–MoS_2 catalysts. In addition, the designed catalysts can be used to understand the nature of the support and additives in terms of the intrinsic activity of CoMoS. Thus the information from the CVD technique is unique and invaluable for the development of highly active HDS catalysts.

Keywords: Hydrodesulfurization catalyst; CVD technique; CoMoS structure; Surface structure; Characterization

1. Introduction

Hydrotreatment, in particular hydrodesulfurization (HDS) of petroleum feedstocks has recently become more and more important to protect the environments by producing sulfur-free fuels [1]. Although the productions of sulfur-free diesel oil and gasoline have started from 2005 in Japan, more active and more selective HDS catalysts are required to reduce the reaction temperature and hydrogen consumption [2]. Zero sulfur emissions and near zero sulfur fuels are also demanded in a near future.

Co–Mo or Ni–Mo or Ni–W binary sulfide catalysts have been used in industry as HDS catalysts for a long time because of high activity and stability [3–5]. Recent better understandings of HDS catalysts at a molecular level have improved the performance of the catalysts very much to meet increasing demands of environmental protections [2]. One of the important features of these binary sulfide catalyst systems is the generation of strong catalytic synergies between the metal components, for example between Co and Mo sulfides, that is, Mo or Co sulfide shows only a very limited activity for HDS reaction but the combination of Co and Mo brings about very high activity [3].

Practical Co–MoS_2 catalysts are composed of several metal sulfide and oxide phases, such as MoS_2 particles, Co_9S_8 clusters, Co^{2+} in Al_2O_3, Mo oxysulfides and so on [3] as illustrated in Fig. 1. On the basis of various characterizations including ^{57}Co Mössbauer emission spectroscopy, it is well established that the so-called Co–Mo–S phase or structure (CoMoS), in which Co atoms are located on the edges of MoS_2 particles, is the active sites of Co–Mo sulfide catalysts [3–5]. HDS activity is linearly correlated with the amount of Co in CoMoS [6,7]. The formation of the new type of Co sulfide species explains the generation of strong catalytic synergies between Co and Mo. In the case of Al_2O_3-supported Co–Mo sulfide catalysts sulfided at a temperature higher than 875 K, it has been reported [6,7] that another type of CoMoS is formed, showing about twice higher intrinsic activity than that formed at a usual sulfidation temperature, e.g., 673 K. The former CoMoS is called CoMoS Type II, while the latter CoMoS Type I. Thus the surface structure of practical HDS catalysts are so complicated that it is not easy to understand the HDS activity in terms of intrinsic activity of CoMoS or TOF (turnover frequency) on CoMoS by ordinary characterization techniques.

In order to overcome these difficulties inherent in conventional HDS catalysts, we tried to prepare designed catalysts, in

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doi:10.1016/j.cattod.2007.12.030

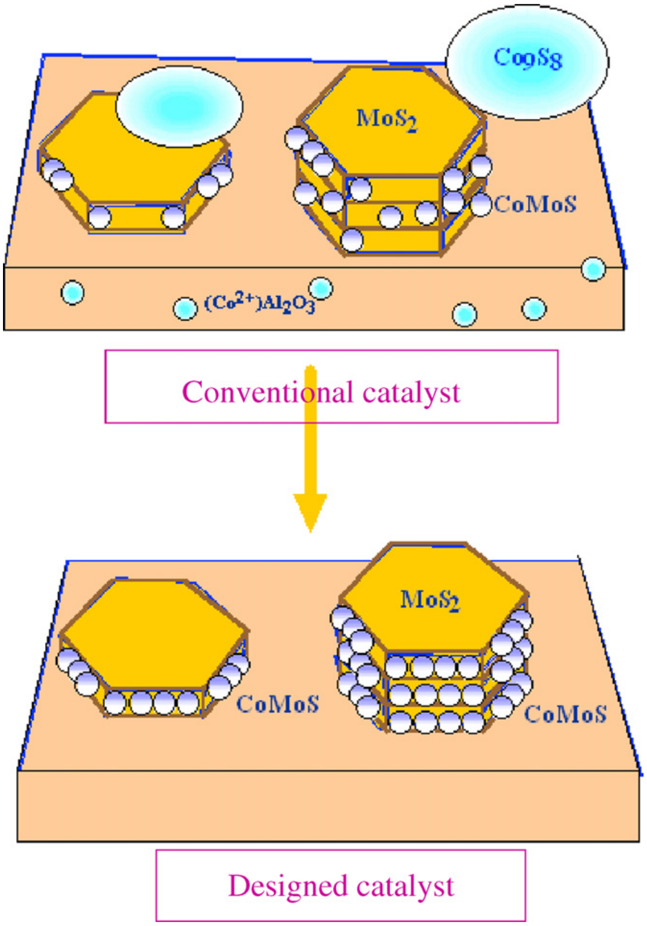

Fig. 1. Surface structure models of a conventional HDS catalyst and the designed catalyst.

which CoMoS is selectively and fully formed and no other Co sulfide species are present (Fig. 1) [8]. We have found that the designed catalysts are very useful to determine the structure of the active sites and HDS reaction mechanism, to characterize the surface structure of Co–MoS_2 catalysts, and to understand the effects of additives and support on the number and intrinsic activity of the active sites, CoMoS, at a molecular level. In this review, our studies on the designed catalysts are summarized and the preparations of highly active HDS catalysts are discussed.

2. Preparation and characterization of designed catalysts by CVD

In the preparation of conventional impregnation catalysts, supported Co and Mo oxides precursors are sulfided in an H_2S/H_2 stream to prepare Co–MoS_2 catalysts. On the other hand, in the designed catalysts, supported Mo oxide precursors were first sulfided at 673 K for 1.5 h to prepare supported MoS_2 catalysts [9,10]. The MoS_2 catalysts were then exposed to a vapor of $Co(CO)_3NO$ at room temperature for 5 min (CVD technique), followed by evacuation at room temperature for 10 min to remove physisorbed $Co(CO)_3NO$ molecules. The $Co(CO)_3NO/MoS_2$ sample was sulfided again at 673 K for 1.5 h. The resultant Co–MoS_2 catalysts are denoted as CVD-Co/MoS_2/support in the present study. The sulfide catalysts were subjected to a variety of characterizations without exposing to air (in situ), such as XPS, Co K-edge XAFS, NO adsorption capacity, FTIR of NO adsorption, and magnetic measurements. The HDS of thiophene was used as a test reaction. The reaction temperature was 623 K. Detailed characterization techniques and reaction conditions have been reported elsewhere [9,10].

