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Effect of sulfidation atmosphere on the hydrodesulfurization activity of SiO_2-supported Co–Mo sulfide catalysts: Local structure and intrinsic activity of the active sites

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ABSTRACT

The effects of the sulfidation atmosphere on the local structure and intrinsic activity of the active sites, Co–Mo–S, are studied with SiO_2-supported Co–Mo sulfide catalysts prepared by a chemical vapor deposition method using $Co(CO)_3NO$. The Co–Mo sulfide catalysts were sulfided in a stream of 10% H_2S/H_2 or 10% H_2S/He or their combinations. The intrinsic activity of $Co–Mo/SiO_2$ presulfided in H_2S/He is 1.6 times as high as that of Co–Mo–S Type II presulfided in H_2S/H_2 for the hydrodesulfurization (HDS) of thiophene, demonstrating that the location and/or local structure of Co–Mo–S are varied by the sulfidation atmosphere as well as by the MoS_2-support interaction. The catalysts were characterized by X-ray absorption fine structure and transmission electron microscope. It is suggested that the intrinsic activities of Co–Mo–S on the S-edge and Mo-edge of MoS_2 particles are distinctly different for HDS. Extended X-ray absorption fine structure analysis shows a good correlation between the coordination number of Co–S and the intrinsic activity of “active Co–Mo–S”.

1. Introduction

Improving the performance of HDS catalysts has been one of the principal issues in the petroleum industry to protect the environment [1–3]. Supported Mo or W sulfide catalysts promoted by Co or Ni have been widely used in industry for the HDS reaction [3–5]. Detailed knowledge of the surface structure of HDS catalysts and the number, intrinsic activity, and local structure of the active sites is required to improve further the catalyst performance to meet the increasingly stricter demands for cleaner fuels.

It is generally accepted that with Co–Mo HDS catalysts the so called Co–Mo–S phase (structure), in which Co atoms are located on the edge of MoS_2 particles, is the active phase [3–5]. The formation of Co–Mo–S explains the generation of strong catalytic synergies between Co and Mo sulfides. In addition, Co–Mo–S is at least classified into two types depending on the intrinsic activity, Type I and Type II, the latter showing activity that is about twice higher than that shown by the former [5–7]. Several groups [7–11] revealed that complete sulfidation of Mo precursors to MoS_2 particles removes the chemical interactions between MoS_2 particles and the support, resulting in the formation of Co–Mo–S Type II. Van Veen et al. [12] showed, however, that Co–Mo–S Type II supported on activated carbon exhibits about twice as high an intrinsic activity as Co–Mo–S Type II prepared on SiO_2 or Al_2O_3. This was later confirmed by Bouwens et al. [10]. These findings may suggest that the intrinsic activity of Co–Mo–S is not determined simply by the interaction between MoS_2 particles and the support.

The location and structure of Co–Mo–S have been studied using a variety of physicochemical techniques [4,5,10,11,13–17]. However, the conclusions are still under debate. Recently, density functional theory (DFT) calculations have provided important insight into the detailed structure of the active sites of Co–Mo catalysts [18,19]. Byskov et al. [20] suggested that Co atoms on the $(\bar{1}\,0\,1\,0)$ edge (S-edge) of MoS_2 particles are energetically more favorable than those on the $(1\,0\,\bar{1}\,0)$ edge (Mo-edge). Schweiger et al. [21] predicted for MoS_2 edges fully promoted by Co atoms that at strongly sulfiding conditions (high chemical potential of sulfur) Co atoms are situated on both edges with 100% sulfur coverage, while at usual HDS conditions Co atoms are present on the S-edge with 50% sulfur coverage and the Co atoms on the Mo-edge are energetically less favorable. In agreement with their predictions, scanning tunneling microscope (STM) studies by Lauritsen et al. [22–24] showed that Co atoms are preferentially located on

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the S-edge of MoS_2 particles with Co–MoS_2/Au(111) prepared at P_{H_2S}/P_{H_2} = ca. 500.

With the effect of the coverage of Co atoms on the edge, Sun et al. [25] suggested by use of DFT calculations that the surface energy of MoS_2 edges with 50% Co coverage is lower than that with 100% Co coverage. More recently, Krebs et al. [26] predicted through DFT calculations that under usual HDS conditions the S-edge of MoS_2 particles is fully promoted by Co, while 50% of the Mo atoms are substituted by Co on the Mo-edge. Thus, it is expected that the location and local structure of Co–Mo–S depend on the sulfidation and reaction conditions. It is of paramount importance to study the intrinsic activity of these possible Co–Mo–S structures for better understanding of HDS catalysts. However, experimental approaches have rarely been reported except for a recent study by Gandubert et al. [27] using X-ray photoelectron spectroscopy (XPS) in conjunction with DFT, suggesting that Co–Mo-mixed sites on the Mo-edge are active for the hydrogenation of toluene, while the S-edge fully promoted by Co shows a lower activity.

In a previous study [11], we investigated the effect of the presulfidation temperature on the catalytic properties of SiO_2-supported Co–Mo sulfide catalysts. X-ray absorption fine structure (XAFS) and magnetic measurements showed that the MoS_2-support interactions strongly modify the local structure and intrinsic activity of Co–Mo–S for the HDS of thiophene. In the present study, we investigate the effect of the sulfidation atmosphere (10% H_2S/H_2 and 10% H_2S/He) on the HDS activity of SiO_2-supported Co–Mo sulfide catalysts and on the local structure and intrinsic activity of Co–Mo–S to get deeper insight into the structure–reactivity relationships. We suggest that the catalytic properties of Co–Mo–S on the S-edge and Mo-edge of MoS_2 particles are distinctly different for HDS.

2. Experimental

2.1. Catalyst preparation

MoO_3/SiO_2 (6.7 wt% Mo) (SiO_2, 370 $m^2\,g^{-1}$) was prepared in a way analogous to the previous study by an impregnation method using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (AHM) as a precursor [11]. MoO_3/SiO_2 was calcined at 773 K for 5 h in air. The MoO_3/SiO_2 catalyst thus prepared (0.1 g) was presulfided at 673 K for 2 h in a 10% H_2S/H_2 or 10% H_2S/He flow (100 mL/min) at atmospheric pressure. The Mo sulfide catalyst is denoted as Mo/Si followed by the sulfidation atmosphere, when necessary.

Cobalt was introduced by the chemical vapor deposition (CVD) technique to Mo/Si [11,28–31]. Briefly, Mo/Si was first evacuated at 673 K for 1 h and subsequently exposed for 5 min at room temperature to a vapor of $Co(CO)_3NO$ kept at 273 K. After evacuation at room temperature for 10 min, the sample was sulfided again at 673 K in a 10% H_2S/H_2 or 10% H_2S/He flow for 1.5 h to prepare Co/Mo/Si. When the first and second sulfidation streams were H_2S/H_2, Co/Mo/Si is denoted as Co/Mo/Si (H_2S/H_2). Similarly, Co/Mo/Si sulfided twice in H_2S/He is designated as Co/Mo/Si (H_2S). When the first and the second sulfidation flows were changed, the catalyst is denoted, for instance, as Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$), in which Mo/Si was sulfided in H_2S/H_2 and then in H_2S/He after the Co addition by the CVD, and vise versa. The amount of Co incorporated by the CVD technique was determined for the catalysts after the HDS reaction by means of X-ray fluorescence analysis (XRF) (Shimadzu EDX-700HS) within an accuracy of ±5%.

Another Mo/Si (6.7 wt% Mo) was prepared by impregnation of the SiO_2 support with $(NH_4)_2MoS_4$ (ATM, Kanto Chemicals) dissolved in *N*,*N*-dimethylformamide [11]. After one-night impregnation, the solvent was removed by evaporation at room temperature, first in air and finally in vacuum, to avoid the oxidation of the thiomolybdate. The dried material was treated in a 10% H_2S/H_2 or 10% H_2S/He stream at 673 K for 2 h. Mo/Si thus prepared is designated as Mo/Si(ATM) hereafter. Co/Mo/Si(ATM) was prepared by the CVD method as described above.

CoO–MoO_3/SiO_2 (6.7 wt% Mo and 1.5 wt% Co) was prepared by a double impregnation technique (Mo first and then Co) using AHM and $Co(NO_3)_2\cdot 6H_2O$. The catalyst was calcined at 773 K for 5 h after each impregnation step. The sulfided catalyst is denoted as Co–Mo/Si(imp).

MoO_3/Al_2O_3 (8.7 wt% Mo, BET surface area of γ-Al_2O_3: 180 m^2/g) was prepared by an impregnation technique using AHM as a precursor. MoO_3/Al_2O_3 was calcined at 773 K for 5 h in air. The sulfided catalysts are denoted as Mo/Al and Co/Mo/Al.

2.2. Reaction procedure

The initial activity of the freshly prepared catalyst for the HDS of thiophene was evaluated at 623 K using a circulation reaction system made of glass under mild reaction conditions (initial H_2 pressure, 20 kPa) [11]. The reaction products were mainly H_2S, butenes, and *n*-butane, accompanying a trace amount of propylene. The HDS activity was calculated on the basis of the accumulated amount of H_2S. The detailed reaction procedures have been reported previously [28,29].

