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Intrinsic catalytic activity of SiO_2-supported Co–Mo and Co–W sulfide catalysts for the hydrodesulfurization of thiophene

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Abstract

SiO_2-supported Co–Mo and Co–W sulfide catalysts with varying Mo(W) content were prepared from Mo(W)S_2/SiO_2 presulfided at 673–873 K with a CVD technique using $Co(CO)_3NO$ as a precursor to Co sulfide. The Al_2O_3-supported counterparts were also briefly studied. The catalysts were characterized by NO adsorption, TEM, XPS, W L_3-edge XANES, and the magnetic measurements of Co. The Co atoms in the Co–W–S phase showed an antiferromagnetic property. The TOF of the hydrodesulfurization of thiophene on the Co–Mo(W)–S phase significantly increased as the presulfidation temperature of Mo(W)S_2/SiO_2 increased from 673 to 873 K, whereas it was independent of the loading of Mo(W). The TOFs on the Co–Mo–S phase and the Co–W–S phase were close to each other but strongly dependent on the support. It is suggested that complete sulfidation and the formation of stacked Mo(W)S_2 particles do not necessarily result in the formation of Co–Mo(W)–S Type II.

Keywords: Hydrodesulfurization; Co–Mo catalysts; Co–W catalysts; Turnover frequency; Xanes; Magnetic susceptibility; CVD

1. Introduction

Development of highly active hydrodesulfurization (HDS) catalysts has been one of the most urgent issues in the petroleum industry related to protection of the environment [1–3]. Supported Mo sulfides promoted by Co or Ni have been extensively used in industry for the HDS reaction [4–7]. Topsøe and co-workers [5,8–11] have proposed that the catalytically active phase in the promoted catalysts is the so-called Co(Ni)–Mo–S phase (structure), in which Co(Ni) atoms are located on the edge of MoS_2 particles. The molecular structure of the Co(Ni)–Mo–S phase and the reaction mechanism thereon are still a matter of debate [12–22].

Supported W sulfide catalysts promoted by Ni have also been widely studied because of the generation of strong catalytic synergies between W and Ni [4–7]. On the other hand, Co–W sulfide catalysts have received much less attention compared with Co–Mo catalysts because of weaker promotional effects of Co in conventionally prepared Co–W catalysts [23]. Recent studies [24,25], however, have shown that this is due, at least in part, to a greater difference in the sulfidation temperature between Co and W than that between Co and Mo, resulting in a lower coverage of Co on the edge of WS_2 particles than that on the edge of MoS_2 particles. The addition of a chelating agent to the impregnation solution of Co increased the sulfidation temperature of Co by about 150 K because of Co-chelate complex formation, accompanying a significant increase in the HDS activity of Co–W catalysts [25]. Nevertheless, the reason for the weak catalytic synergy between Co and W sulfides is not clear at present.

The HDS activity of Co-promoted Mo or W catalysts is determined by the amount of the Co–Mo(W)–S phase and its intrinsic activity. It is therefore intriguing to compare the intrinsic activities of the Co–Mo–S phase and the Co–W–S phase for HDS reaction in order to understand the nature of Co–W catalysts and to obtain important insights into the role

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of Co situated on the MoS_2 or WS_2 edge in the HDS reaction thereon, and into the role of the MoS_2 or WS_2 edge. With carbon-supported Ni–Mo and Ni–W sulfide catalysts, Louwers and Prins [26] suggested that the intrinsic catalytic activities of the Ni–Mo–S phase and the Ni–W–S phase are identical for the HDS of thiophene. It seems, however, that there remain some ambiguities about their assumptions that all of the Ni atoms are situated on the edge of MoS_2 or WS_2 particles in the catalyst systems, since no sufficient characterizations were presented, except for EXAFS.

For the purpose of comparing the intrinsic catalytic activities of the Co(Ni)–Mo–S phase and the Co(Ni)–W–S phase, it is very desirable to prepare Co(Ni)–Mo and Co(Ni)–W catalysts, in which the edges of MoS_2 or WS_2 particles are selectively covered by the Co(Ni)–Mo–S phase or the Co(Ni)–W–S phase without a concomitant formation of Co(Ni) sulfide clusters with a low catalytic activity. In a previous study [27–30] we showed that supported Co–Mo sulfide catalysts, in which the edge of MoS_2 particles is fully covered by Co atoms forming the Co–Mo–S phase, can be selectively prepared when sulfided Mo catalysts are exposed to $Co(CO)_3NO$ vapor (CVD technique), followed by evacuation and resulfidation. The Co–Mo catalysts thus prepared by the CVD technique are designated CVD-Co/MoS_2/support here. The amount of Co accommodated in CVD-Co/MoS_2/support (support: Al_2O_3, TiO_2, ZrO_2, or SiO_2) is proportional to the amount of NO adsorption on the MoS_2/support, suggesting that Co atoms are preferentially located at the edge of MoS_2 particles [27]. The Co2p XPS [27] and Co K-edge XANES [30] spectra clearly demonstrated a selective formation of Co–MoS_2 interaction species. The FTIR results of CO adsorption by Maugé et al. [31] also suggested the selective formation of the Co–Mo–S phase in ex-carbonyl catalysts. However, no clear experimental evidence was reported about selective formation of the Co–W–S phase by the CVD technique, except for spectral indications from Co K-edge XANES [25].

In the present study, we prepared CVD-Co/MoS_2/SiO_2 and CVD-Co/WS_2/SiO_2 with a varying Mo or W loading to compare the intrinsic activities of the Co–Mo–S phase and the Co–W–S phase for the HDS of thiophene. The effect of presulfidation temperature was also examined. We studied mainly SiO_2-supported Co–Mo(W) sulfide catalysts and briefly Al_2O_3-supported counterparts, even though the latter catalysts have been widely employed as practical HDS catalysts, to avoid strong and complicated interactions between the active phase and support and thereby to directly extract the nature of the active sites. It is concluded that the turnover frequencies (TOFs) of the HDS of thiophene on the Co–Mo–S phase and the Co–W–S phase are close to each other and significantly depend on the presulfidation temperature and support.

2. Experimental

2.1. Catalyst preparation

A series of SiO_2-supported MoO_3 catalysts (MoO_3/SiO_2) with 5, 10, 15, and 20 wt% MoO_3 was prepared by an impregnation technique using $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Kanto Chemicals; analytical grade). After evaporation of the impregnation solution to dryness at ca. 350 K with stirring, the catalyst was dried at 373 K for 16 h. The catalyst was calcined in air at 773 K for 5 h with an electric furnace. A corresponding series of WO_3/SiO_2 catalysts (5, 10, 15, and 20 wt% WO_3) was prepared in an analogous way with $(NH_4)_6W_{12}O_{39} \cdot 5H_2O$ (Kanto Chemicals; analytical grade) as a starting precursor. The SiO_2 supports (JRC-SIO-8, 323 $m^2\,g^{-1}$ for MoO_3/SiO_2, and JRC-SIO-9, 370 $m^2\,g^{-1}$ for WO_3/SiO_2) were supplied by the Catalysis Society of Japan as reference catalysts.

The MoO_3/SiO_2 catalyst thus prepared was presulfided at 673, 773, or 873 K in a 10% H_2S/H_2 flow at an atmospheric pressure for 1.5 h (673 K) or 2 h (773 and 873 K). The Mo sulfide catalyst is designated MoS_2/SiO_2, followed by the presulfidation temperature in parentheses if necessary. WO_3/SiO_2 was sulfided at 673, 773, or 873 K for 2 h to prepare WS_2/SiO_2.