The chemical state of Co in the CVD catalysts was examined by XPS. Fig. 2 shows the Co 2p XP spectra for Co/MoS_2/Al_2O_3 catalysts [9]. The Co $2p_{3/2}$ binding energy for CVD-Co/MoS_2/Al_2O_3 is higher by 0.9 eV than that for Co sulfide clusters prepared by the CVD technique in the absence of Mo sulfides. Fig. 3 shows the Co 2p XP spectra for SiO_2-, ZrO_2- and TiO_2-supported CVD-Co/MoS_2 catalysts [9]. The Co $2p_{3/2}$ binding energies are 779.3 ± 0.1 eV irrespective of the support and in agreement with that for CoMoS reported by Alstrup et al. [11] and Bouwens et al. [12], demonstrating selective formation of unique Co–MoS_2 interaction species [9,10]. The formation of Co–MoS_2 interaction species was also confirmed by means of Co K-edge XANES differential spectra [13].

In order to examine the location of the Co atoms in CVD catalysts, the amount of Co anchored by the CVD technique, as expressed by Co/Mo mole ratio, is shown in Fig. 4 against the amount of NO adsorption on the MoS_2 catalysts before the introduction of Co [9]. Since it is well established that NO molecules are preferentially adsorbed on the edge sites of MoS_2 particles [3], a proportional correlation in Fig. 4 indicates that Co is preferentially located on the edge sites of MoS_2 particles. The FT-IR spectra of NO adsorption showed that NO adsorption sites on Mo sites are replaced by Co sites in CVD catalysts [14]. Accordingly, it is concluded that CoMoS is selectively prepared by the CVD technique using $Co(CO)_3NO$,

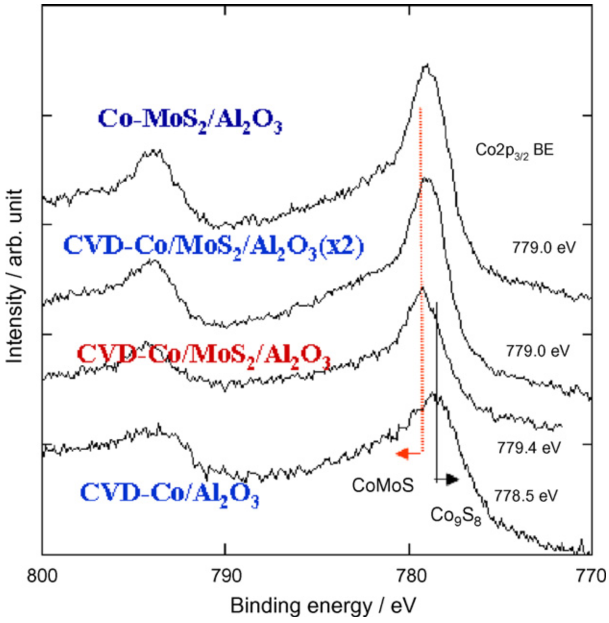

Fig. 2. XP spectra of the Co 2p level for CVD-Co/Al_2O_3, CVD-Co/MoS_2/Al_2O_3, CVD-Co/MoS_2/Al_2O_3 after the second CVD and sulfidation, and a Co–MoS_2/Al_2O_3 impregnation catalyst.

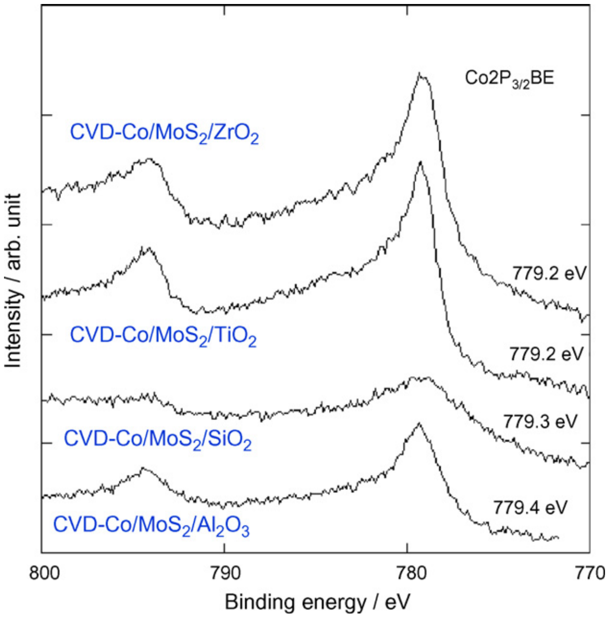

Fig. 3. XP spectra of the Co 2p level for CVD-Co/MoS_2 catalysts supported on Al_2O_3, SiO_2, TiO_2 and ZrO_2.

that is, Co–MoS_2 interaction species located on the edges of MoS_2 particles [9,10].

The effects of the number of the CVD cycle on the HDS activity and the amount of Co anchored were examined for CVD-Co/MoS_2/Al_2O_3 [14]. A single exposure of MoS_2/Al_2O_3 to a vapor of $Co(CO)_3NO$ significantly increased the HDS of thiophene. However, when CVD-Co/MoS_2/Al_2O_3 was exposed to the Co carbonyl and sulfided again, the HDS activity was not increased at all, whereas the amount of Co was almost doubled. This fact indicates that under the present CVD conditions, a single dose of $Co(CO)_3NO$ completely fills the edges of MoS_2 particles and that excess Co admitted by the second CVD is present as Co sulfide clusters on the Al_2O_3 surface. This is supported by the XS spectrum in Fig. 2 showing a shift of the Co $2p_{3/2}$ binding energy from 779.4 to 779.0 eV by the second CVD [9].

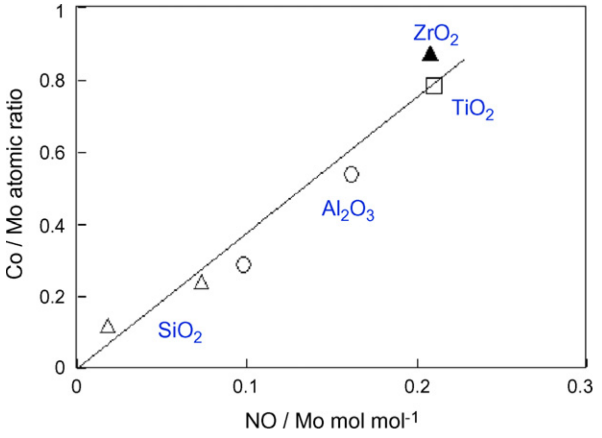

Fig. 4. Correlation between the Co/Mo atomic ratio and NO/Mo mole ratio for CVD-Co/MoS_2 catalysts supported on SiO_2, Al_2O_3, TiO_2 and ZrO_2.