The HDS of dibenzothiophene (DBT) was carried out in a liquid phase using an autoclave (200 mL) at 1.4 MPa of H_2 pressure and 603 K. Sulfided Co/Mo/Si (0.1 g) was dispersed in 50 mL of decalin containing 1 wt% of DBT in a glove bag filled with N_2 to avoid contact with air. After setting the reactant solution and the catalyst in the autoclave vessel, the air was replaced first by N_2 and then H_2 five times each at room temperature. The H_2 pressure was increased and then the temperature was raised to 603 K (12 K/min) while stirring (300 rpm) the reaction mixture. After 3–5 h of reaction at 603 K, we analyzed the reaction mixture by GLC furnished with a flame ionization detector (Shimadzu GC-14B).

2.3. Characterization

TEM images of Mo/Si were taken on an electron microscope JEM-2010 with an accelerating voltage of 200 keV, as reported previously [11]. The distributions of MoS_2 particle size and stacking number were calculated over 150 particles in several arbitrary chosen areas.

The Co K-edge XAFS spectra of the catalysts and reference compounds were measured at room temperature at BL-9C (proposal 2006G331) of the Institute of Material Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF) with 2.5 GeV ring energy and 350–280 mA stored current in a fluorescence mode by using a Lytle type detector [11]. The higher harmonics were eliminated by detuning the incident X-ray intensity to 60%. The scan step was 0.5 eV. The synchrotron radiation was monochromatized by a Si (1 1 1) double crystal monochromator. The catalyst was evacuated at room temperature after sulfidation and then transferred to an in situ XAFS cell with Kapton windows without exposure to air.

The EXAFS data were analyzed with the same procedure as described previously [11]. The analysis involved pre-edge extrapolation and back ground removal by a cubic smoothing method to obtain EXAFS oscillations, which were Fourier transformed from *k*-space to *R*-space. Curve fittings were performed on the *k*-range between 30 and 145 nm^{-1} with k^3-weighted $\chi(k)$ and an *R*-window of 0.10–0.33 nm. The data were analyzed by a curve fitting procedure to obtain the coordination number *N*, atomic distance *R*, and Debye–Waller factor σ, inner potential E_0 using Eqs. (1) and (2)

$$k^3\chi(k) = k^2NF(k)\exp(-2\sigma^2k^2)\sin(2kR + \phi(k))/R^2 \tag{1}$$

$$k = (2m/\hbar^2(E - E_0))^{1/2} \tag{2}$$

where m is the mass of an electron, and E and E_0 are X-ray photon energy and threshold energy for photoemission, respectively.

The parameters (back scattering amplitude $F(k)$ and phase shift $\varphi(k)$) for the curve fittings were obtained by using FEFF calculations (FEFF codes: 8.2) [32,33] for the three scattering paths (Co–Co, Co–S, and Co–Mo). A S_0^2 value of 0.95 and a Debye–Waller factor value of 0.006 nm were employed in the FEFF calculations. The degree of error bars in the present analysis is estimated to be 0.5 for N, 0.001 nm for R, 3 eV for ΔE_0, and 0.0003 nm for σ, respectively, using the diagonal elements of the covariance matrix.

The normalized XANES spectra were obtained by subtracting the pre-edge background from the raw data assuming a straight line. Normalization was carried out by the edge height.

3. Results

3.1. Catalytic activity of Co/Mo/Si

Table 1 summarizes the catalytic activity of Co/Mo/Si presulfided in a variety of sulfidation atmospheres for the HDS of thiophene. In agreement with the previous results [11], the HDS activity of Co/Mo/Si (H_2S/H_2) is varied little by the sulfidation at 873 K. A great activity increase, however, is observed when Co/Mo/Si is presulfided at 673 K in 10% H_2S/He (without H_2). The amounts of H_2S detected in blank experiments, in which 20 kPa of H_2 has been circulated over Co/Mo/Si (H_2S) at 623 K without thiophene, were less than 0.1 mmol/h g, confirming that the activity increase observed for Co/Mo/Si (H_2S) is ascribed neither to the desorption of H_2S from the catalyst adsorbed during the presulfidation nor to the H_2S formation due to the hydrogenation of excess sulfur in the catalyst.

Table 1 shows that Co/Mo/Si(ATM) (H_2S) also exhibits a considerably higher activity than Co/Mo/Si(ATM) (H_2S/H_2). The HDS activity of the Co–Mo/Si impregnation catalyst is almost doubled by the presulfidation in H_2S/He compared to the sulfidation in H_2S/H_2. A considerably higher activity is also observed for Co/Mo/Al (H_2S) than for Co/Mo/Al (H_2S/H_2). Thus, it is evident that the HDS activity of the catalyst is significantly increased when presulfided in H_2S/He compared to H_2S/H_2 irrespective of the support and preparation method.

Table 1
Effect of sulfidation atmosphere on the thiophene HDS activity, Co content, and TOF for Co/Mo/Si, Co/Mo/Si (ATM), Co/Mo/Si (imp), and Co/Mo/Al.

Catalyst	Sulfidation conditions[a]	HDS activity (mmol g^{-1} h^{-1})	Co content		TOF (h^{-1})
			Wt%	Co/Mo atomic ratio	
Co/Mo/Si	H_2S/H_2	2.20	0.95	0.23	11.9
	H_2S/H_2[b]	2.24	0.81	0.20	16.2
	H_2S/He	3.10	0.71	0.17	26.2
	$H_2S/H_2 \rightarrow H_2S/He$	2.74	0.90	0.22	18.0
	$H_2S/He \rightarrow H_2S/H_2$	2.52	0.74	0.18	20.2
Co/Mo/Si (ATM)	H_2S/H_2	2.67	1.1	0.24	16.0
	H_2S/He	3.25	0.67	0.16	28.5
Co–Mo/Si (imp)	H_2S/H_2	1.14	1.5	0.36	–
	H_2S/He	2.23	1.5	0.36	–
Co/Mo/Al	H_2S/H_2	3.14	2.5	0.46	7.6
	H_2S/He	3.83	2.1	0.39	14.2

[a] The Mo catalyst was first presulfided for 2 h, followed by the introduction of Co by the CVD method and subsequent second sulfidation for 1.5 h. The first and the second sulfidation streams (10% H_2S/H_2 or 10% H_2S/He) were the same. When they were changed, the sequence is indicated by an arrow. The sulfidation temperature was 673 K unless otherwise noted.

[b] The first sulfidation was carried out at 873 K and the second one at 673 K.

In the present study, we employed a mild reaction condition to intend to conserve the original surface states, prepared by the presulfidation, during the reaction as much as possible to establish a structure–reactivity relationship. The stability of the catalytic activity was studied first by repeating the 1 h-reaction, intermediated by 10 min-evacuation at the reaction temperature and subsequent admission of the fresh reactants (thiophene and hydrogen). Fig. 1 shows the activity of the Co/Mo/Si catalysts presulfided in H_2S/H_2 and H_2S/He for the HDS of thiophene as a function of the reaction time. The activities of both catalysts decrease gradually during the reaction. However, the activity ratio of the catalysts is constant regardless of the reaction time: Co/Mo/Si (H_2S) shows a 1.4 times higher activity than the catalyst presulfided in H_2S/H_2, indicating that Co/Mo/Si (H_2S) is as stable as Co/Mo/Si (H_2S/H_2) under the present reaction conditions. The activity decrease may be due to the carbon deposition during the reaction rather than to the degradation of active sites.

We have shown previously that Co–Mo–S is selectively and fully prepared by the present CVD technique [28–31]. Besides, the amount of Co deposited on SiO_2 surface has been marginally small [28]. As a consequence, the intrinsic activity of the catalyst, as expressed by the turnover frequency (TOF) of the thiophene HDS on Co–Mo–S, is evaluated on the basis of the amount of Co anchored by the CVD technique: TOF (h^{-1}) = (activity (mol/g h))/(amount of Co (mol/g)). The reproducibility of TOF thus calculated was better than 10%.

The TOF is given in Table 1 together with the amount of Co (wt%), which is also expressed by the Co/Mo atomic ratio. As demonstrated previously with Co/Mo/Si [11], the TOF attained by the sulfidation at 873 K is higher than that at 673 K and corresponds to the TOF for "Co–Mo–S Type II", which is defined here, like other researchers [3–5], as Co–Mo–S formed *at usual H_2S/H_2 conditions* and without any strong interactions with the support. Nevertheless, when Co/Mo/Si is sulfided in H_2S/He, the TOF is significantly increased and 1.6 times greater even than that for Co–Mo–S Type II. In agreement with our previous study [11], the TOF of Co/Mo/Si(ATM) (H_2S/H_2) reveals the formation of Co–Mo–S Type II at 673 K. The presulfidation of Co/Mo/Si(ATM) in H_2S/He greatly increases the TOF to 28.5 h^{-1}, 1.8 times of Co–Mo–S Type II. Obviously, the sulfidation of Co/Mo/Si in H_2S/He leads to the formation of extraordinary active Co–Mo–S on SiO_2 regardless of the precursor of Mo. We call this highly active Co–Mo–S as "Co–Mo–S Type III" hereafter just for convenience. Fig. 1 shows

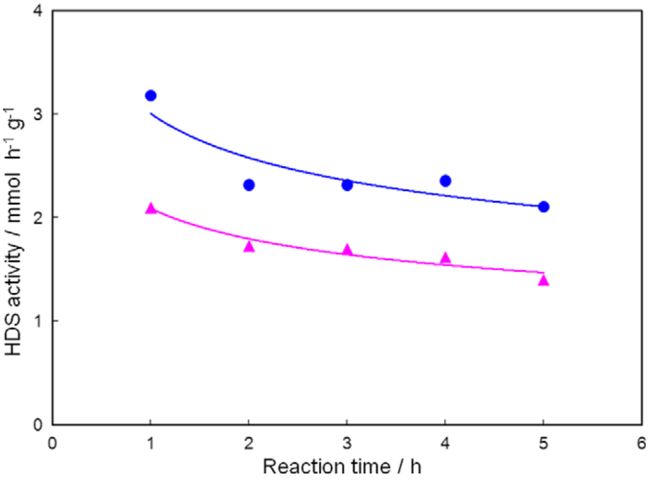

Fig. 1. Catalytic activity of Co/Mo/Si catalysts for the HDS of thiophene at 623 K as a function of reaction time. ●, Co/Mo/Si (H_2S) and ▲, Co/Mo/Si (H_2S/H_2).

that Co–Mo–S Type III is stable under the present reaction conditions. It is noteworthy in Table 1 that the amount of Co accommodated in Mo/Si presulfided in H_2S/He is smaller than that in H_2S/H_2.