WO_3/Al_2O_3 (22 wt% WO_3) and MoO_3/Al_2O_3 (13 wt% MoO_3) were prepared in a similar way. The surface area of the Al_2O_3 support (JRC-ALO-7) was 180 $m^2\,g^{-1}$. MoS_2/Al_2O_3 and WS_2/Al_2O_3 were presulfided at 673 or 773 K for 1.5 and 2 h, respectively.

Cobalt was introduced to MoS_2/SiO_2 and WS_2/SiO_2 by a CVD technique [27–30]. Briefly, MoS_2/SiO_2 was first evacuated at 673 K for 1 h and subsequently exposed for 5 min at room temperature to a vapor of $Co(CO)_3NO$ (Strem Chemicals) kept at 273 K (CVD technique). After evacuation for 10 min at room temperature, the sample was sulfided again at 673 K for 1.5 h to prepare CVD-Co/MoS_2/SiO_2 regardless of the presulfidation temperature of MoS_2/SiO_2. CVD-Co/WS_2/SiO_2, CVD-Co/MoS_2/Al_2O_3, and CVD-Co/WS_2/Al_2O_3 were prepared in a similar manner. CVD-Co/SiO_2 was prepared similarly with the use of presulfided SiO_2 (JRC-SIO-9). The amount of Co incorporated by the CVD technique was determined by means of XRF (Rigaku RIX2000) within an accuracy of 5% [30].

2.2. Reaction procedure

The initial activity of the freshly prepared catalyst for the HDS of thiophene was evaluated at 623 K with a circulation reaction system made of glass under mild reaction conditions (initial H_2 pressure, 20 kPa). The HDS activity was calculated on the basis of the accumulated amount of H_2S. The details of the reaction procedures have been reported previously [27].

2.3. Characterization

The amount of NO adsorption on the catalyst was measured at room temperature by a pulse technique after the catalyst sample was cooled from the presulfidation temperature in a 10% H_2S/H_2 stream. The sample was purged for 15 min with a He stream before periodic admissions of a pulse of 10% NO/He. Details of the procedures have been reported elsewhere [19,27].

The W L_3-edge X-ray absorption near-edge structure (XANES) spectra of the catalysts and reference compounds were measured in transmission mode at room temperature at BL-10B of KEK-IMSS-PF with the use of an in situ XAFS cell with Kapton windows, with a 2.5-GeV ring energy and 250–290 mA of stored current.

The static magnetic susceptibility measurement of the sulfided catalyst was made in situ with a Faraday method with the use of a Cahn 2000 Electro-Balance system between 4.2 and 300 K [19]. The catalyst sample was evacuated at 673 K for 1 h (ca. 10^{-2} Pa) before it was fused into a glass ampoule (Al_2O_3-supported catalysts) or a quartz ampoule (SiO_2-supported catalysts). The magnitude of the magnetic field was fixed at 10,000 G. We obtained the effective magnetic moment and magnetic susceptibility by subtracting the magnetic contributions of the glass or quartz ampoule and the corresponding supported MoS_2 or WS_2 catalyst or Al_2O_3 measured separately under identical conditions.

The XPS spectra of 20% WS_2/SiO_2 (673) were measured on an X-ray photoelectron spectrometer, an ESCA 5400 (ULVAC-PHI). The catalyst was mounted on double-sided adhesive tape in an N_2-filled glove box and transferred to the pretreatment chamber with the use of a specially designed cell to avoid air contamination. Mg-$K_{\alpha_{1,2}}$ radiation (1253.6 eV) was used, and the pass energy was adjusted to 35.75 eV. The binding energies were referenced to the Si2p level at 103.8 eV due to SiO_2.

TEM observations were made on a JEM-2010 (200 kV) for 10% MoS_2/SiO_2 (673) and 20% WS_2/SiO_2 (673). The catalyst sample was dispersed in heptane in a N_2-filled glove bag. The distributions of MoS_2 or WS_2 slab size and stacking number were calculated over 100–250 particles [28].

3. Results

The catalytic activities of CVD-Co/MoS_2/SiO_2 and CVD-Co/WS_2/SiO_2 catalysts for the HDS of thiophene are shown in Fig. 1 as a function of Mo or W loading, S_{Mo} or S_W (atoms nm^{-2}). CVD-Co/MoS_2/SiO_2 exhibited a considerably higher HDS activity than CVD-Co/WS_2/SiO_2 over the whole range of metal loading. Regardless of the presulfidation temperature, the HDS activities of CVD-Co/MoS_2/SiO_2 and CVD-Co/WS_2/SiO_2 weakly depended on S_{Mo} and S_W, with broad maximum activities around 2.3 Mo atoms nm^{-2} and 0.8 W atoms nm^{-2}, respectively. The HDS activity of CVD-Co/Mo(W)S_2/SiO_2 increased with increasing presulfidation temperature, particularly at a lower S_{Mo} or S_W. CVD-Co/SiO_2 showed only a negligible HDS activity (0.02 mmol g^{-1} h^{-1}). This is due to a very limited anchoring capacity of Co on SiO_2 by the CVD technique and to the formation of less active Co sulfide clusters [27].

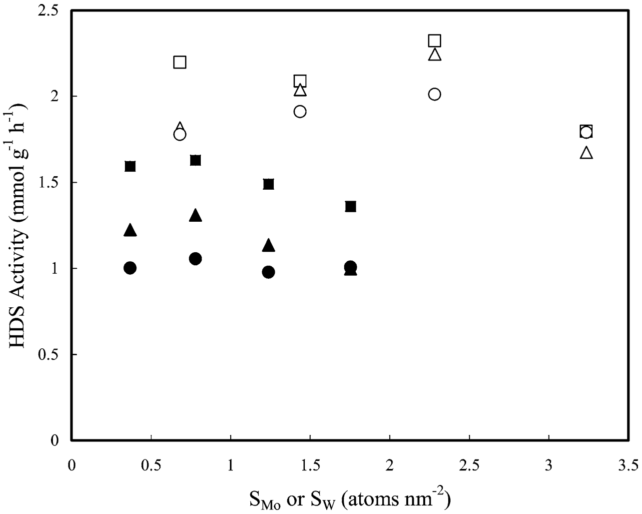

Fig. 1. Catalytic activity of CVD-Co/MoS_2/SiO_2 (open symbols) and CVD-Co/WS_2/SiO_2 (closed symbols) for the HDS of thiophene at 623 K as a function of loading (atoms nm^{-2}) of Mo (S_{Mo}) or W (S_W). Presulfidation temperature: ○ and ●, 673 K; △ and ▲, 773 K; and □ and ■, 873 K.

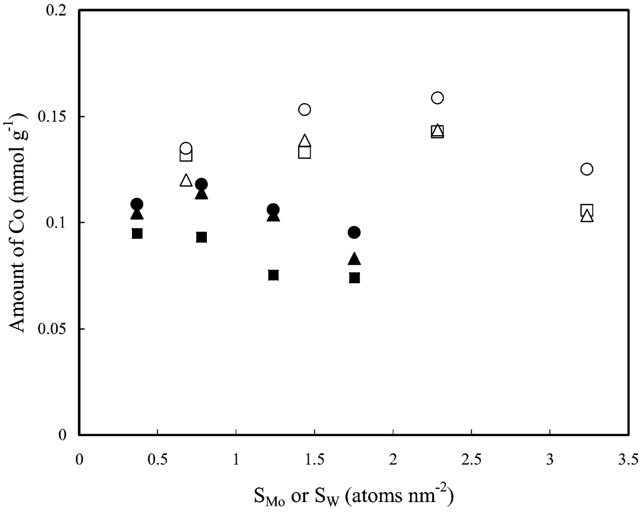

Fig. 2. Amount of Co in CVD-Co/MoS_2/SiO_2 (open symbols) and CVD-Co/WS_2/SiO_2 (closed symbols) as a function of loading (atoms nm^{-2}) of Mo (S_{Mo}) or W (S_W). Presulfidation temperature: ○ and ●, 673 K; △ and ▲, 773 K; and □ and ■, 873 K.