A schematic model in Fig. 5 shows the fate of adsorbed $Co(CO)_3NO$ molecules on sulfidation [10]. The Co carbonyl molecules adsorbed on or near the edges of MoS_2 particles are selectively transformed into CoMoS on sulfidation. On the other hand, the Co carbonyl molecules adsorbed on the MoS_2 edges already occupied by Co are transformed into Co_9S_8 clusters when sulfided again. It should be noted that with the designed catalysts (CVD-catalysts), the Co content presents the number of CoMoS, the active sites of the Co–MoS_2 catalysts. Accordingly, we can discuss catalytic activity in terms of TOF or intrinsic activity. Another important point of the CVD catalysts is that the CVD catalysts should show the maximum activity for given Mo sulfide catalysts, since the amount of CoMoS is maximized or fully promoted. The maximum activity is called the maximum potential activity [10,13]. These features of the designed catalysts allow us to characterize HDS catalysts in a unique way.

3. Molecular structure of CoMoS

The designed catalysts are obviously appropriate for the determination of the molecular structure of the active sites and the reaction mechanism because of the selective preparation of CoMoS by the CVD technique. The structure of CoMoS has been studied by many workers with conventionally prepared Co–MoS_2 catalysts, sometimes in the presence of a chelating agent, by using mainly EXAFS techniques [3,12,15–17] or recently by using DFT calculations and STM [18–23]. Several models have been proposed but the CoMoS structure is still under debate [24,25]. We used the designed catalysts for the determination of the CoMoS structure.

Fig. 6 shows the magnetic susceptibility and magnetic moment of Co in CVD-Co/MoS_2/Al_2O_3 as a function of temperature [26]. The magnetic susceptibility increased as the temperature decreased and took a maximum at 16 K, followed by a drastic decrease. The temperature dependency of the magnetic susceptibility shows antiferromagnetic interactions between Co atoms in CoMoS. The magnetic susceptibility (χ) in Fig. 6 was found to be satisfactorily simulated by a theoretical equation (1) for dinuclear Co clusters:

$$\chi = N_A g^2 \mu_B / k_B T \left[3 + \exp\left(\frac{-2J}{k_B T}\right)\right] \tag{1}$$

where N_A is the Avogadro's constant, μ_B the Bohr magneton, g the gyromagnetic factor (assumed to be 2, here), k_B the Boltzman's constant and J is the magnetic interaction strength defined by $H = -2J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$. It is suggested from Fig. 6 that the Co atoms in CoMoS are not isolated each other but paired to form dinuclear clusters with a Co–S–Co bond. The formation of dinuclear clusters was also confirmed by the analysis of the Fourier transforms of Co K-edge EXAFS, which showed well resolved fine structures due to Co–S, Co–Mo and Co–Co shells because of the selective formation of CoMoS in the CVD-Co/MoS_2 catalysts [27]. On the basis of the EXAFS structural parameters, it is possible to construct the Co dinuclear clusters both on the Mo-edge and S-edge of MoS_2 particles. Fig. 7 illustrates a possible CoMoS structure on the S-edge. The

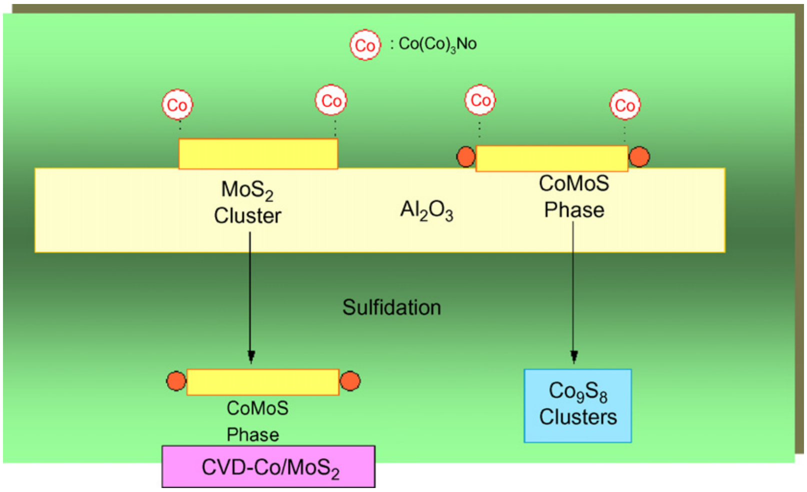

Fig. 5. A schematic model illustrating the fate on sulfidation of $Co(CO)_3NO$ molecules adsorbed on the edge of MoS_2 particle and on the MoS_2 edge already occupied by Co.

formation of dinuclear clusters on the edge of MoS_2 particles readily explains the NO adsorption capacity of CoMoS, that is, only a half of the Co atoms in CoMoS can adsorb NO molecules in a dinitrosyl form [26,28], as shown in Fig. 7.

4. Intrinsic activity of CoMoS

As illustrated in Figs. 5 and 8, CVD-Co/MoS_2 catalysts are fully promoted and no other Co species than those in CoMoS are formed. This feature of the CVD-catalysts allows us to calculate the intrinsic activity of CoMoS and to determine the type of CoMoS, Type I or Type II. We examined the effect of the sulfidation temperature on the intrinsic activity of CoMoS for SiO_2-supported Co–MoS_2 catalysts (Fig. 9) [29]. With increasing sulfidation temperature, the TOF of thiophene HDS increased and reached a plateau. Since the TOF on CoMoS Type I (TOF for CVD-Co/MoS_2/Al_2O_3 sulfided at 673 K) was below 10, the plateau value shows the formation of CoMoS Type II at >873 K. The increase of the TOF is ascribed to a complete sulfidation of Mo oxides to MoS_2 on the basis of temperature programmed sulfidation results.

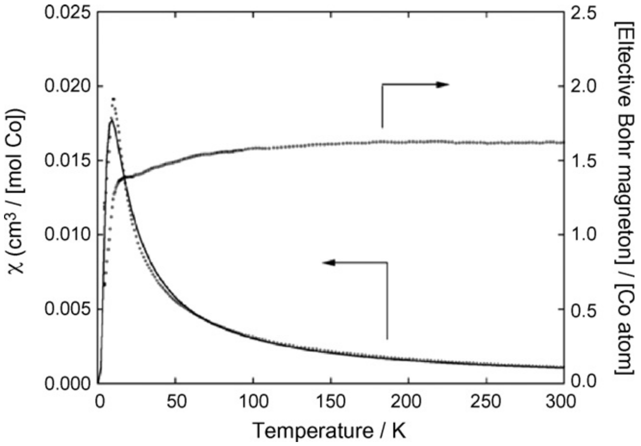

Fig. 6. Magnetic susceptibility (χ) and magnetic moment of Co as a function of temperature for CVD-Co/MoS_2/Al_2O_3.