In order to study the formation and stability of Co–Mo–S Type III, the combinations of the first and second presulfidation steps were changed. Mo/Si was first sulfided at 673 K for 2 h in H_2S/H_2 and subsequently Co was introduced by the CVD method, followed by the second sulfidation at 673 K for 1.5 h in H_2S/He. The activity of Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$) is presented in Table 1. The HDS activity and TOF are increased by the second sulfidation in H_2S/He compared with those for Co/Mo/Si (H_2S/H_2), but are smaller than those for Co/Mo/Si (H_2S). The reversed combination of the sulfidation atmosphere forms Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$) with intermediate HDS activity and TOF. It should be noted that the TOF values of these Co/Mo/Si catalysts are higher than that for Co–Mo–S Type II. Table 1 clearly shows that the amount of Co anchored in Co/Mo/Si is determined by the sulfidation atmosphere of Mo/Si.

The catalytic activity of Co/Mo/Si (H_2S) was measured for the HDS of DBT at a H_2 pressure of 1.4 MPa to examine the stability of the catalyst. The HDS of DBT has been found to be first order with respect to the concentration of DBT. The HDS product was predominantly biphenyl with a small amount of hexylbenzene (1–2%). Table 2 compares the rate constant and TOF, which is calculated by dividing the rate constant by the amount of Co. Co/Mo/Si (H_2S) shows a 1.2 times higher HDS activity than Co/Mo/Si sulfided at 873 K (Type II catalyst), compared to the 1.4 times activity increase shown in Table 1 for the HDS of thiophene under 20 kPa of H_2. The relative intrinsic activity of Co–Mo–S is increased by 40% for the HDS of DBT in comparison with 60% increase for the HDS of thiophene. These results suggest that Co–Mo–S Type III is fairly stable even during the HDS of DBT at 603 K and 1.4 MPa of H_2.

Table 2
Effect of sulfidation atmosphere on the activity of Co/Mo/Si for the HDS of dibenzothiophene.[a]

Sulfidation condition	Rate constant (h^{-1} g^{-1})	Co content[c] (mmol g^{-1})	TOF[d] (h^{-1} mol-Co^{-1})
H_2S/H_2 (873 K)[b]	0.55	0.14 (0.20)	3.9×10^3
H_2S/He (673 K)	0.66	0.12 (0.17)	5.5×10^3

[a] H_2 pressure: 1.4 MPa, reaction temperature: 603 K.
[b] The second sulfidation was carried out at 673 K after the addition of Co by the CVD.
[c] The Co/Mo atomic ratio is given in the parentheses.
[d] TOF was evaluated by dividing the rate constant by the amount of Co (mol g^{-1}).

3.2. Morphology

A representative TEM image of Mo/Si (H_2S) is presented in Fig. 2. As reported previously [11], in the case of Mo/Si (H_2S/H_2) sulfided at 673 K, nanosized entities ascribable to amorphous MoS_2 particles and/or Mo (oxy)sulfides have been observed by TEM along with MoS_2 particles. However, no such entities are detected in the TEM image shown in Fig. 2A, suggesting complete sulfidation of Mo oxides in H_2S/He at 673 K in contrast to Mo/Si (H_2S/H_2). The average size and stacking number of MoS_2 particles calculated from the TEM images are summarized in Table 3. The dispersion of MoS_2 particles is lower and the stacking is more extensive for Mo/Si (H_2S/H_2) than those for the previous catalyst [11]. However, the TOF value presented in Table 1 is the same as the previous one within the accuracy.

The TEM analysis of Mo/Si(ATM) (H_2S/H_2) and (H_2S) was similarly conducted. A typical TEM image for Mo/Si(ATM) (H_2S/H_2) is shown in Fig. 2B. In contrast to the TEM image for Mo/Si (H_2S/H_2) [11], no nanosized entities are detected in both catalysts prepared using ATM. The morphological parameters are listed in Table 3. The dispersion of MoS_2 particles is not varied very much by the Mo precursors.

3.3. XAFS analysis

Fig. 3 shows the Co K-edge XANES spectra for Co/Mo/Si presulfided in various atmospheres and reference compounds (Co_9S_8 and CoS_2) for comparison. The spectra for Co/Mo/Si (H_2S/H_2) and Co/Mo/Si(ATM) (H_2S/H_2) are taken from our previous study [11]. The 1s–3d pre-edge peak around 7709 eV is compared in Fig. 3B for clarity. It is apparent that the pre-edge peak intensity for the Co/

Table 3
TEM analysis of Mo/Si presulfided at 673 K for 2 h.

Catalyst	Sulfidation atmosphere	Average size (nm)	Average stacking number	Co/Mo atomic ratio	
				Estimated from TEM[a]	Observed
Mo/Si	H_2S/H_2	4.0	3.7	0.24	0.23
	H_2S/He	3.2	4.4	0.28	0.18
Mo/Si (ATM)	H_2S/H_2	3.9	3.7	0.24	0.24
	H_2S/He	4.1	4.3	0.24	0.16

[a] Assuming a regular hexagon, according to a model proposed by Kastzelan et al. [34].

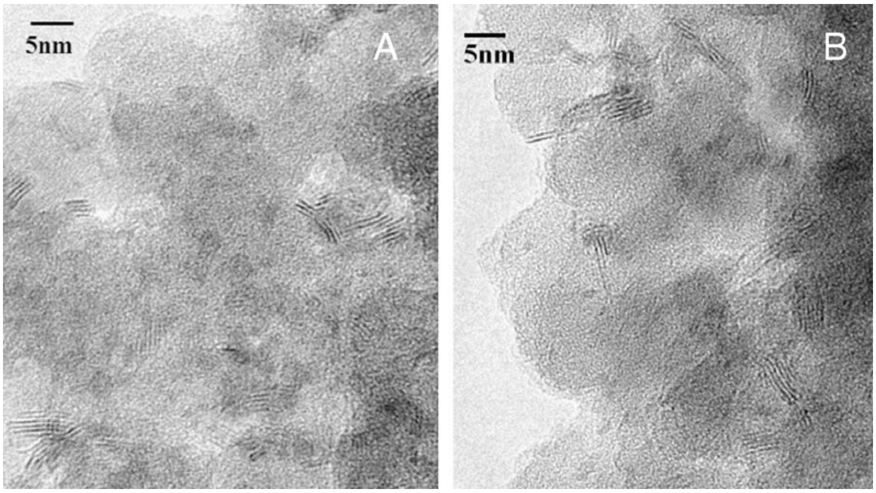

Fig. 2. Representative TEM images of Mo/Si. (A) Mo/Si (H_2S) and (B) Mo/Si(ATM) (H_2S/H_2).

Mo/Si catalysts treated in H_2S/He is considerably lower than that for Co/Mo/Si (H_2S/H_2) and even than that for Co/Mo/Si(ATM) (H_2S/H_2) and is close to the intensity for CoS_2, in which Co is in an octahedral symmetry. Fig. 3B thus indicates that the Co atoms of Co–Mo–S in the Co/Mo/Si catalysts sulfided in H_2S/He are in a higher symmetry than in a square pyramidal configuration. In our previous study [11], we have pointed out that a shoulder peak around 7720 eV grows as Co–Mo–S shifts from Type I to Type II. Fig. 3A shows that the shoulder peak for Co/Mo/Si once treated in H_2S/He is as prominent as that for Co/Mo/Si(ATM) (H_2S/H_2) (Type II catalyst). Co_9S_8 and CoS_2 show a corresponding peak but the energy is several eVs lower than that for Co–Mo–S, suggesting that the local structure and/or electronic state of Co–Mo–S are different from those of the bulk sulfides. With Co/Mo/Al (H_2S), the XANES features are close to those for Co/Mo/Si (H_2S/H_2), but apparently different from those for Co/Mo/Al (H_2S/H_2) (Type I catalyst) presented in [11]. The slight but distinct differences in the XANES spectra clearly suggest the modifications of the local structure and/or electronic state of Co–Mo–S by the presulfidation atmosphere.