Fig. 2 shows the amount of Co anchored by the CVD technique as a function of S_{Mo} or S_W. The amount of Co exhibited a broad maximum around 2.3 Mo and 0.8 W atoms nm^{-2} for CVD-Co/MoS_2/SiO_2 and CVD-Co/WS_2/SiO_2, respectively, except for CVD-Co/WS_2/SiO_2 (873), in which the amount of Co decreased monotonically with increasing W content. The amount of Co in CVD-Co/MoS_2/SiO_2 decreased slightly as the presulfidation temperature of

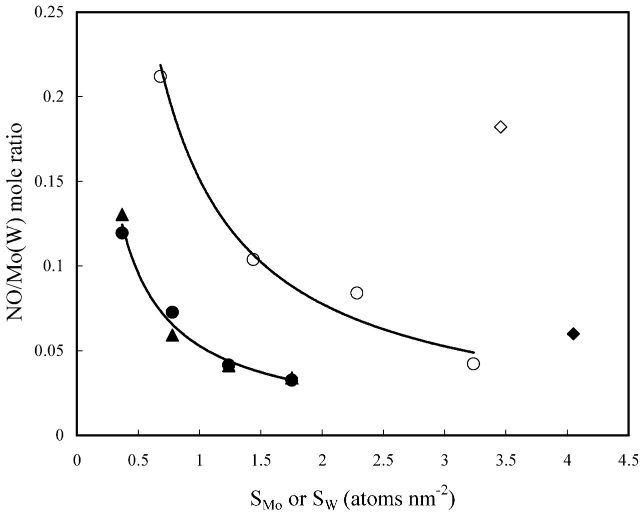

Fig. 3. The NO/Mo(W) mole ratios for MoS_2/SiO_2 (○), WS_2/SiO_2 (● and ▲), 13% MoS_2/Al_2O_3 (◇), and 22% WS_2/Al_2O_3 (◆) as a function of loading (atoms nm^{-2}) of Mo (S_{Mo}) or W (S_W). Presulfidation temperature: ○, ●, ◇, ◆, 673 K and ▲, 773 K.

MoS_2/SiO_2 increased from 673 to 773 K, but no further decrease was observed for the catalyst presulfided at 873 K. In CVD-Co/WS_2/SiO_2, the amount of Co was decreased considerably by the presulfidation between 773 and 873 K.

For MoS_2/SiO_2 and WS_2/SiO_2 catalysts sulfided at 673 or 773 K, the NO/Mo and NO/W mole ratios are plotted in Fig. 3 against S_{Mo} and S_W. The NO/Mo and NO/W ratios decreased as S_{Mo} and S_W increased, indicating decreasing dispersion of MoS_2 or WS_2 particles. Fig. 3 also presents the NO/Mo and NO/W mole ratios for 13% MoS_2/Al_2O_3 (673) and 22% WS_2/Al_2O_3 (673). Apparently, the dispersion of Mo and W sulfides on the Al_2O_3-supported catalysts is much higher than that on the SiO_2-supported counterparts.

The morphology of MoS_2 and WS_2 particles in 10% MoS_2/SiO_2 (673) and 20% WS_2/SiO_2 (673) was observed by TEM (not shown for brevity). The average stacking numbers were calculated as 2.1 and 3.7, and the average slab lengths were 2.7 and 6.7 nm for the Mo and W catalysts, respectively. Obviously, MoS_2 particles are more highly dispersed than WS_2 particles at a similar loading of Mo (1.44 atoms nm^{-2}) and W (1.75). In both catalyst systems, stacked MoS_2 and WS_2 particles were predominant.

Fig. 4 shows a correlation between the Co/W mole ratio for CVD-Co/WS_2/SiO_2 and the NO/W mole ratio for WS_2/SiO_2 presulfided at 673 or 773 K. The results for 22% WS_2/Al_2O_3 are also shown in Fig. 4. A single proportional line was obtained for the series of WS_2/SiO_2 and 22% WS_2/Al_2O_3 within experimental accuracy, regardless of the presulfidation temperature. A similar proportional correlation was observed for MoS_2/SiO_2 (673), as shown previously for supported MoS_2 catalysts [27,28]. The correlation in Fig. 4 suggests [27–29] that the Co–W–S phase is selectively formed by the CVD technique, with $Co(CO)_3NO$ as a precursor to Co sulfides.

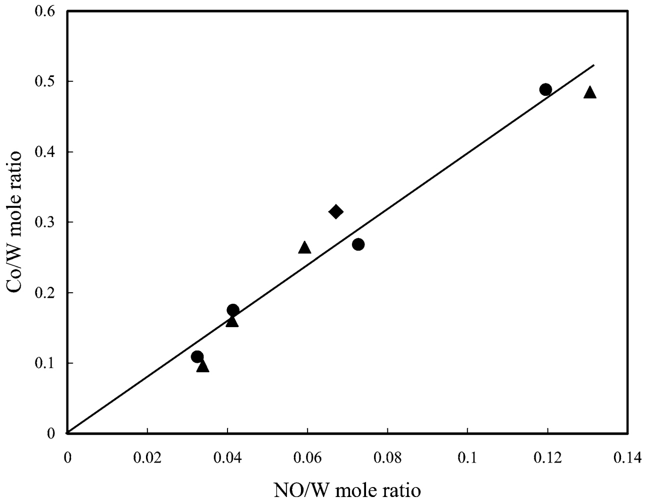

Fig. 4. Correlation between the Co/W mole ratio for CVD-Co/WS_2/SiO_2 and the NO/W mole ratio for WS_2/SiO_2. The results for CVD-Co/WS_2/Al_2O_3 (◆) are also included. Presulfidation temperature: ● and ◆, 673 K and ▲, 773 K.

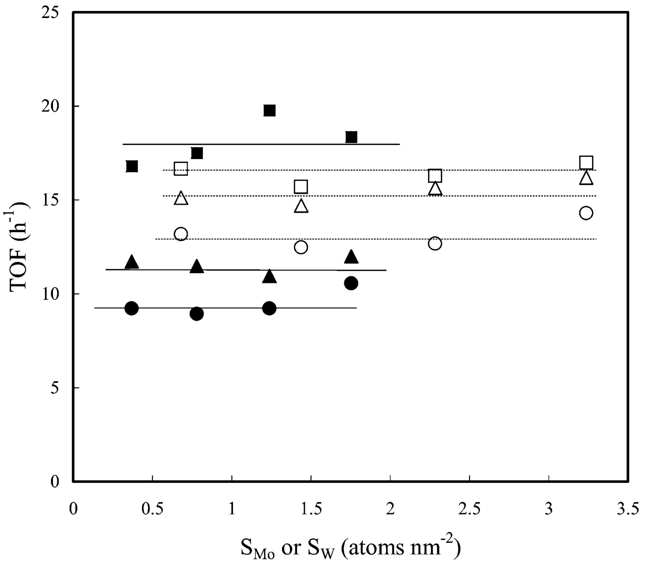

Fig. 5. TOF of the thiophene HDS at 623 K over CVD-Co/MoS_2/SiO_2 (open symbols) and CVD-Co/WS_2/SiO_2 (closed symbols) as a function of S_{Mo} or S_W. Presulfidation temperature: ○ and ●, 673 K; △ and ▲, 773 K; and □ and ■, 873 K.