Fig. 9 also shows the dependency of TOF of CoWS (the active sites of CVD-Co/WS_2/SiO_2) on the sulfidation temperature [29]. Obviously, CoWS Type II is formed at >973 K for SiO_2-supported catalysts. What is interesting in Fig. 9 is that the TOF of CoWS Type II is 1.5 times greater than that of CoMoS Type II, although Co–WS_2 catalysts have never been used in industry because of low activity. This is due to a greater difficulty of sulfidation of W oxides and to an easier sintering of WS_2 particles than those of Mo counterparts. Better preparations of Co–WS_2 catalysts would open a new challenge.

The effects of boron addition on the HDS activity of Co–MoS_2/Al_2O_3 were studied by the CVD technique [30,31].

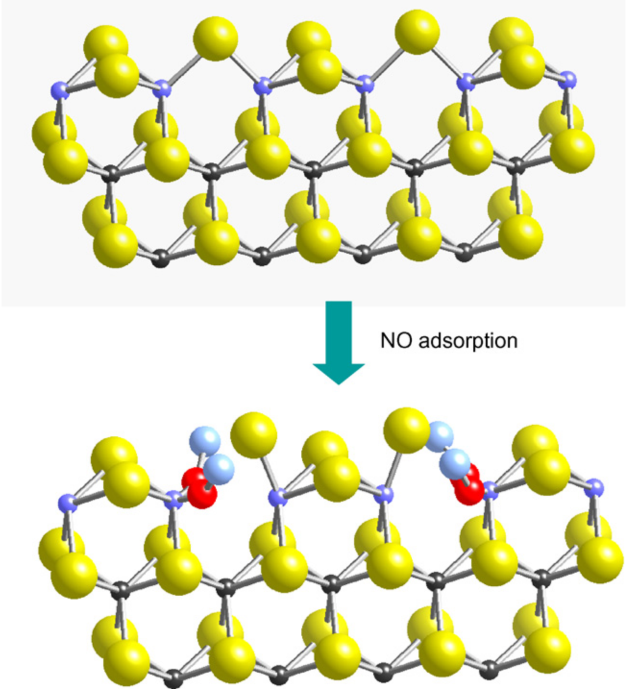

Fig. 7. Proposed structure of CoMoS on the S-edge of MoS_2 and the NO adsorption. Large gray balls: sulfur; small gray balls: cobalt; small black balls: molybdenum; middle size balls: oxygen and nitrogen.

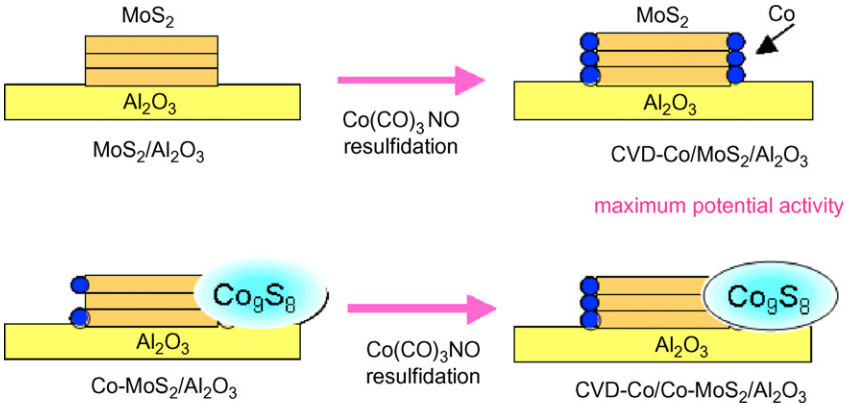

Fig. 8. Surface model illustrating the application of the CVD technique for the determination of TOF and for the evaluation of the extent of blockings and Co coverage.

As shown in Fig. 10, the thiophene HDS activity of CVD-Co/MoS_2/B/Al_2O_3 was increased by the addition of a small amount of boron, followed by a considerable decrease at higher boron content. On the other hand, the TOF was increased by the addition of boron and reached a constant value as shown in Fig. 11. The TOF shows the formation of CoMoS with an intrinsic activity between Type I and Type II. So we call this type of CoMoS pseudo-Type II [30]. The addition of boron increases the TOF on CoMoS and thus increases the HDS activity. The decrease of the activity at higher boron content is due to a loss of the dispersion of MoS_2 particles.

The addition of boron consumes the basic surface hydroxyl groups on Al_2O_3 surface, which are used to form strong Mo oxides–support interactions via Mo–O–Al bonds, as illustrated by the FT-IR spectra in Fig. 12 [32]. The TOF in Fig. 11 is shown in Fig. 13 as a function of the amount of the residual basic OH groups (3772 cm^{-1} band as a representative) [33]. The TOF increases linearly as the basic OH groups are consumed by the addition of boron. With B/Al_2O_3-supported CVD-Co/MoS_2 catalysts, Fig. 14 shows a linear correlation between the TOF on CoMoS and the TOF on MoS_2 edge sites, which was evaluated on the basis of the NO adsorption capacity on unpromoted MoS_2 catalysts. This fact suggests that the intrinsic activities of CoMoS and MoS_2 particles are similarly affected by the addition of boron. Accordingly, it is considered that the boron addition weakens the Mo oxides–support interactions and thus MoS_2-support interactions, accompanying the increases of the intrinsic activity of CoMoS and MoS_2

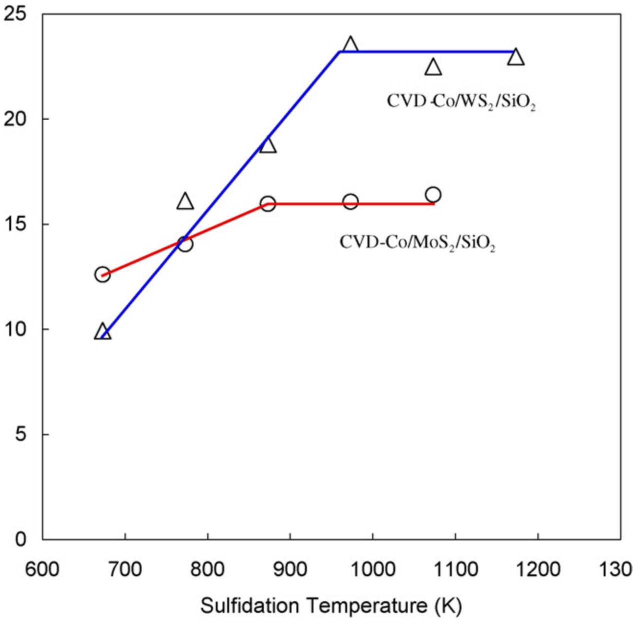

Fig. 9. TOF of the HDS of thiophene on CoMoS (circles) and CoWS (triangles) as a function of the sulfidation temperature for SiO_2-supported CVD-Co/MoS_2 (10 wt% MoO_3) and CVD-Co/WS_2 (20 wt% WO_3).