Fig. 4 presents the Co K-edge $k^3\chi(k)$ EXAFS oscillations. Fig. 5 shows the Fourier transforms (FT) for Co/Mo/Si, Co/Mo/Si(ATM), and Co/Mo/Al sulfided only in H_2S/He. Fig. 6 compares the FTs of Co/Mo/Si sulfided at a various conditions at 673 K. The EXAFS results for Co/Mo/Si (H_2S/H_2) sulfided at 673 K and 873 K and for Co/Mo/Al (H_2S/H_2) have already been reported previously [11]. The FTs for Co/Mo/Si in Figs. 5 and 6 show well resolved three peaks around 0.18, 0.24, and 0.28 nm (phase shifts: uncorrected) irrespective of the sulfidation atmosphere and support, as reported previously for Co/Mo/Si (H_2S/H_2) [11]. The FTs were analyzed by the use of FEFF parameters, assuming Co–S, Co–Mo, and Co–Co atomic pairs in order of increasing distance. The structural parameters are summarized in Table 4. The accuracy of the coordination number (CN) of Co–S was estimated to be ±0.5 using the diagonal elements of the covariance matrix. We confirmed, however, with a few catalysts that the CN of Co–S was reproducible within ±0.1 as long as we used the same sulfidation conditions and EXAFS analysis procedures. In the present study, we discuss mainly the relative values of CN of Co–S to compare the local structure of Co–Mo–S as a function of the sulfidation atmosphere. A comparison between

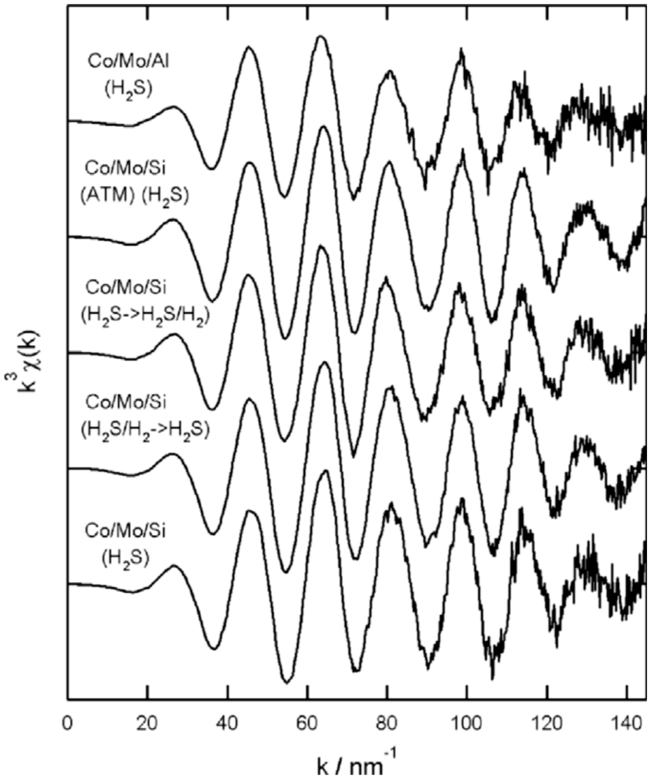

Fig. 4. Co K-edge $k^3\chi(k)$ EXAFS oscillations for Co/Mo/Si (H_2S), Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$), Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$), Co/Mo/Si(ATM) ($H_2S$), and Co/Mo/Al ($H_2S$).

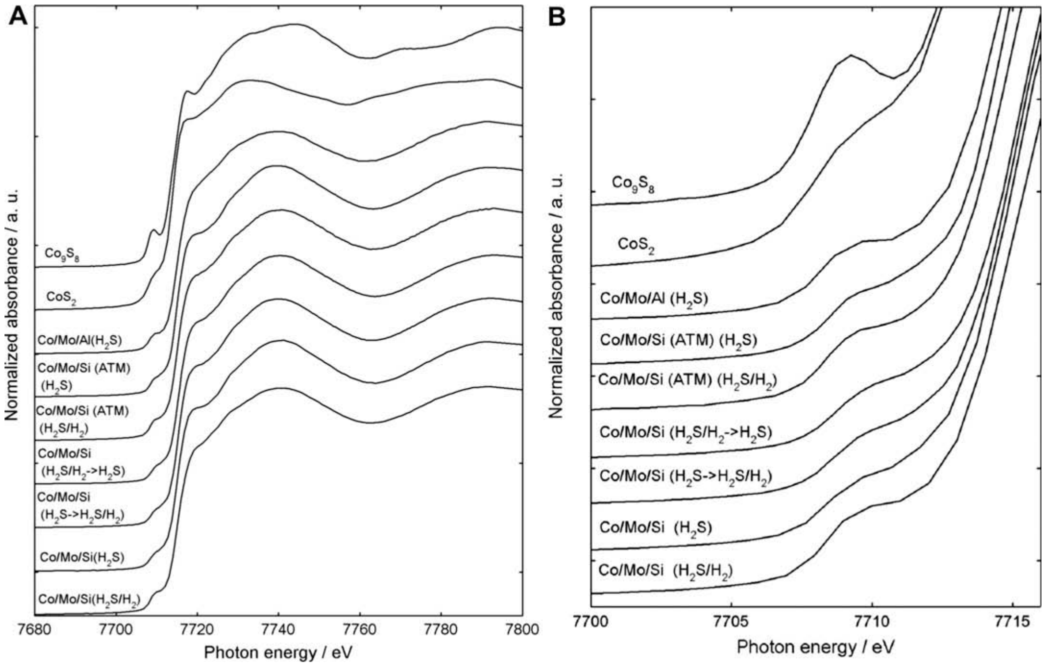

Fig. 3. (A) Co K-edge XANES spectra for Co/Mo/Si (H_2S), Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$), Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$), Co/Mo/Si(ATM) ($H_2S$), Co/Mo/Al ($H_2S$), and reference compounds (Co_9S_8 and CoS_2). The XANES spectra for Co/Mo/Si (H_2S/H_2) and Co/Mo/Si(ATM) (H_2S/H_2) are taken from [11] for comparison. (B) The pre-edge region of Co K-edge spectra is shown for clarity.

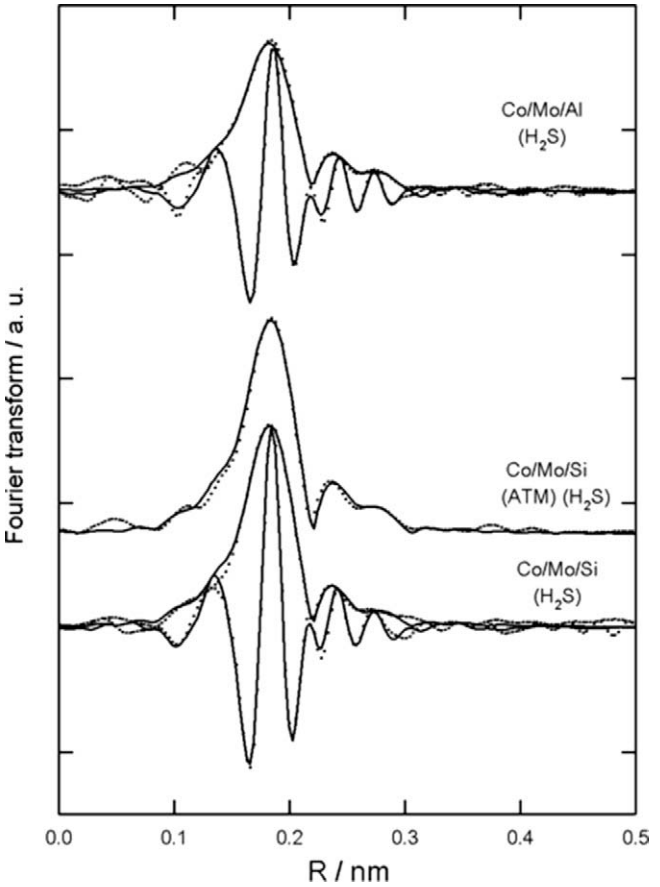

Fig. 5. Co K-edge k^3-weighted Fourier transforms for Co/Mo/Si (H_2S), Co/Mo/Si(ATM) (H_2S), and Co/Mo/Al (H_2S). Dots: observed Fourier transforms, and solid line: best curve-fittings.

the intensity of the pre-edge peak shown in Fig. 3B and the CN of Co–S shows a small but clear tendency that the pre-edge peak intensity decreases as the CN of Co–S increases, implying that the relative CN of Co–S is a reliable parameter to describe the change in the local structure of Co–Mo–S in spite of the estimated error bar of ±0.5 for the absolute values.

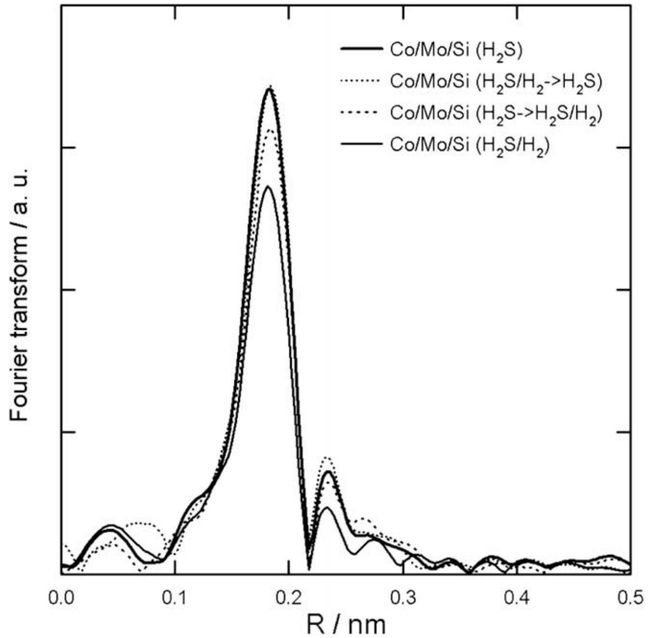

Fig. 6. Co K-edge k^3-weighted Fourier transforms for Co/Mo/Si (H_2S), Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$), Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$), and Co/Mo/Si ($H_2S/H_2$). The Fourier transform for Co/Mo/Si (H_2S/H_2) is taken from [11] for comparison.