The intrinsic activity of the catalyst was evaluated in terms of a TOF calculated on the basis of the amount of Co anchored by the CVD technique, assuming that the Co–Mo(W)–S phase is selectively prepared by the present technique. As shown in our previous study [27,29], the HDS reaction on unpromoted $Mo(W)S_2$ edges in the CVD-Co/MoS_2 catalysts can be neglected. Fig. 5 shows the TOF values over CVD-Co/MoS_2/SiO_2 and CVD-Co/WS_2/SiO_2 as a function of S_{Mo} or S_W. The TOF was almost independent of the surface concentration of Mo or W, except for a slight tendency toward a higher TOF at the highest loading for the Mo and W catalysts presulfided at 673 K. However, the TOF strongly depended on the catalyst component and

Table 1
TOF of thiophene HDS on the Co–Mo–S phase and the Co–W–S phase supported on SiO_2 and Al_2O_3

Support	Mo/W	Amount of oxides (wt%)	Presulfidation temperature (K)	TOF (h^{-1})	Relative TOF	
					SiO_2 (T_1)/Al_2O_3(673)[a]	TOF(T_2)/TOF(673)[b]
SiO_2	Mo	5–20	673	12.8	1.8	1.0
			773	15.4	2.1	1.2
			873	16.5	2.3	1.3
SiO_2	W	5–20	673	9.1	1.3	1.0
			773	11.2	1.6	1.2
			873	17.9	2.5	2.0
Al_2O_3	Mo	13	673	7.3	–	1.0
			773	8.7	–	1.2
	W	22	673	7.1	–	1.0
			773	7.7	–	1.1

[a] Relative TOF is defined as the ratio of the TOF value on the SiO_2-supported CVD-Co/Mo(W)S_2 catalyst to the one on the corresponding Al_2O_3-supported CVD-Co/Mo(W)S_2 catalyst sulfided at 673 K. Presulfidation temperature $T_1 = 673$, 773, or 873 K.

[b] Relative TOF is defined as the ratio of the TOF on the CVD-Co/Mo(W)S_2 catalyst sulfided at 773 K to the one in the corresponding CVD-Co/Mo(W)S_2 catalyst sulfided at 673 K. Presulfidation temperature $T_2 = 773$ or 873 K.

the presulfidation temperature of MoS_2/SiO_2 and WS_2/SiO_2. Table 1 summarizes the TOF values over SiO_2- and Al_2O_3-supported CVD-Co/MoS_2 and CVD-Co/WS_2 catalysts presulfided at 673, 773, or 873 K.

The TOF values over CVD-Co/MoS_2/Al_2O_3 and CVD-Co/WS_2/Al_2O_3 presulfided at 673 K were the same within experimental accuracy, suggesting that the Co–Mo–S phase and the Co–W–S phase exhibit the same intrinsic activity. The high-temperature presulfidation of the Al_2O_3-supported CVD-Co/MoS_2 and CVD-Co/WS_2 catalysts caused a 10–20% increase in the TOF. The TOF on CVD-Co/MoS_2/SiO_2 (673) was 1.8 times as high as that on CVD-Co/MoS_2/Al_2O_3 (673), in excellent agreement with the previous observations [27]. On the other hand, the TOF on CVD-Co/WS_2/SiO_2 (673) was only 1.3 times as high as that on the Al_2O_3-supported counterpart. With regard to the SiO_2-supported catalysts presulfided at 673 K, the Co–Mo–S phase showed a considerably higher intrinsic activity than the Co–W–S phase. When the catalysts were presulfided at 773 K, the TOF values on both CVD-Co/MoS_2/SiO_2 and CVD-Co/WS_2/SiO_2 increased by about 20%. When CVD-Co/MoS_2/SiO_2 was presulfided at 873 K, the TOF increased further, but to a smaller extent (7%). However, the effect of the high-temperature presulfidation was very significant for CVD-Co/WS_2/SiO_2, and the TOF increased by 60% compared with that for CVD-Co/WS_2/SiO_2 (773). The TOF on the Co–W–S phase was comparable to or even higher than that on the Co–Mo–S phase at a presulfidation temperature of 873 K.

Fig. 6 presents the W L_3-edge XANES spectra of 10 and 20% WS_2/SiO_2 sulfided at 673 and 773 K for examination of the chemical state of W in the sulfided catalysts, since it is well known that supported-W oxides are not easily sulfided compared with the Mo oxide counterparts [5,13,32,33]. The XANES spectra of 10% WO_3/SiO_2 and a crystalline WS_2 reference are also shown for comparison. WS_2/SiO_2 (773) showed a XANES spectrum very close to the one due to crystalline WS_2 regardless of the W loading, indicating complete sulfidation of W oxides to WS_2 particles. On the other hand, the white line around 10208 eV for the WS_2/SiO_2 (673) catalysts was much broader than that for crystalline WS_2. It is assumed that the peak is broadened by a superposition of the peaks due to W oxides and sulfides, judging from the peak position (10210 eV) for WO_3/SiO_2. The peak was successfully deconvoluted into two peaks due to WS_2 and W oxides, as exemplified in Fig. 6B for 20% WS_2/SiO_2 (673), allowing the estimation of the sulfidation degree of W. The contribution of the WS_2 peak for 20% WS_2/SiO_2 (673) was 56% and much lower than that for 10% WS_2/SiO_2 (673) (81%). Since the sulfidation degree of W was lower at a higher W content, it is assumed that large WO_3 crystallites are only partially sulfided to WS_2 particles. The XPS spectrum of the W4f level for 20% WS_2/SiO_2 (673) (not shown for brevity) showed a clear contribution of W oxides (W4$f_{7/2}$: 36.3 eV) to WS_2 (32.6 eV). A deconvolution of the spectrum indicated that 21% of W remained unsulfided after the presulfidation at 673 K, suggesting the formation of the surface WS_2 layers around W oxide cores. Similar phenomena were observed by XPS for the sulfidation of poorly dispersed MoO_3/SiO_2 [34]. On the basis of extensive physicochemical characterizations, van der Vlies et al. [35,36] have proposed a detailed mechanism of sulfidation of crystalline monoclinic WO_3 and $WO_3 \cdot H_2O$ to WS_2, involving the formations of hydrogen tungsten bronze, shear oxides, and various oxysulfide intermediates, and eventual transformations of the oxysulfidic phases to WS_2.