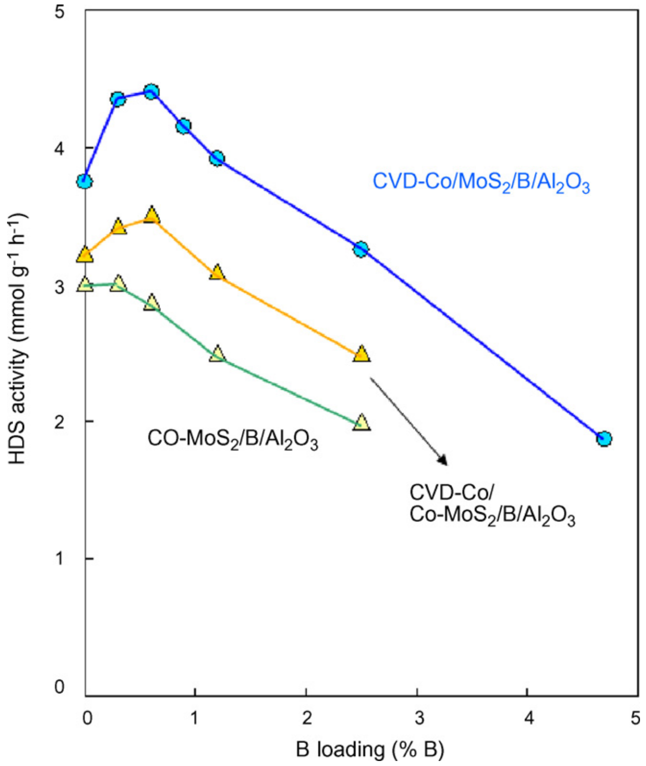

Fig. 10. Catalytic activity of thiophene HDS as a function of boron content for Co–MoS_2/B/Al_2O_3 impregnation catalysts, CVD-Co/Co–MoS_2/B/Al_2O_3 after the addition of Co by the CVD method, and CVD-Co/MoS_2/B/Al_2O_3.

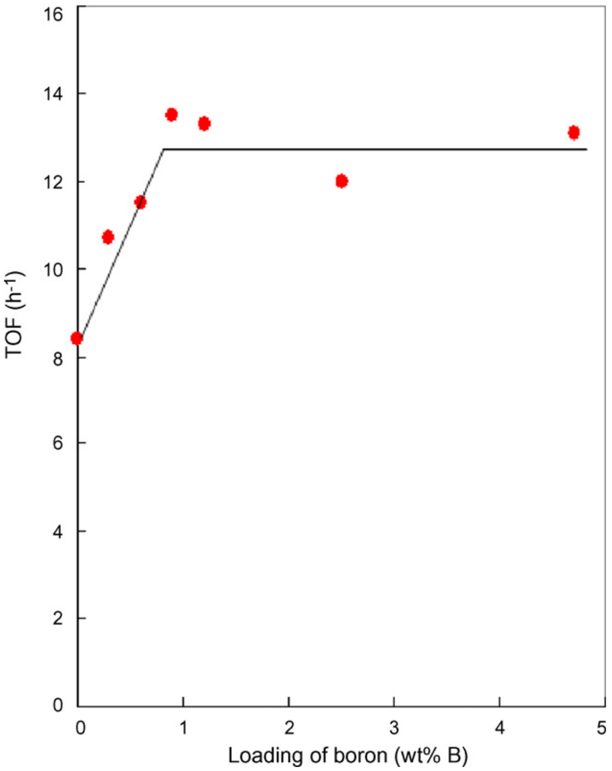

Fig. 11. TOF on CoMoS as a function of boron content for CVD-Co/MoS$_2$/B/Al$_2$O$_3$.

edges. In addition, the relative TOF was found to be correlated to the J value in Eq. (1) for SiO$_2$-, Al$_2$O$_3$- and B/Al$_2$O$_3$-supported CVD-Co/MoS$_2$ catalysts [34], indicating that the effects of support and additives can be understood in terms of the MoS$_2$–support interactions, which modify the electronic state of MoS$_2$ particles and concomitantly the electronic state and then intrinsic activity of CoMoS. In conformity with the suggestions, Hinnemann et al. [35] showed by DFT calculations that MoS$_2$–O–Al$_2$O$_3$ interactions modify the electronic state of MoS$_2$ particles and reduce the reactivity of MoS$_2$ edges. The effect of phosphoric acid addition on Co–MoS$_2$/Al$_2$O$_3$ can be explained in a similar way [36–38].

The thermal stability of CoMoS was studied by use of the CVD technique [39]. In order to remove the possibility of the destruction of CoMoS induced by the sintering of MoS$_2$ particles, supported MoS$_2$ was sulfided at a high temperature (873 K) for a prolonged time. It was found that CoMoS is thermally stable at 623 K in a stream of 10% H$_2$S/H$_2$ at atmospheric pressure but that it is gradually decomposed at a temperature higher than 673 K, the extent of destruction being dependent on the support, SiO$_2$ > B/Al$_2$O$_3$ > Al$_2$O$_3$. CoMoS Type II is slightly more fragile than CoMoS Type I.

5. Surface structure

The CVD technique can be used to characterize the surface structure of HDS catalysts [13,31]. By comparing the maximum potential HDS activity and the activity of Co–MoS$_2$ catalysts after the CVD, we can estimate the extent of blockings of the active sites by catalytically inactive Co sulfide clusters (Fig. 8). Furthermore, we can estimate the Co coverage on the edges of MoS$_2$ particles by comparing the HDS activities before and after the CVD.