With Co/Mo/Si (H_2S), the Co–S, Co–Mo, and Co–Co atomic distances are 0.220, 0.282, and 0.315 nm and close to those for Co/Mo/Si (H_2S/H_2) sulfided at 873 K or the Co–Mo–S Type II catalyst in [11]. The coordination number (CN) of the Co–S bonds is, however, larger than that for the Type II catalyst (4.5–4.9) [11], while the CN of Co–Mo is not changed (1.5 ± 0.5). Essentially identical structural parameters are obtained for Co/Mo/Si(ATM) (H_2S) and Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$). On the other hand, Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$) shows a smaller CN of Co–S (4.8) compared with Co/Mo/Si (H_2S) (5.3). With Co/Mo/Al (H_2S), the atomic distances of Co–Mo and Co–Co are slightly elongated compared with those for Co/Mo/Al (H_2S/H_2) (Co–Mo–S Type I by definition [5–7]) in [11]. However, the CN of Co–S is not significantly varied by the sulfidation in H_2S/He (from 4.2 to 4.3) in contrast to Co/Mo/Si (from 4.5 to 5.3).

We have previously noted a tendency of an increasing TOF with the increasing CN of Co–S [11]. The significantly high intrinsic activity of Co–Mo–S Type III may be correlated to the relatively high CN of Co–S. Fig. 7 presents the TOF as a function of the CN of Co–S for Co/Mo/Si and Co/Mo/Al prepared in H_2S/H_2 and H_2S/He, including the previous results [11]. Table 5 lists the CN of Co–S for the catalysts relevant in the present study. Fig. 7 shows a clear tendency that the TOF increases as the CN of Co–S increases from Co–Mo–S Type I for Co/Mo/Al (H_2S/H_2) through Co–Mo–S Type II for Co/Mo/Si (H_2S/H_2) presulfided at 873 K to Co–Mo–S Type III for Co/Mo/Si (H_2S) despite of some scattering in the correlation. Bouwens et al. [10] reported a similar correlation including Al_2O_3-, SiO_2-, and activated carbon-supported Co–Mo sulfide catalysts.

On the basis of the structural parameters shown in Table 4, we tentatively propose a structure model of Co–Mo–S Type III in Fig. 8. The structure of Co–Mo–S Type III may be described as a dinuclear Co sulfide clusters as proposed for Co–Mo–S Type I and Co–Mo–S Type II [11,16]. Since we have assumed a single Co–S peak for five-six Co–S bonds in the analysis of the EXAFS data, it is conjectured that the CN of Co–S of 5.3-5.4 presented in Table 4 is compatible with the model within the accuracy (±0.5). It seems that the CN of Co–Co is not incompatible with the model within the accuracy (±0.5). The weak 1s–3d pre-edge peak in Fig. 3 for Co/Mo/Si (H_2S) is consistent with a preferential formation of Co in a distorted octahedral configuration. We tentatively propose that Co–Mo–S Type III has a S-dimer between the two Co atoms as illustrated in Fig. 8.

4. Discussion

4.1. Location of Co–Mo–S

In our previous study [11], we have estimated the amount of Co required to fully decorate the edges of MoS_2 particles on the basis of the average size of MoS_2 particles evaluated from the TEM analysis and the structural model proposed by Kasztelan et al. [34], assuming a regular hexagon and a 1:1 substitution of Mo by Co. An excellent agreement between the calculated and observed amounts of Co for Co/Mo/Si prepared by the CVD technique suggested that Co atoms fully occupy the substitutional sites of Mo on both Mo-edge and S-edge of MoS_2 particles [11]. We estimated the Co/Mo ratios on the basis of the TEM results presented in Table 3 for Mo/Si (H_2S/H_2) and Mo/Si (H_2S) and for the Mo/Si(ATM) counterparts. They are compared in Table 3 with the observed Co/Mo ratios. With Mo/Si (H_2S/H_2) and Mo/Si(ATM) (H_2S/H_2), the calculated ratios are in excellent agreement with the observed ratios,

Table 4
Structural parameters[a] derived from Co K-edge EXAFS analysis of Co/Mo/Si and Co/Mo/Al catalysts.

Catalyst[b] (presulfidation atmosphere)	Atomic pair	CN	R (nm)	ΔE_0 (eV)	σ (10^{-3} nm)	R_f (%)
Co/Mo/Si (H_2S/H_2 → H_2S/He)	Co–S	5.3	0.219_7	2.0	8.2	2.5
	Co–Mo	1.4	0.281_0	3.8	9.4	
	Co–Co	0.9	0.315_1	−7.8	10.8	
Co/Mo/Si (H_2S/He → H_2S/H_2)	Co–S	4.8	0.220_9	2.0	8.1	1.0
	Co–Mo	1.4	0.279_9	4.3	10.0	
	Co–Co	0.5	0.315_4	−7.8	11.5	
Co/Mo/Si (H_2S/He)	Co–S	5.3	0.219_8	3.1	8.2	1.3
	Co–Mo	1.4	0.281_9	5.6	9.8	
	Co–Co	0.8	0.315_0	−8.7	11.2	
Co/Mo/Si (ATM) (H_2S/He)	Co–S	5.4	0.220_5	2.9	8.0	1.3
	Co–Mo	1.6	0.282_0	4.3	9.2	
	Co–Co	1.0	0.315_1	−8.9	10.8	
Co/Mo/Al (H_2S/He)	Co–S	4.3	0.220_5	1.2	8.6	1.1
	Co–Mo	1.5	0.283_1	4.1	9.5	
	Co–Co	1.0	0.315_3	−8.5	10.7	

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

[b] The Mo catalyst was first presulfided for 2 h, followed by the introduction of Co by the CVD method and subsequent second sulfidation for 1.5 h. The first and the second sulfidation streams (10% H_2S/H_2 or 10% H_2S/He) were the same. When they were changed, the sequence is indicated by an arrow. The sulfidation temperature was 673 K.

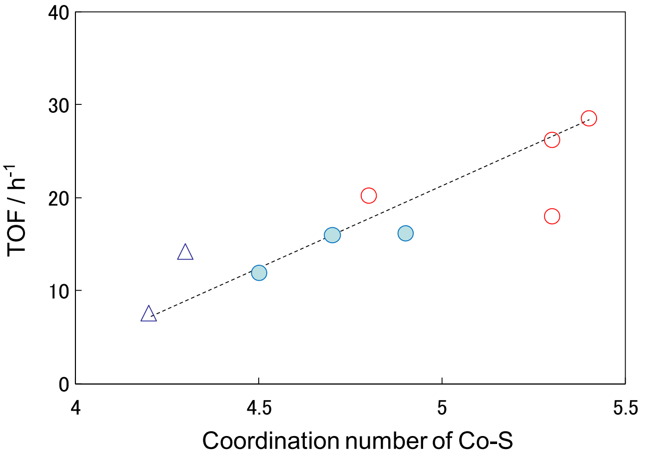

Fig. 7. Correlation between the TOF on Co–Mo–S for the HDS of thiophene and the coordination number of Co–S bonds. Closed circles, Co/Mo/Si (H_2S/H_2) (673 K and 873 K) and Co/Mo/Si(ATM) (H_2S/H_2); triangles, Co/Mo/Al (H_2S/H_2) and (H_2S); and open circles, Co/Mo/Si (H_2S), Co/Mo/Si (H_2S → H_2S/H_2), Co/Mo/Si (H_2S/H_2 → H_2S), and Co/Mo/Si(ATM) (H_2S). Refer to Table 5 for the CN of Co–S.

Table 5
Effect of sulfidation atmosphere on the coordination number of Co–S bonds and the TOF of "active Co–Mo–S".

Catalyst	Sulfidation conditions[a]	CN of Co–S	TOF on "active Co–Mo–S" (h^{-1})
Co/Mo/Si	H_2S/H_2	4.5[c]	18.3
	H_2S/H_2[b]	4.9[c]	24.9
	H_2S/He	5.3	26.2
	H_2S/H_2 → H_2S/He	5.3	27.7
	H_2S/He → H_2S/H_2	4.8	20.2
Co/Mo/Si (ATM)	H_2S/H_2	4.7[c]	24.6
	H_2S/He	5.4	28.5
Co/Mo/Al	H_2S/H_2	4.2[c]	11.7
	H_2S/He	4.3	14.2

[a] The Mo catalyst was first presulfided for 2 h, followed by the introduction of Co by the CVD method and subsequent second sulfidation for 1.5 h. The first and the second sulfidation streams (10% H_2S/H_2 or 10% H_2S/He) were the same. When they were changed, the sequence is indicated by an arrow. The sulfidation temperature was 673 K unless otherwise noted.

[b] The first sulfidation was carried out at 873 K and the second one at 673 K.

[c] Taken from [11].