We measured the magnetic property of the Co species in the CVD-Co/Mo(W)S_2 catalysts to study the effects of the support and metal sulfide component on the structure and electronic state of Co [18,19]. Fig. 7 presents the effective magnetic moment and magnetic susceptibility χ of Co for CVD-Co/WS_2/Al_2O_3 (773) as a function of temperature. The catalyst was treated in a H_2 stream at 673 K for 30 min after the second sulfidation. With decreasing temperature, the magnetic susceptibility χ of Co increased and had a maximum around 15 K, followed by a sharp decrease at a lower

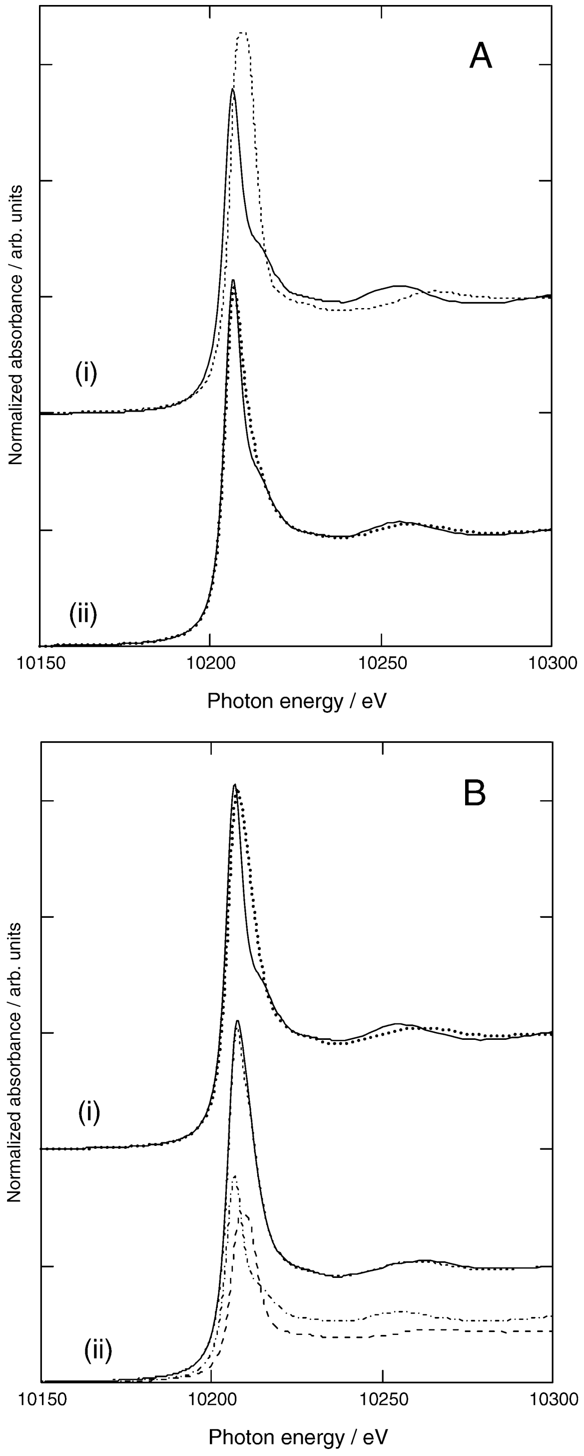

Fig. 6. W L_3-edge XANES spectra for 10% WS_2/SiO_2, 20% WS_2/SiO_2, and references. (A) (i) polycrystalline WS_2 (solid line) and 10% WO_3/SiO_2 (dotted line), (ii) 10% WS_2/SiO_2 (673) (dotted line) and 10% WS_2/SiO_2 (773) (solid line). (B) (i) 20% WS_2/SiO_2 (673) (dotted line) and 20% WS_2/SiO_2 (773) (solid line), (ii) deconvolution of the XANES spectrum of 20% WS_2/SiO_2 (673) (solid line, observed; dotted line, convoluted spectrum) into two components (WS_2, dash-dot line; WO_3, dash line).

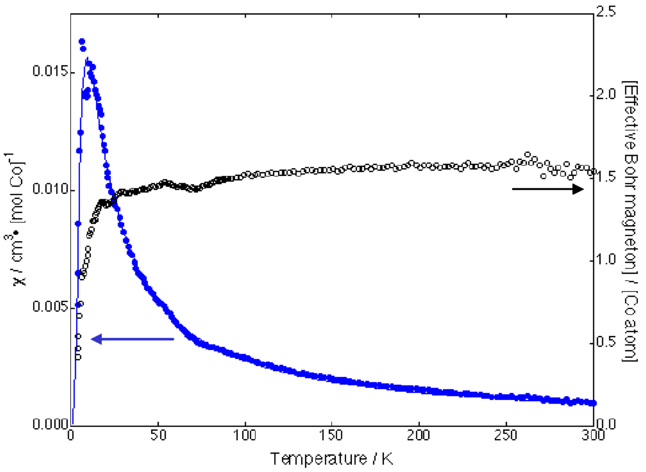

Fig. 7. Magnetic susceptibility χ and effective magnetic moment (μ_B) of Co as a function of temperature for CVD-Co/WS_2/Al_2O_3 (773) treated in an H_2-stream at 673 K. The best fitting curve, assuming a dinuclear Co sulfide cluster, for the observed magnetic susceptibility is also shown.

Table 2
Magnetic parameters[a] obtained by fitting the experimental magnetic susceptibility of Co assuming the formation of dinuclear Co clusters on the edge of MoS_2 or WS_2 particles

Catalyst	Mo(W)O_3 content (wt%)	Presulfidation temperature (K)	J (K)	α
CVD-Co/MoS_2/Al_2O_3[b]	13	673	−7.1	0.84
CVD-Co/MoS_2/Al_2O_3[b,c]	13	673	−6.9	0.96
CVD-Co/WS_2/Al_2O_3[c]	22	773	−7.4	0.77
CVD-Co/MoS_2/SiO_2	10	673	−8.5	1.2
CVD-Co/WS_2/SiO_2[c]	20	673	−9.6	0.98

[a] Eq. (1).
[b] Previous results [19].
[c] H_2-trated at 673 K for 30 min.

temperature. This temperature dependency of χ is a typical antiferromagnetic behavior. A similar magnetic property of Co was previously reported for CVD-Co/MoS_2/Al_2O_3 (673) [18,19]. With CVD-Co/MoS_2/Al_2O_3, the magnetic susceptibility χ of Co was reasonably fitted by Eq. (1) [37], assuming the formation of a dinuclear Co sulfide cluster on the edge of MoS_2 particles (spin-pair model)

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

where N_A is Avogadro's constant, μ_B is the Bohr magneton, g is the gyromagnetic factor (assumed to be 2 here), k_B is Boltzmann's constant, J is the magnetic interaction strength (defined by $H = -2J\boldsymbol{S}_1 \times \boldsymbol{S}_2$), and α is the fraction of the paramagnetic spin per Co atom. It was found that the temperature dependency of the observed χ for CVD-Co/WS_2/Al_2O_3 (773) was also rationally fitted by using the theoretical Eq. (1) as shown in Fig. 7. The fitting parameters, J and α, are summarized in Table 2 together with the previous results for CVD-Co/MoS_2/Al_2O_3 [19]. The effective magnetic moment for CVD-Co/WS_2/Al_2O_3 is close to the theoretical value for Co(II) at a low spin state, 1.73μ_B, at around 300 K. As presented in Table 2, the magnetic property of CVD-Co/MoS_2/Al_2O_3 was not changed by the treatment in a H_2 stream at 673 K for 30 min [19]. It should be noted that the J values for CVD-Co/MoS_2/Al_2O_3 (673) and CVD-Co/WS_2/Al_2O_3 (673) are the same within experimental accuracy (±0.5 K).