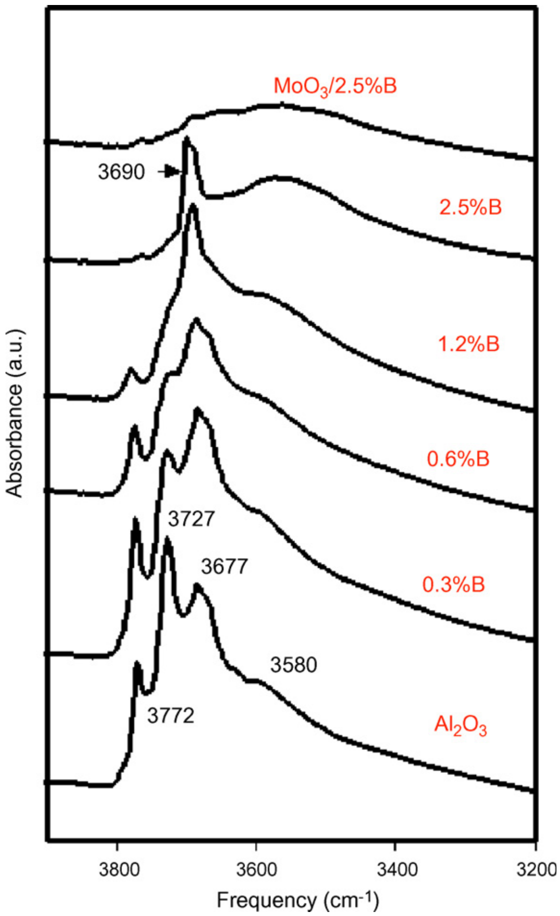

Fig. 12. FT-IR spectra of the surface hydroxyl groups on boron-modified Al$_2$O$_3$.

The HDS activity of Co–MoS$_2$/Al$_2$O$_3$ prepared by a double impregnation method is shown in Fig. 15 against the amount of Co. The catalyst showed a maximum activity at 3–4 wt% Co. When Co was added by the CVD to the impregnation catalyst, the activity was increased as shown in Fig. 15. The extent of blockings calculated from the activity increase is shown in Fig. 16 for Co–MoS$_2$/(1.2 wt%) B/Al$_2$O$_3$ catalysts [31]. It increases as the amount of Co increases but depends strongly on the catalyst preparation: the calcination significantly decreases the blockings, while the addition of boron considerably increases it. The detrimental effect of boron is ascribed to the decrease of the dispersion of Co oxides by the addition of boron [31], since boric acid occupies the tetrahedral sites of the Al$_2$O$_3$ surface [40]. The CVD technique using Co(CO)$_3$NO was also applied to evaluate the surface structure of Ni–MoS$_2$/Al$_2$O$_3$ catalysts [13]. The addition of Co to Ni–MoS$_2$/Al$_2$O$_3$ caused no synergistic effects between Co and Ni, indicating that Co and Ni atoms occupy the same sites of MoS$_2$ edges to form CoMoS and NiMoS.

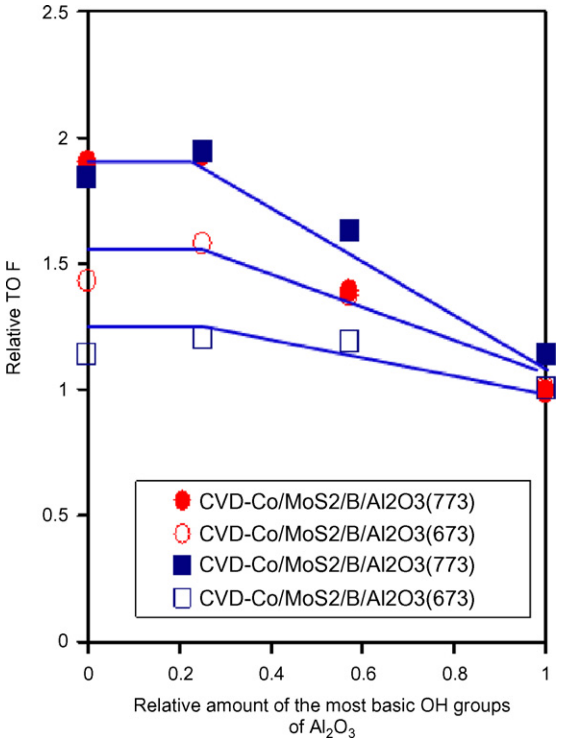

Fig. 13. Relative TOF on CoMoS for CVD-Co/MoS$_2$/B/Al$_2$O$_3$ as a function of the relative amount of the basic OH groups of Al$_2$O$_3$. MoS$_2$/B/Al$_2$O$_3$ was sulfided at 673 or 773 K before the introduction of Co by the CVD technique.

6. Preparation of highly active HDS catalysts

In order to prepare highly active HDS catalysts, we need to prepare CoMoS Type II by controlling the MoS$_2$–support interactions. Weakened interactions often accompany the formation of well-stacked MoS$_2$ particles which are beneficial for the hydrogenation of aromatic rings [36]. Furthermore, we need to increase the amount of CoMoS Type II by increasing the dispersion of MoS$_2$ particles and the Co coverage and by preventing the blockings of the active sites by Co sulfide clusters. In addition, we need to add acidity to the support for ultra-deep HDS catalysts [2,5,41].

The addition of a chelating agent to an impregnation solution is sometimes effective to increase the coverage of Co on the

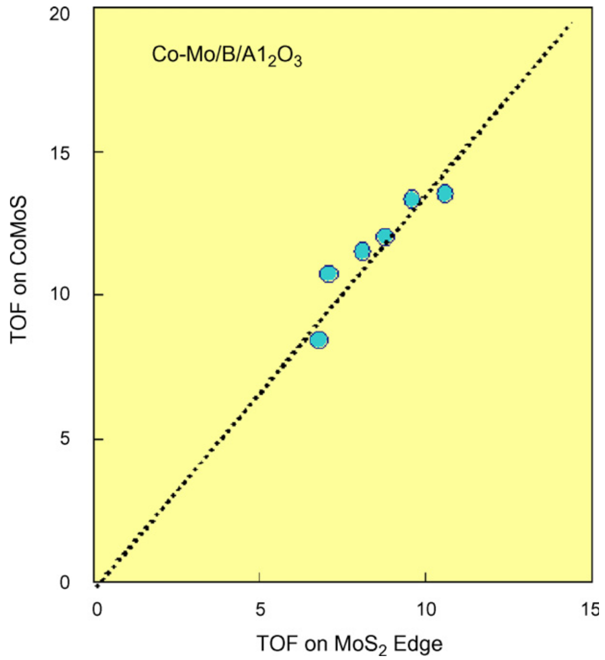

Fig. 14. Correlation between the TOF on CoMoS and the TOF on MoS$_2$ edges, as calculated by the NO adsorption capacity, for CVD-Co/MoS$_2$/B/Al$_2$O$_3$.