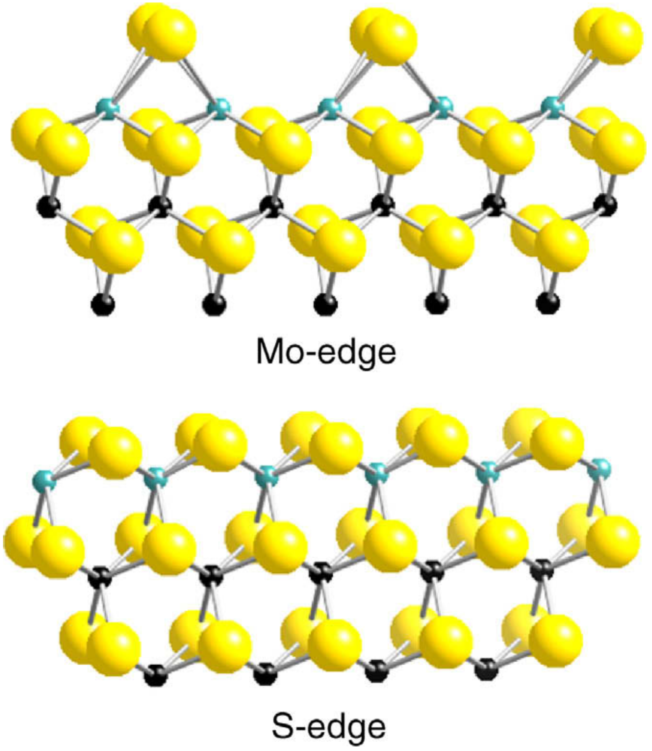

Fig. 8. Structural models of Co–Mo–S in Co/Mo/Si sulfided in H_2S/He at 673 K. Large light ball (yellow), sulfur; small light ball (blue), cobalt; and small dark ball (black), molybdenum. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

confirming the previous conclusion that Co–Mo–S is formed on both edges of MoS_2 particles [11].

In sharp contrast to the excellent agreement between the observed and calculated Co/Mo ratios for Co/Mo/Si presulfided in H_2S/H_2, the experimental Co/Mo ratios are considerably smaller for Co/Mo/Si (H_2S) and Co/Mo/Si(ATM) (H_2S) than the calculated ones (Table 3). The disagreement suggests that only 65% (0.18/0.28 = 0.64 and 0.16/0.24 = 0.67) of the edges of MoS_2 particles in Mo/Si presulfided in H_2S/He is decorated with Co after the CVD.

According to the DFT calculations [20,25,35–39], both Mo-edge and S-edge of MoS_2 particles are expected to be fully covered by sulfur (100% sulfur coverage), when Mo/Si or Mo/Si(ATM) is sulfided in H_2S/He (without H_2). Schweiger et al. [36] predicted by DFT calculations coupled with thermodynamics that the surface energy of the Mo-edge with 100% sulfur coverage is considerably lower than that of the corresponding S-edge and, as a consequence, that the shape of MoS_2 particles is almost triangular consisting of the Mo-edge (ca. 90%). The STM study on MoS_2/Au(1 1 1) substantiated the calculations [22]. Although the Mo sulfide-support interactions and the chemical processes during the sulfidation may modify the morphology of the resultant MoS_2 particles, it is expected that after the sulfidation in H_2S/He, the Mo-edge prevails over the S-edge in the fraction, both of which have 100% sulfur coverage: the Mo-edge is covered by S-dimers and the sulfur atoms coordinate to only a single Mo atom, while the S-edge is covered by relatively coordinatively saturated sulfur atoms [20,36,39]. In the present preparation of Co–Mo sulfide catalysts, $Co(CO)_3NO$ molecules are allowed to contact the edges of MoS_2 particles and subsequently react with the sulfur atoms on the edges to form Co–Mo–S if the sulfur atoms are reactive enough. Taking into consideration the configuration and fraction of the Mo-edge and S-edge, we propose that with Co/Mo/Si (H_2S) Co–Mo–S is formed selectively on one of the edges (65% of the total edges) of MoS_2 particles, presumably on the Mo-edge, while the other edge, possibly the S-edge, remains intact. Under strongly sulfiding conditions (high chemical potential of sulfur) such as those in H_2S/He, Schweiger et al. [36] and Krebs et al. [26] suggested that Co atoms are stabilized on both Mo-edge and S-edge from the point of edge energy. It is considered that the preferential location of Co on one of the edges (the Mo-edge) in the present catalyst preparation is not thermodynamics-controlled, but is kinetics-controlled due to a higher reactivity of this edge (the Mo-edge) toward $Co(CO)_3(NO)$ molecules.

Schweiger et al. [36] predicted for MoS_2 particles that under typical sulfidation conditions the 50% sulfur coverage is stabilized on both Mo-edge and S-edge involving coordinatively unsaturated sulfur atoms. It is conceived that due to coordinative unsaturation these edges are highly reactive toward $Co(CO)_3NO$ molecules, facilitating the formation of Co–Mo–S on both edges of MoS_2 particles for Mo/Si sulfided in H_2S/H_2. According to the theoretical calculations by Byskov et al. [20] and Schweiger et al. [21], the full substitution of Mo atoms by Co on the Mo-edge is energetically more expensive than that on the S-edge, suggesting the preferential formation of Co–Mo–S on the S-edge under usual sulfidation or reaction conditions such as those employed in the present study. Sun et al. [25] and Krebs et al. [26], however, suggested under these conditions that Co atoms are stabilized even on the Mo-edge when the Mo atoms are partially substituted by the Co atoms (50%). Instead, we tentatively propose from Table 3 that both edges of MoS_2 particles are fully covered by Co in the present preparations of Co/Mo/Si and Co/Mo/Si(ATM) presulfided in H_2S/H_2, since we need to assume a 60–70% larger (Mo_{edge}/Mo_{total}) ratio than that expected from the model proposed by Kasztelan et al. [34] when the Mo-edge is only 50% covered by Co [25,26].

When the Co atoms located on the Mo-edge of Mo/Si presulfided in H_2S/He are exposed to H_2S/H_2, the EXAFS analysis of Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$) presented in Table 4 and the XANES spectrum presented in Fig. 3 show no sign of the degradation of Co–Mo–S to Co sulfide clusters (vide infra), suggesting that Co–Mo–S, presumably, on the Mo-edge is stable even in H_2S/H_2 once it is formed. In line with the DFT calculations [20,21,26], the EXAFS and XANES results of Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$) indicate the stability of Co–Mo–S on both edges at highly sulfiding conditions (H_2S/He).

4.2. Formation of Co–Mo–S Type III

In the present study on SiO_2-supported Co–Mo sulfide catalysts, it is distinctly demonstrated that the intrinsic activity of Co–Mo–S strongly depends on the sulfidation atmosphere. Co–Mo–S Type III that is formed by the sulfidation in H_2S/He at 673 K is 1.6–1.8 times as active as Co–Mo–S Type II, which is about twice as active as Co–Mo–S Type I, for the HDS of thiophene. Co–Mo–S Type III is as stable as Co–Mo–S Type I/II during the present mild reaction conditions (Fig. 1). When Co/Mo/Si (H_2S) is used for the HDS of DBT at 1.4 MPa of H_2 pressure, the differences in the activity and TOF between Co–Mo–S Type III and Type II become smaller than those observed for the HDS of thiophene. This may be accounted for by a partial transformation of Co–Mo–S Type III to Co–Mo–S Type II during the reaction at a higher H_2 pressure, suggesting limited stability of Co–Mo–S Type III in practical HDS conditions. It is considered that the degradation of Type III to Type II accompanies the reduction of a S-dimer to a bridging sulfur (Co–S–Co [11,16]).

Before discussing the nature of Co–Mo–S Type III, it is noted that the intrinsic activity of Co–Mo–S is determined mainly by the interaction of MoS_2 particles with the support surface [11], the location of Co–Mo–S, and the local structure of Co–Mo–S. It is conceived that these three determining factors are strongly controlled by the sulfidation atmosphere and reaction conditions. In the present study, we discuss the change in the intrinsic activity of Co–Mo–S with the sulfidation atmosphere in terms of these three points.

Table 1 shows that Co/Mo/Si(ATM) (H_2S/H_2) exhibits a TOF characteristic of Co–Mo–S Type II because of complete sulfidation of ATM to MoS_2 in H_2S/H_2 at 673 K, in contrast to Co/Mo/Si (H_2S/H_2) which needs a sulfidation temperature of >873 K to form Co–Mo–S Type II, as revealed previously [11]. The temperature programed sulfidation profile of MoO_3/SiO_2 in H_2S/H_2 has shown that the sulfidation of Mo oxides proceeds through O–S exchange to form $MoO_{3-x}S_y$ (<450 K), followed by H_2-reduction to $MoS_{2-x}O_y$ at 480 K and subsequent sulfidation to MoS_2 (>500 K) [11,40,41]. Crystalline MoO_3 present in MoO_3/SiO_2 is in part sulfided via MoO_2 because of diffusion limitations. It has been shown that MoS_2–O–SiO_2 and/or MoS_2–O–MoO_2 interactions are completely eliminated at >873 K to form Co–Mo–S Type II. On the other hand, it is considered that such detrimental interactions are minimized by using ATM as a precursor and thus Co–Mo–S Type II is formed in H_2S/H_2 even at 673 K. Accordingly, it is rational to assume complete sulfidation of Mo to MoS_2 in Mo/Si(ATM) in H_2S/H_2 at 673 K. In agreement with the assumption, the TEM image of Mo/Si(ATM) (H_2S/H_2) presented in Fig. 2B shows no nanosized particles, which are ascribed to Mo (oxy)sulfides [42,43].