With CVD-Co/MoS_2/SiO_2 (673) and CVD-Co/WS_2/SiO_2 (673), it was found that the temperature dependency of the magnetic susceptibility χ of Co was also reasonably fitted by Eq. (1) (not shown for brevity). The magnetic parameters are presented in Table 2. It seems that the J values for the SiO_2-supported Mo and W catalysts are rather close to each other but are slightly greater in the absolute value than those for the Al_2O_3-supported catalysts. The values of α are close to unity for the CVD catalysts regardless of the support and catalyst composition, indicating that the dinuclear Co species are preferentially formed in these catalysts by the CVD technique. The effective magnetic moments around 300 K indicate that Co(II) species in the CVD catalysts are in a low spin state characteristic of sulfur environments even after the H_2 treatment at 673 K.

4. Discussion

4.1. *Selective formation of the Co–W–S phase and its structure*

In our previous study on various CVD-Co/MoS_2/support (support: Al_2O_3, TiO_2, ZrO_2, or SiO_2) catalysts, it has been shown by XPS [27] and Co-K-edge XANES [30] spectra that the Co sulfide species, admitted by the CVD technique with $Co(CO)_3NO$, preferentially interact with MoS_2 particles. Furthermore, the amount of anchored Co as expressed by the Co/Mo mole ratio was proportional to the amount of NO adsorption (NO/Mo mole ratio) on the MoS_2/support catalyst, substantiating the conclusion that the Co sulfide species are located on the edge of MoS_2 particles [27–29], since it is well established that NO molecules adsorb selectively on the edge of MoS_2 particles. These results allowed us to conclude that the Co–Mo–S phase [5] or the Co–Mo–S structure, in which Co atoms interact with a MoS_2 edge, is preferentially and fully formed by the CVD technique. The FTIR spectra of NO adsorption on CVD-Co/MoS_2/Al_2O_3 substantiated the conclusions [29].

Fig. 4 shows a proportional correlation between the Co/W and NO/W ratios for the WS_2 catalysts regardless of the W loading, sulfidation temperature, and support, demonstrating that the Co–W–S phase is selectively formed by the CVD technique as observed for the Co–Mo–S phase. The selective formation of Co–WS_2 interaction species was suggested by the Co-K-edge XANES spectra for CVD-Co/WS_2/Al_2O_3 [25]. The value of α in Table 2 shows the fraction of paramagnetic spin per Co atom accommodated in the CVD-Co/Mo(W)S_2 catalysts. As discussed elsewhere [18,19], the Co species in the Co–Mo–S phase are described as a dinuclear Co sulfide cluster model with an antiferromagnetic property, since Co_9S_8 shows a Pauli paramagnetic behavior ($\chi = 1.2 \times 10^{-4}\ \mathrm{cm^3\,mol^{-1}\,Co^{-1}}$) [38]. Accordingly, the selective formation of the Co–W–S phase is confirmed by the finding that the value of α is essentially unity within experimental accuracy.

As shown in Fig. 7, the magnetic property of CVD-Co/WS_2/Al_2O_3 (773) can be described by Eq. (1), indicating that the Co species in the Co–W–S phase form a dinuclear Co sulfide structure, as observed for the Co–Mo–S phase in CVD-Co/MoS_2/Al_2O_3 (673) [18,19]. With the SiO_2-supported CVD-Co/Mo(W)S_2 catalysts, the same conclusions can be derived from Table 2. Together with the spectroscopic and adsorption results for CVD-Co/MoS_2/Al_2O_3 (Fig. 4), the value of α in Table 2 and Co-K-edge XANES [25] strongly indicate that the antiferromagnetically coupled Co atoms in CVD-Co/WS_2 catalysts are in sulfur environments and are situated at the edge of WS_2 particles.

The parameter J, which shows the magnitude of the magnetic interactions between the adjacent Co atoms of CVD-Co/WS_2/Al_2O_3 (773), is very close to that of CVD-Co/MoS_2/Al_2O_3 (673), suggesting that the local structure and electronic state of the Co(II) species in the Co–W–S phase and the Co–Mo–S phase are very similar to each other. The value of J for CVD-Co/WS_2/SiO_2 is slightly larger than or rather close to that for CVD-Co/MoS_2/SiO_2 within the experimental accuracy (±0.5 K). On the other hand, the values of J for the SiO_2-supported catalysts are slightly but significantly greater in the absolute value than those for the Al_2O_3-supported counterparts. Although it is assumed that the difference in the J value resulted from the differences in the local structure and electronic state of the Co species in the Co–Mo(W)–S phase, caused by the interactions with the support, we have to await more systematic experiments and theoretical calculations for a more detailed discussion on the Co–Mo(W)–S structure, magnetic property, the effect of support, the effect of pretreatment (evacuation at 673 K in the present study), and the TOF of the HDS reaction. However, it is worth noting here that the magnetic property of the Co–Mo(W)–S phase can differentiate slight changes in the nature of the Co species between the SiO_2- and Al_2O_3-supported catalysts, in contrast to XPS (the same $Co2p_{3/2}$ binding energy [27]).

4.2. *Intrinsic activity of the Co–Mo–S phase and the Co–W–S phase*

As shown in Fig. 5 and Table 1, the TOF values of the thiophene HDS on the Co–Mo–S phase and the Co–W–S phase strongly depend on the support, metal sulfide component, and presulfidation temperature. With the CVD-Co/MoS_2/Al_2O_3 and CVD-Co/WS_2/Al_2O_3 catalysts sulfided at 673 K, the TOF values on the Co–Mo–S phase and the Co–W–S phase are identical under the present reaction conditions. Louwers and Prins [26] suggested that the intrinsic activities of the Ni–Mo–S phase and the Ni–W–S phase supported on activated carbon are identical, on the basis of the activity increase with the addition of Ni. The present results directly demonstrate, for the first time, that the TOF values on the Co–Mo–S phase and the Co–W–S phase supported on Al_2O_3 are identical, on the basis of the actual number of the active sites for the HDS of thiophene. Topsøe et al. defined two types of the Co–Mo–S phase depending on the intrinsic activity, Co–Mo–S Type I and II [5,39,40]. Co–Mo–S Type II, which is formed by high-temperature sulfidation (875–1275 K), is about two times more active for the HDS of thiophene than Co–Mo–S Type I formed by low temperature sulfidation (675 K). Since CVD-Co/MoS_2/Al_2O_3 and CVD-Co/WS_2/Al_2O_3 were presulfided at 673 K, it is concluded that Co–Mo–S Type I and Co–W–S Type I show the same TOF of the HDS of thiophene, in conformity with a close J value in Table 2.

The TOF over CVD-Co/MoS_2/SiO_2 (673) is 1.8 times that of CVD-Co/MoS_2/Al_2O_3 (673), in agreement with the previous study [27]. On the basis of the results, we previously concluded that there was formation of Co–Mo–S Type II in CVD-Co/MoS_2/SiO_2 (673). However, as shown in Fig. 5 and Table 1, the TOF over CVD-Co/MoS_2/SiO_2 is increased by the presulfidation at 773 K and further increased, although to a lesser extent, by the sulfidation at 873 K. The TOF over CVD-Co/MoS_2/SiO_2 (873) is 2.3 times that over CVD-Co/MoS_2/Al_2O_3 (673); the extent of the increase in TOF is consistent with that reported by Topsøe et al. [5,39] for the shift from Co–Mo–S Type I to II. Accordingly, it is concluded that the Co–Mo–S phase in CVD-Co/MoS_2/SiO_2 (873) is classified as “real” Co–Mo–S Type II defined by Topsøe et al. [5,37]. The Co–Mo–S phase in CVD-Co/MoS_2/SiO_2 (673), with a TOF intermediate between those of Co–Mo–S Type II and I, is designated as Co–Mo–S pseudo-Type II hereinafter for convenience. In the present study, the TOF calculated here is averaged over the Co–Mo–S structures existing in the catalysts. However, it is unlikely that Co–Mo–S pseudo-Type II in CVD-Co/MoS_2/SiO_2 (673) is a simple mixture of Co–Mo–S Type I and II, since the TOF on Co–Mo–S pseudo-Type II is independent of the Mo content or MoS_2 particle size within the experimental accuracy and since MoS_2 particles only weakly interact with SiO_2 surface [41,42] and are completely sulfided at 673 K [34,43,44].