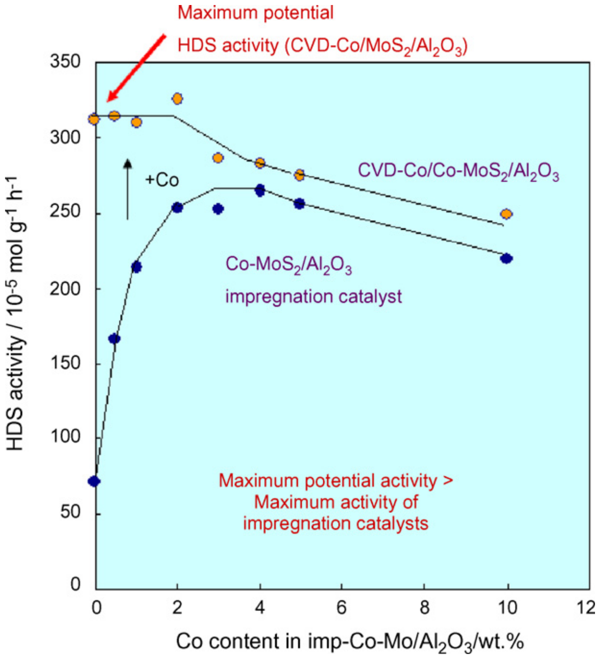

Fig. 15. HDS activity of Co–MoS$_2$/Al$_2$O$_3$ impregnation catalysts before and after the Co-addition by the CVD technique.

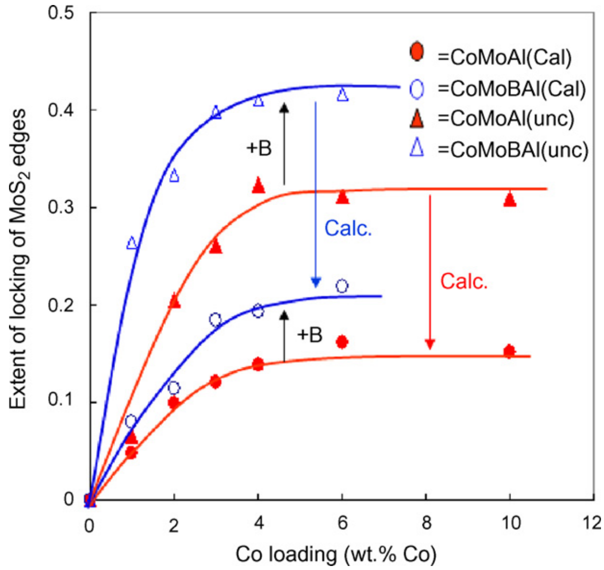

Fig. 16. Extent of blockings of the active sites by catalytically inactive Co sulfide clusters as a function of Co content for Co–MoS$_2$/Al$_2$O$_3$ and Co–MoS$_2$/(1.2 wt%) B/Al$_2$O$_3$ catalysts. Calcined Mo oxides catalysts were impregnated with Co. The Co–Mo precursors were calcined at 773 K or remained uncalcined (dried).

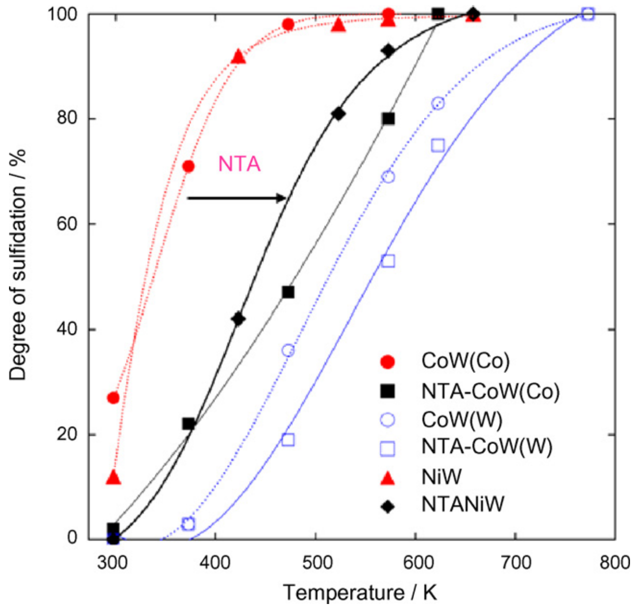

Fig. 17. Degree of sulfidation of Co, Ni and W as a function of sulfidation temperature for Al_2O_3-supported Co(Ni)–W catalysts. An impregnation solution containing NTA (nitrilotriacetic acid) and Co or Ni salt was added to calcined 22 wt% WO_3/Al_2O_3.

MoS_2 edges [36]. The basic idea is to increase the sulfidation temperature of Co by the formation of thermally stable Co-complexes. Thus it is expected that Co is sulfided after the sulfidation of Mo oxides to MoS_2 or at least Co and Mo are simultaneously sulfided, facilitating the location of Co on the edge of MoS_2 particles. Fig. 17 shows the sulfidation degrees of Co(Ni) and W oxides to the corresponding sulfides as a function of sulfidation temperature for a Co(Ni)–WS_2/Al_2O_3 impregnation catalyst, as measured by XAFS [42]. Actually, the addition of a chelating agent, NTA (nitrilotriacetic acid), increased the sulfidation temperature of Co(Ni) by 150 K and the HDS activity was almost doubled. XPS [43] and FT-IR [44] studies showed that the addition of a chelating agent increase the sulfidation temperature of the promoter. Furthermore, the addition of a chelating agent is reportedly effective for the formation of CoMoS Type II [36,45].

The modification of the support surface by the addition of boron or phosphorus is beneficial for the formation of CoMoS Type II [30,36]. The addition of a chelating agent leads to the maximum amount of CoMoS Type II. Actually, the combination of these preparations and the addition of acidity have significantly increased HDS activity to meet the demands of the production of sulfur-free fuels [41].

7. Concluding remarks

Precise characterizations of HDS catalysts under study are must for the effective development of HDS catalysts. The CVD technique provides a novel characterization technique combined with the catalyst preparation. The resultant designed catalysts are very appropriate for determining the CoMoS structure and reaction mechanism due to a selective formation of CoMoS. The CVD technique is also very effective to prepare highly active HDS catalysts, since full promotion of MoS_2 particles can be achieved. The CVD technique can be applied to estimate the surface structure of supported Co–MoS_2 catalysts. In addition, the designed catalysts can be used to understand the nature of the support and additives in terms of the intrinsic activity of CoMoS. Thus the information from the CVD technique is unique and invaluable for the development of highly active HDS catalysts. Furthermore, the CVD technique can be applied to prepare highly active unsupported Co–MoS_2 catalysts in which highly dispersed MoS_2 particles are prepared by a sonochemical method [46,47].