The TEM image of Mo/Si (H_2S) presented in Fig. 2A shows the absence of nanosized Mo (oxy)sulfide particles that have been observed for Mo/Si (H_2S/H_2) [11]. Besides, the Co K-edge XANES spectra (Fig. 3A) for Co/Mo/Si once presulfided in H_2S/He show a distinct shoulder peak at 7720 eV characteristic of Co–Mo–S Type III and Type II. Furthermore, it is evident from Table 1 that the TOF of Co/Mo/Si (H_2S) is the same as that of Co/Mo/Si(ATM) (H_2S) within the accuracy. All these findings indicate that the sulfidation of Mo oxides supported on SiO_2 is completed in H_2S/He at as low as 673 K and thereby strong interactions such as MoS_2-O-support and/or MoS_2-O-MoO_2 are absent, since it is considered that the sulfidation of MoO_3 to MoS_2 proceeds through the formation of a MoS_3 intermediate and its subsequent decomposition to MoS_2 in H_2S/He without possible formation of MoO_2, which is estimated to be the origin of MoS_2-O-MoO_2 detrimental interactions. Similarly, it is very likely that the sulfidation of Mo oxides is completed when Mo/Si is once sulfided in a stream of H_2S/He at 673 K for >1.5 h. In the case of Co/Mo/Al (H_2S), however, the TOF is still lower than that of the Type II catalysts, suggesting incomplete sulfidation of Mo oxides even in H_2S/He due to strong Mo–O–Al linkages [4,5,44]. It is concluded that both Co–Mo–S Type III and Co–Mo–S Type II are formed only when Mo precursors are completely sulfided to MoS_2 particles without any strong interactions with the support.

Nevertheless, Type III is a type of Co–Mo–S formed only at strongly sulfiding conditions (H_2S/He in the present study), whereas Type II is the one produced at usual sulfidation (H_2S/H_2 here) or reaction conditions. It should be noted again that "Co–Mo–S Type II" is defined in the present study and tacitly in most of the studies [4,5] as Co–Mo–S formed *at usual H_2S/H_2 conditions* and without any strong interactions with the support.

4.3. Local structure and intrinsic activity of Co–Mo–S

Table 4 shows that the structural parameters of Co–Mo–S on Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$) are very similar to those for Co/Mo/Si (H_2S). Furthermore, the parameters for Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$) are almost identical with those reported previously [11] for Co/Mo/Si (H_2S/H_2) sulfided at 873 K. These findings clearly demonstrate that the local structure of Co–Mo–S is determined by or, possibly, equilibrated with the second sulfidation atmosphere, so long as there are no strong interactions between MoS_2 particles and the support or MoO_2. On the other hand, the local structure of Co–Mo–S, in particular, the CN of Co–S for Co/Mo/Al (H_2S) is considerably smaller than that of the SiO_2-supported counterparts. In addition, the CN of Co–S for Co/Mo/Si (H_2S/H_2) was 4.5 [11] and slightly smaller than that for Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$) or Co/Mo/Si(ATM) ($H_2S/H_2$). It is concluded that the MoS_2-support (or MoO_2) interactions strongly modify the edge structure and thereby the intrinsic activity of Co–Mo–S, possibly, due to increased metal-sulfur bond energies [45]. Our previous magnetic study on Co–Mo–S [11] has shown that the local structure and intrinsic activity of Co–Mo–S are affected by such strong interactions through the electronic modifications of MoS_2 particles and that the difference between Co–Mo–S Type I and Co–Mo–S Type II is caused by the MoS_2-support interactions.

In our previous study [11], we have pointed out that the Co–S–Co angle is slightly increased by the transformation of Co–Mo–S Type I to Co–Mo–S Type II. We estimated the Co–S–Co angle from the structural parameters given in Table 4 to be 91.5 ± 0.1° for Co–Mo–S Type III, which is identical with the angle 91.4 ± 0.1° for Type II and is larger than the angle 90.3° for Type I.

As presented in Table 1 and illustrated in Fig. 7, the TOF values of Co/Mo/Si (H_2S) and Co/Mo/Si(ATM) (H_2S) are significantly different from that of Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$), despite of their very similar local structures of Co–Mo–S. Co/Mo/Si(ATM) (H_2S/H_2) and Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$) provide another such pair. With all these catalysts, the effect of support can be neglected due to the complete sulfidation of Mo as discussed above. In order to solve these discrepancies, we propose in the present study that the intrinsic activity of Co–Mo–S strongly depends on which edge of MoS_2 particles it is located, that is, the intrinsic activities of Co–Mo–S on the Mo-edge and S-edge are significantly different for HDS. As discussed in Section 4.1., we propose that Co–Mo–S is fully situated on only one of the edges of MoS_2 particles for Co/Mo/Si which has been sulfided in H_2S/He before the Co addition. On the other hand, Co–Mo–S is fully formed on both edges of MoS_2 particles and, accordingly, the TOF is averaged over the TOF values of Co–Mo–S on Mo-edge and S-edge for Co/Mo/Si which has been sulfided in H_2S/H_2 before the exposure to $Co(CO)_3NO$ vapor. The findings in Table 1 that Co/Mo/Si (H_2S) and Co/Mo/Si(ATM) (H_2S) show significantly higher TOF than Co/Mo/Si (H_2S/H_2) sulfided at 873 K or Co/Mo/Si(ATM) (H_2S/H_2) (Type II catalysts) prompt us to propose that Co–Mo–S situated on one of the edges of MoS_2 particles, possibly on the Mo-edge, exhibits a remarkably higher intrinsic activity for the HDS of thiophene and DBT than does Co–Mo–S on the other edge, possibly the S-edge. Such an active Co–Mo–S structure is denoted simply as "active Co–Mo–S" hereafter. With Co/Mo/Si sulfided first in H_2S/H_2, the TOF given in Table 1 is an average TOF over "active" and "less active" Co–Mo–S structures. When we assume, for simplicity, that the morphology of MoS_2 particles is not significantly varied in the H_2S/H_2 and H_2S/He atmospheres (the fraction of the Mo-edge for "active Co–Mo–S"; 65%) and that "less active Co–Mo–S" shows no activity, we can estimate the TOF on "active Co–Mo–S" by simply dividing the observed TOF by 0.65 for the Co/Mo catalysts presulfided in H_2S/H_2 before the addition of Co. The first assumption may be verified by the DFT calculations by Schweiger et al. [36] for MoS_2 particles, predicting 70% Mo-edge at typical sulfidation and reaction conditions vs. 90% at strongly sulfiding conditions. The fraction of the Mo-edge, 65%, in the present study is compatible with these DFT predictions. The TOF on "active Co–Mo–S" thus estimated is summarized in Table 5 together with the CN of Co–S bonds. Fig. 9 shows a correlation between the TOF on "active Co–Mo–S" and "the average CN of Co–S bonds" over "active" and "less active" Co–Mo–S for all the Co/Mo/Si and Co/Mo/Al catalysts examined in the present and previous [11] studies. A considerably improved correlation is obtained in Fig. 9, which includes Co–Mo–S Type I, Type II, and Type III catalysts, compared with a rather scattered one shown in Fig. 7. The satisfactory correlation in Fig. 9 may substantiate our propositions: one of the edges of MoS_2 particles is selectively decorated by Co–Mo–S in the Co/Mo catalysts presulfided in H_2S/He before the admission of Co and only the Co–Mo–S structure located on this edge of MoS_2 particles is catalytically active for HDS, while the Co–Mo–S structure on the other edge is much less active. As discussed in Section 4.1., it is suggested that "active Co–Mo–S" is presumably situated on the Mo-edge rather than on the S-edge. Very recently, Gandubert et al. [27] suggested that Co–Mo-mixed sites on the Mo-edge are active for the hydrogenation of toluene, while the S-edge fully promoted by Co is much less active. The present and their results suggest that the catalytic properties of Co–Mo–S on the Mo-edge and S-edge are considerably different.

In order to examine the nature of "less active Co–Mo–S", we carefully analyzed the XANES spectra presented in Fig. 3. It is well established that separate Co sulfide clusters show much lower activity for HDS than does Co–Mo–S [4,5,46]. Accordingly, it is considered that Co sulfide clusters might be the strongest candidate as "less active Co–Mo–S". Hence, we tried to examine whether the XANES spectrum for Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$), which is proposed to contain 35% of Co as "less active Co–Mo–S" and 65% as "active Co–Mo–S", can be simulated using the XANES spectrum for Co/Mo/Si (H_2S) shown in Fig. 3, which has exclusively "active

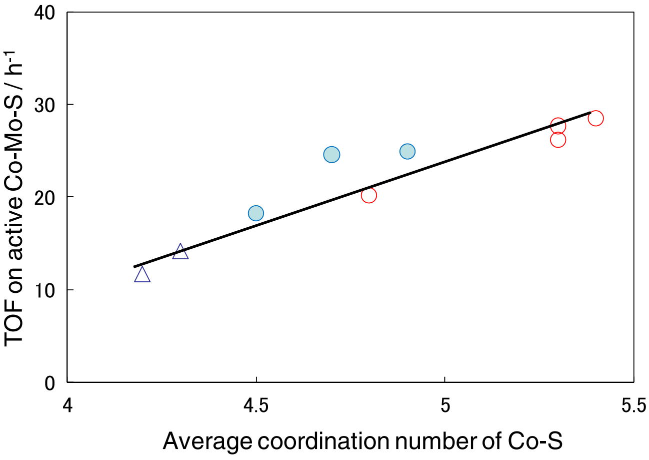

Fig. 9. Correlation between the TOF on "active Co–Mo–S" for the HDS of thiophene and the average coordination number of Co–S bonds over "active" and "less active" Co–Mo–S. Closed circles, Co/Mo/Si (H_2S/H_2) (673 K and 873 K) and Co/Mo/Si(ATM) (H_2S/H_2); triangles, Co/Mo/Al (H_2S/H_2) and (H_2S); and open circles, Co/Mo/Si (H_2S), Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$), Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$), and Co/Mo/Si(ATM) ($H_2S$). Refer to Table 5 for the CN of Co–S and the TOF on "active Co–Mo–S".