The origin of Co–Mo–S Type I has been attributed to strong interactions between Mo oxides and support and, accordingly, to incomplete sulfidation of Mo oxides to MoS_2 particles and their resultant single-slab structure with residual anchoring bonds with the support such as Mo–O–Al, whereas that of Type II has been attributed to complete sulfidation and the formation of stacked MoS_2 particles [5,39]. The formation of MoS_2 stackings (averaged stacking number 2.1) was confirmed by TEM for 10% MoS_2/SiO_2 (673). It is therefore assumed that full sulfidation and the formation of stacked MoS_2 particles are not enough to form Co–Mo–S Type II. On the basis of the dependence of the TOF on the support and presulfiding temperature (Fig. 5 and Table 1), we instead propose that Co–Mo–S pseudo-Type II and Type II are formed on the edge of fully sulfided MoS_2 particles with no strong interactions with the support, in contrast to Co–Mo(W)–S Type I, and that pseudo-Type II is correlated with a distorted structure of MoS_2 particles, whereas Type II is correlated with a well-crystallized MoS_2 structure. It seems rational to assume that the crystallinity of MoS_2 particles is mainly determined by the sulfidation temperature at a fixed H_2S/H_2 pressure. Recently, Kooyman et al. [45] clearly showed by HRTEM that the crystallinity of supported MoS_2 particles is improved by sulfidation at 873 K compared with those formed at 673 K.

With the W-based catalysts, we propose the formation of Co–W–S pseudo-Type II in CVD-Co/WS_2/SiO_2 (773), in which WO_3 is completely sulfided to WS_2, as indicated by the W L_3-edge XANES spectra in Fig. 6. The TOF on CVD-Co/WS_2/SiO_2 is significantly increased by the presulfidation of WS_2/SiO_2 at 873 K, suggesting the formation of Co–W–S Type II simply on the basis of a 2.5 times increase in TOF relative to Co–W–S Type I observed for CVD-Co/WS_2/Al_2O_3 (673). It is confirmed that full sulfidation (Fig. 6) and the formation of WS_2 stackings (averaged stacking number 3.7) are not enough to form Co–W–S Type II. The formation of Co–W–S pseudo-Type II requires a higher presulfidation temperature (773 K) than Co–Mo–S pseudo-Type II (673 K). This is correlated with a higher difficulty of the full sulfidation of W oxides than that of Mo oxides to the corresponding sulfides, as evidenced by the XANES spectra in Fig. 6. With CVD-Co/WS_2/SiO_2 (673), the relatively low TOF may have resulted from the incomplete sulfidation of W oxides (XANES in Fig. 6 and XPS). It should be noted that there remains a possibility that a presulfidation temperature higher than 873 K is needed for the formation of “real” Co–W–S Type II, in contrast to the formation of Co–Mo–S Type II at 873 K [10,11].

As for the Al_2O_3-supported catalysts, it is assumed by definition [5,39] that Co–Mo–S Type I and Co–W–S Type I are formed, when presulfided at 673 K. These phases show identical TOFs. When Mo(W)S_2/Al_2O_3 is presulfided at 773 K, the TOF is increased by 10–20%; this is ascribed to partial formation of Co–Mo(W)–S pseudo-Type II in these catalysts.

The TOF values increase in the order Co–Mo(W)–S Type I (7.1–7.3 h^{-1}) < Co–Mo(W)–S pseudo-Type II (11.2–12.8 h^{-1}) < Co–Mo(W)–S Type II (16.5–17.9 h^{-1}). The different intrinsic activities of these phases stem from a slight difference in the local structures and electronic states of the Co species in the active phase. If we compare the TOFs in Table 1 and the J values in Table 2, it seems that these values are closely correlated with each other. However, a further systematic study is needed to establish the correlation between the magnetic property and TOF.

It is well known that only a weak synergetic effect appears between Co and W sulfides compared with the other combinations [23]. Kishan et al. [24] and Kubota et al. [25] have demonstrated that the HDS activity of Co–W catalysts is greatly increased by the addition of a chelating agent to impregnation solutions containing Co, suggesting that the weak catalytic synergy between Co and W sulfides is caused by a difference in the sulfidation temperatures between Co and W precursors that is greater than those between Co and Mo counterparts. The present results clearly demonstrate that if Co–W sulfide catalysts were prepared properly, strong synergetic effects would be generated, even between Co and W sulfides, as observed for Co–Mo sulfide catalysts. The fact in Fig. 1 that the HDS activity of CVD-Co/WS_2/SiO_2 (873) is lower than that of CVD-Co/MoS_2/SiO_2 (873) does not result from a lower intrinsic activity of the Co–W–S phase than that of the Co–Mo–S phase, but is due simply to a lower edge dispersion of WS_2 particles compared with that of MoS_2 particles, as suggested by the NO/Mo(W) ratio in Fig. 3 and the TEM observations.

Close similarities in TOF between the Co–Mo–S phase and the Co–W–S phase may imply the reaction mechanism of HDS on the Co–Mo(W)–S phase or the genesis of the catalytic synergy between Co and Mo or W sulfides. There are mainly two proposed reaction mechanisms of HDS on the Co–Mo(W)–S phase; one model assumes that the reaction takes place on coordinatively unsaturated Co sites and that MoS_2(WS_2) edges provide only a “support” to form highly active Co species (Co-only model) [26,46,47], and another model assumes that the sulfur vacancy between Co and Mo(W) atoms, Co–□–Mo(W), provides an active site and the Co and Mo(W) atoms simultaneously participate in the activation of organic sulfur compounds, thus generating catalytic synergy [45]. As discussed by Louwers and Prins [26], the present results suggest the reaction mechanism in which coordinatively unsaturated Co atoms play a major role under the present reaction conditions (623 K). If the reactants were activated on the active sites, Co–□–Mo(W), the intrinsic activities of the Co–Mo–S phase and the Co–W–S phase would be expected to be significantly different, reflecting the difference in the bond energy between Mo–S and W–S bonds, the latter being greater than the former [48]. However, the involvement of the MoS_2 or WS_2 edge or corner sites, in part, in the reaction (e.g., through the activation of hydrogen and formations of Mo(W)–SH groups [49]) cannot be ruled out.