Acknowledgements

I express sincere gratitude to Dr. Takeshi Kubota and Dr. Usman for their useful discussions.

References

[1] C. Song, Catal. Today 86 (2003) 211.
[2] K. Segawa, Shokubai (Catalysts and Catalysis) 48 (2006) 228.
[3] H. Topsøe, B.S. Clausen, F.E. Massoth, Catal. Sci. Technol. 11 (1996) 1.
[4] R. Prins, in: G. Ertl, H. Knözinger, H.J. Weitkamp (Eds.), Handbook of Hetergeneous Catalysis, VHC, Weinheim, 1997, p. 1908.
[5] D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345.
[6] R. Candia, H. Topsøe, B.S. Clausen, Proc. 9th Iberoamerican Symp. on Catalysis, Lisbon, Portugal, (1984), p. 211.
[7] H. Topsøe, B.S. Clausen, Appl. Catal. 25 (1986) 273.
[8] Y. Okamoto, J. Jpn. Petrol. Inst. 46 (2003) 343.
[9] Y. Okamoto, K. Ochiai, M. Kawano, K. Kobayashi, T. Kubota, Appl. Catal. A 226 (2002) 115.
[10] Y. Okamoto, S. Ishihara, M. Kawano, M. Sato, T. Kubota, J. Catal. 217 (2003) 12.
[11] I. Alstrup, I. Chorkendorff, R. Candia, B.S. Clausen, H. Topsøe, J. Catal. 77 (1982) 397.
[12] S.M.A.M. Bouwens, F.B.M. van Zon, M.P. van Dijik, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen, D.C. Koningsberger, J. Catal. 146 (1994) 375.
[13] Y. Okamoto, K. Ochiai, M. Kawano, T. Kubota, J. Catal. 222 (2004) 143.
[14] Y. Okamoto, T. Kubota, Catal. Today 86 (2003) 31.
[15] W. Niemann, B.S. Clausen, H. Topsøe, Catal. Lett. 4 (1990) 355.
[16] S.M.A.M. Bouwens, J.A.R. van Veen, D.C. Koningsberger, V.H.J. de Beer, R. Prins, J. Phys. Chem. 95 (1991) 123.
[17] S.P.A. Louwers, R. Prins, J. Catal. 133 (1992) 94.
[18] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, Catal. Lett. 64 (2000) 95.
[19] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Houlhoat, J. Catal. 190 (2000) 128.
[20] J.V. Lauritsen, S. Helveg, E. Lagsgaad, I. Stengaad, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Catal. 197 (2001) 1.
[21] A. Travert, H. Nakamura, R.A. van Santen, S. Cristol, J.-F. Paul, E. Payen, J. Am. Chem. Soc. 124 (2002) 7084.
[22] H. Schweiger, P. Raybaud, H. Toulhoat, J. Catal. 212 (2002) 33.
[23] J.V. Lauritsen, R.T. Vang, F. Besenbacher, Catal. Today 111 (2006) 34.
[24] R. Prins, V.H.J. de Beer, G.A. Somorjai, Catal. Rev. Sci. Eng. 31 (1989) 1.
[25] S. Eijsbouts, Appl. Catal. A 158 (1997) 53.
[26] Y. Okamoto, M. Kawano, T. Kawabata, T. Kubota, I. Hiromitsu, J. Phys. Chem. B 109 (2005) 288.
[27] T. Kubota, M. Ito, Y. Okamoto, Preprint of 4th International Symp. Molecular Aspects of Catalysis by Sulfides, Doorn, The Netherlands, (2007), p. 82.
[28] Y. Okamoto, M. Kawano, T. Kubota, J. Chem. Soc., Chem. Commun. (2003) 1086.

[29] Y. Okamoto, A. Kato, Usman, K. Sato, T. Kubota, Chem. Lett. 34 (2005) 1258.

[30] Usman, T. Kubota, Y. Araki, K. Ishida, Y. Okamoto, J. Catal. 227 (2004) 523.

[31] Usman, T. Kubota, I. Hiromitsu, Y. Okamoto, J. Catal. 247 (2007) 78.

[32] Usman, M. Takaki, T. Kubota, Y. Okamoto, Appl. Catal. A 286 (2005) 148.

[33] Usman, T. Kubota, Y. Okamoto, Bull. Chem. Soc. Jpn. 79 (2006) 637.

[34] Y. Okamoto, T. Kubota, I. Hiromitsu, unpublished results.

[35] B. Hinnemann, J.K. Nørskov, H. Topsøe, J. Phys. Chem. B 109 (2005) 2245.

[36] M. Sun, D. Nicosia, R. Prins, Catal. Today 86 (2003) 173.

[37] R. Iwamoto, J. Grimblot, Adv. Catal. 44 (2000) 417.

[38] T. Usman, T. Yamamoto, Y. Kubota, Okamoto, Appl. Catal. A 328 (2007) 219.

[39] Usman, T. Kubota, Y. Okamoto, Ind. Eng. Chem. Res. 45 (2006) 3537.

[40] M.A. Stranick, M. Houalla, D.M. Hercules, J. Catal. 104 (1987) 396.

[41] T. Fujikawa, Catal. Surv. Asia 10 (2006) 89.

[42] T. Kubota, N. Hosomi, K.K. Bando, T. Matsui, Y. Okamoto, Phys. Chem. Chem. Phys. 5 (2003) 4510.

[43] G. Kishan, L. Coulier, V.H.J. de Beer, J.A.P. van Veen, J.W. Niemantsverdriet, J. Catal. 196 (2000) 180.

[44] T. Fujikawa, M. Kato, T. Ebihara, K. Hagihara, T. Kubota, Y. Okamoto, J. Jpn. Petrol. Inst. 48 (2005) 114.

[45] J.A.R. van Veen, E. Gerkema, A.M. van der Kraan, A. Knoester, J. Chem. Soc., Chem. Commun. (1987) 1684.

[46] J.J. Lee, H. Kim, J.H. Koh, A. Jo, S.H. Moon, Appl. Catal. B 58 (2005) 89.

[47] J.J. Lee, H. Kim, J.H. Koh, A. Jo, S.H. Moon, Appl. Catal. B 61 (2005) 274.