Co–Mo–S", and the spectrum for Co/Al (H_2S/H_2) prepared by the CVD [11,46], which has only highly dispersed Co sulfide clusters. We synthesized a XANES spectrum by adding 65% of the spectral intensity for Co/Mo/Si (H_2S) and 35% of that for Co/Al (H_2S/H_2). The convoluted spectrum is compared in Fig. 10 with that for Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$). The difference spectrum is also shown in the inset for clarity. The simulated spectrum is slightly but distinctly different from the XANES spectrum for Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$), showing that "less active Co–Mo–S" is not ascribed to Co sulfide clusters, but to Co–Mo–S. The analysis of the difference spectrum between Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$) and Co/Mo/Si ($H_2S$) in the inset of Fig. 10 suggested that the proportion of Co sulfide clusters in the former catalyst is, if any, much less than 10% of the total amount of Co atoms incorporated by the CVD. Besides, a similar simulation of the XANES spectrum for Co/Mo/Si ($H_2S \rightarrow H_2S/H_2$) using the spectra for Co/Mo/Si (H_2S) and Co/Al (H_2S/H_2) clearly indicated that "active Co–Mo–S" once formed in H_2S/He is not degraded to Co sulfide clusters during the successive sulfidation in H_2S/H_2 at 673 K. With the Al_2O_3-supported catalysts, it was difficult from a similar XANES analysis to estimate the possible fraction of Co sulfide clusters because of broadened nature of the XANES spectra. However, it cannot be ruled out that a small fraction of Co sulfide clusters is present on Co/Mo/Al and thus somewhat reduces the TOF of Co/Mo/Al.

We analyzed EXAFS Fourier transforms assuming a single Co–S peak and hence the CN of Co–S is modified by the presence of the five-six Co–S bonds with close distances for Co–Mo–S on the Mo-edge and S-edge (Fig. 8). Hence, the absolute CN of Co–S of "active Co–Mo–S" may be subject to small changes (±0.5 from the error bar estimation). In addition, the local structures of Co–Mo–S of "active" and "less active" Co–Mo–S cannot be discriminated in the present EXAFS analysis ("average CN of Co–S" in Fig. 9). However, the relative CN obtained in the same series of the EXAFS analysis is fairly reliable and consistent with the pre-edge intensity of XANES (Fig. 3B). As a consequence, we believe that the correlation in Fig. 9 shows a distinct structure–reactivity relationship with the Co–Mo–S structure for HDS.

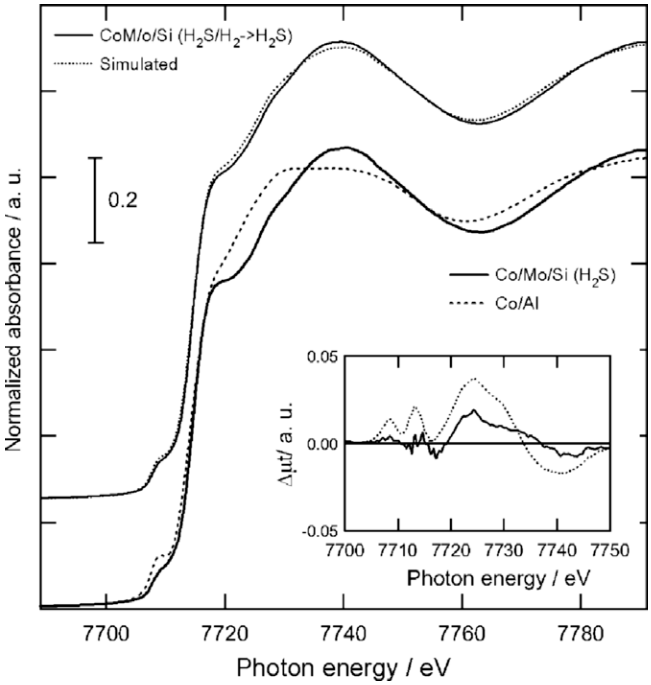

Fig. 10. A comparison of the Co K-edge XANES spectrum (solid line) for Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$) with a spectrum (dotted line) simulated using the XANES spectra for Co/Al (H_2S/H_2) (35%) and Co/Mo/Si (H_2S) (65%). The latter two spectra are shown for clarity. The inset shows the difference XANES spectra between Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$) and simulated one (dotted line) and between Co/Mo/Si ($H_2S/H_2 \rightarrow H_2S$) and Co/Mo/Si ($H_2S$) (solid line).

In our previous study [11] on the effect of the sulfidation temperature on the intrinsic activity of the Co/Mo catalysts sulfided in a conventional H_2S/H_2 stream, we have proposed that the local structures of Co–Mo–S Type I and Co–Mo–S Type II are essentially identical and that the higher intrinsic activity of Co–Mo–S Type II is ascribed to the absence of the interactions between MoS_2 particles and the support (or MoO_2) and thereby to the change in the electronic state of dinuclear Co sulfide clusters on the edge of MoS_2 particles. The electronic modifications of Co–Mo–S by the support have been substantiated by the magnetic property of Co. The effect of the support has been discussed in the same framework [11]. It is considered that the increase of the CN of Co–S by the shift from Co–Mo–S Type I to Co–Mo–S Type II (Figs. 7 and 9) reflects the change of the adsorptive properties of Co–Mo–S toward sulfur to form S-dimers bonded to Co–Mo–S, the change which is induced by the electronic modifications of Co due to the interactions with the support. As discussed above, both Co–Mo–S Type III and Co–Mo–S Type II have no strong interactions with the support. However, the number of S-dimers on the Type II catalysts (Co/Mo/Si (H_2S/H_2) sulfided at 873 K and Co/Mo/Si(ATM) (H_2S/H_2)) is considerably limited because of the thermodynamic equilibration with the gas phase (10% H_2S/H_2 at 873 K and 673 K, respectively), while much more abundant S-dimers are thermodynamically allowed to form on Co–Mo–S Type III. In other words, the concept of "Co–Mo–S Type II", which has been tacitly defined as Co–Mo–S formed *at usual H_2S/H_2 conditions* and without any strong interactions with the support, can be extended to include "Co–Mo–S Type III" formed abundantly *at strongly sulfiding conditions*. It is concluded in the present study that highly active Co–Mo–S Type III is characterized by a dinuclear Co sulfide cluster [11,16] with a S-dimer between two Co atoms and situated on the Mo-edge of MoS_2 particles, as illustrated in Fig. 8. Recently, Krebs et al. [26] suggested a Co–S–S–Co dinuclear structure for 100% promoted Co–Mo–S on the Mo-edge with a 50% coverage of S at a high P_{H_2S}/P_{H_2}.

The formation of the Co–(S_2)–Co structure illustrated in Fig. 8 is thermodynamically favored only under the strongly sulfiding atmosphere (high chemical potential of sulfur). According to DFT calculations [20,36,39], the sulfur atoms are stabilized as dimers on the fully sulfided edge of MoS_2 (100% S coverage). Besides, it is proposed by use of DFT that H_2 molecules are easily activated on S-dimer species [38,39]. It is concluded that the significantly high intrinsic activity of Co–Mo–S Type III is correlated to the absence of interactions between MoS_2 particles and the support and to the presence of S-dimers with a high probability in the Co–Mo–S structure for hydrogen activation. The structure–reactivity relationship presented in Fig. 9 verifies the second conclusion.

5. Conclusions

In the present study, we investigated the effect of the sulfidation atmosphere on the local structure and intrinsic HDS activity of Co–Mo–S supported on SiO_2. We employed the sulfidation procedures of the Co–Mo catalysts at 673 K in 10% H_2S/H_2, 10% H_2S/He, and their combinations to vary the sulfidation atmosphere. We characterized the sulfide catalysts by TEM and XAFS. The salient findings in the present study are as follows:

- The intrinsic activity of Co–Mo–S is strongly affected by the sulfidation atmosphere. The presulfidation of Co–Mo–S in a strongly sulfiding atmosphere (H_2S/He) forms the Co–Mo–S structure with a high intrinsic activity for the HDS of thiophene and DBT.

- It is proposed that Co–Mo–S on one of the edges of MoS_2 particles, possibly on the Mo-edge, is highly active for the HDS, while Co–Mo–S on the other edge, possibly on the S-edge, is less active.
- The local structure of the highly active Co–Mo–S formed in H_2S/He is described as a dinuclear Co sulfide cluster with a sulfur-dimer between the two Co atoms.
- The intrinsic activity of the "active Co–Mo–S" increases as the coordination number of Co–S bond increases. A structure–reactivity relationship is proposed with the Co–Mo–S structure for HDS, accounting for the effects of the sulfidation temperature and atmosphere as well as the effect of the support on Co–Mo sulfide catalysts.
- We demonstrate in the present study that the intrinsic HDS activity of Co–Mo–S is strongly affected by the location and the local structure, which is equilibrated with the sulfidation atmosphere or reaction conditions, as well as by the MoS_2-support interactions.

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