5. Conclusions

In the present study, we tried to compare the intrinsic catalytic activities of the Co–Mo–S phase and the Co–W–S phase for the HDS of thiophene. The CVD technique was used to prepare supported Co–Mo and Co–W sulfide catalysts, in which all of the Co atoms form active sites. The catalysts were characterized by NO adsorption, TEM, XPS, W L_3-edge XANES, and the measurements of the magnetic susceptibility and effective magnetic moment of Co. The salient findings of the present study are as follows:

1. The Co–W–S phase supported on SiO_2 and Al_2O_3 was selectively formed by the CVD technique with the use of $Co(CO)_3NO$, as shown previously for the Co–Mo–S phase. The Co–W–S phase showed an antiferromagnetic property.
2. The TOF of the Co–Mo–S phase and the Co–W–S phase increased as the presulfidation temperature of MoS_2/SiO_2 and WS_2/SiO_2 increased from 673 to 873 K, whereas it was independent of the loading of Mo and W (5–20 wt% MoO_3 and WO_3).
3. The TOFs on the Co–Mo–S phase and the Co–W–S phase were very close for the HDS of thiophene; that is, Co–Mo–S Type I $\approx$ Co–W–S Type I $<$ Co–Mo–S Type II $\approx$ Co–W–S Type II. The magnetic results suggest that the TOF is changed by a slight modification in the local structure and electronic state of Co in the Co–Mo(W)–S phase.
4. It is suggested that Co–Mo(W)–S Type II is not necessarily formed by full sulfidation and stackings of Mo(W)S_2 slabs, but by a high-temperature treatment.

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References

[1] C. Song, Catal. Today 86 (2003) 211.
[2] C. Song, X. Ma, Appl. Catal. B 41 (2003) 207.
[3] K.G. Knudsen, B.H. Cooper, H. Topsøe, Appl. Catal. A 189 (1999) 205.
[4] R. Prins, in: G. Ertl, H. Knözinger, H.J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997, p. 1908.
[5] H. Topsøe, B.S. Clausen, F.E. Massoth, in: J.R. Anderson, M. Boudard (Eds.), Catalysis Science and Technology, vol. 11, Springer, Berlin, 1996.
[6] T. Kabe, A. Ishihara, W. Qian, Hydrodesulfurization and Hydrodenitrogenation, Kodansha, Tokyo, 1999.
[7] D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345.
[8] B.S. Clausen, S. Mørup, H. Topsøe, R. Candia, J. Phys. Colloq. C 6 (1976) 37.
[9] N.-Y. Topsøe, H. Topsøe, J. Catal. 75 (1982) 354.
[10] H. Topsøe, B.S. Clausen, N.-Y. Topsøe, E. Pederson, Ind. Eng. Chem. Fundam. 25 (1986) 25.
[11] R. Candia, O. Sørensen, J. Villadsen, N.-Y. Topsøe, B.S. Clausen, H. Topsøe, Bull. Soc. Chim. Belg. 93 (1984) 763.
[12] R. Prins, V.H.J. de Beer, G.A. Somorjai, Catal. Rev. Sci. Eng. 31 (1989) 1.
[13] S. Eijsbouts, Appl. Catal. A 158 (1997) 53.
[14] S. Helveg, J.V. Lauritsen, E. Lagsgaad, I. Stensgaad, J.K. Nørskov, B.S. Clausen, H. Topsøe, F. Besenbacher, Phys. Rev. Lett. 84 (2000) 951.
[15] J.V. Lauritsen, S. Helveg, E. Lagsgaad, I. Stensgaad, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Catal. 197 (2001) 1.
[16] M.V. Bollinger, J.V. Lauritsen, K.W. Jacobsen, J.K. Nørskov, S. Helveg, F. Besenbacher, Phys. Rev. Lett. 87 (2001) 196803.
[17] Y. Okamoto, M. Kawano, T. Kubota, J. Chem. Soc., Chem. Commun. (2003) 1086.

[18] Y. Okamoto, T. Kawabata, T. Kubota, I. Hiromitsu, Chem. Lett. 32 (2003) 1150.
[19] Y. Okamoto, M. Kawano, T. Kawabata, T. Kubota, I. Hiromitsu, J. Phys. Chem. B 109 (2005) 288.
[20] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, J. Catal. 187 (1999) 109.
[21] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, T. Toulhoat, J. Catal. 190 (2000) 128.
[22] H. Schweiger, P. Raybaud, H. Toulhoat, J. Catal. 212 (2002) 33.
[23] S.P. Ahuja, M.L. Derrien, J.F. Le Page, Ind. Eng. Chem. Prod. Res. Div. 9 (1970) 272.
[24] G. Kishan, L. Coulier, J.A.R. van Veen, J.W. Niemantsverdriet, J. Catal. 200 (2001) 194.
[25] T. Kubota, N. Hosomi, K. Bando, T. Matsui, Y. Okamoto, Phys. Chem. Chem. Phys. 5 (2003) 4510.
[26] S.P.A. Louwers, R. Prins, J. Catal. 139 (1993) 525.
[27] Y. Okamoto, K. Ochiai, M. Kawano, K. Kobayashi, T. Kubota, Appl. Catal. A 226 (2002) 115.
[28] Y. Okamoto, S. Ishihara, M. Kawano, M. Satoh, T. Kubota, J. Catal. 217 (2003) 12.
[29] Y. Okamoto, T. Kubota, Catal. Today 86 (2003) 31.
[30] Y. Okamoto, K. Ochiai, M. Kawano, T. Kubota, J. Catal. 222 (2004) 143.
[31] F. Maugé, A. Vallet, J. Bachelier, J.C. Duchet, J.C. Lavalley, J. Catal. 162 (1996) 88.
[32] B. Scheffer, B.P. Mangnus, J.A. Moulijn, J. Catal. 121 (1990) 18.
[33] H. Shimada, N. Matsubayashi, T. Sato, Y. Yoshimura, M. Imamura, T. Kameoka, H. Yanase, A. Nishijima, Jpn. J. Appl. Phys. 32 (1993) 463.
[34] Y. Okamoto, T. Imanaka, S. Teranishi, J. Phys. Chem. 85 (1981) 3798.
[35] A.J. van der Vlies, G. Kishan, J.W. Niemantsverdriet, R. Prins, T. Weber, J. Phys. Chem. B 106 (2002) 3449.
[36] A.J. van der Vlies, R. Prins, T. Weber, J. Phys. Chem. B 106 (2002) 9277.
[37] O. Kahn, Molecular Magnetism, VCH, 1993, Chapt. 6.
[38] O. Knop, C. Huang, K.I.G. Reid, J.S. Carlow, F.W.D. Woodhams, J. Solid State Chem. 16 (1976) 97.
[39] R. Candia, J. Villadsen, N.-Y. Topsøe, B.S. Clausen, H. Topsøe, Bull. Soc. Chim. Belg. 93 (1984) 763.
[40] H. Topsøe, B.S. Clausen, Catal. Rev. Sci. Eng. 26 (1984) 395.
[41] M. Breysse, J.L. Portefaix, M. Vrinat, Catal. Today 10 (1991) 489.
[42] F. Luck, Bull. Soc. Chim. Belg. 100 (1991) 781.
[43] M. de Boer, A.J. van Dillen, D.C. Koningsberger, J.W. Geus, J. Phys. Chem. 98 (1994) 7862.
[44] R. Cattaneo, Th. Weber, T. Shido, R. Prins, J. Catal. 191 (2000) 225.
[45] P.J. Kooyman, J.G. Buglass, H.R. Reinhoudt, A.D. van Langeveld, E.L.M. Hensen, H.W. Zandbergen, J.A.R. van Veen, J. Phys. Chem. B 106 (2002) 11795.
[46] J.P.R. Vissers, V.H.J. de Beer, R. Prins, J. Chem. Soc., Faraday Trans. 1 83 (1987) 2145.
[47] R.G. Leliveld, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, J. Catal. 175 (1998) 108.
[48] P. Raybaud, G. Kresse, J. Hafner, T. Toulhoat, J. Phys. Condense Matter. 9 (1997) 11085.
[49] N.-Y. Topsøe, H. Topsøe, J. Catal. 139 (1993) 641.