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# Simultaneous promotion of hydrogenation and direct desulfurization routes in hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiW catalyst by use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support in combination with *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid

### Naoto Koizumi<sup>a,\*</sup>, Yusuke Hamabe<sup>a</sup>, Shohei Yoshida<sup>a</sup>, Muneyoshi Yamada<sup>b</sup>

<sup>a</sup> Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai 980-8579, Japan <sup>b</sup> Akita National College of Technology, 1-1, Iijima-Bunkyo-cho, Akita 011-8511, Japan

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#### ABSTRACT

Effect of novel SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on surface structure and hydrodesulfurization (HDS) activity of the NiW catalyst prepared using trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CyDTA) was investigated by combination of quasi in situ TEM, in situ diffuse reflectance FTIR spectroscopy (DRIFTS) coupled with NO adsorption, and 4,6-dimethyldibenzothiophene (4,6-DMDBT) HDS activity measurement. When the catalysts were prepared without using CyDTA, quasi in situ TEM observation showed that WS<sub>2</sub>-like slabs in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported W and NiW catalysts had higher stacking degree, but smaller basal plane sizes compared with the Al<sub>2</sub>O<sub>3</sub> supported counterparts. In situ DRIFTS coupled with NO adsorption further revealed that the formation of the Ni–W–S phase was suppressed by use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support. The SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst showed higher activity for hydrogenation (HYD) of 4,6-DMDBT into tetrahydro-DMDBT (THDMDBT) than the Al<sub>2</sub>O<sub>3</sub> supported counterpart. However, this catalyst failed to promote the HYD route because of lower activity for C-S bond cleavage of THDMDBT, and showed lower HDS activity than the Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst. On the other hand, the formation of the Ni-W-S phase was promoted when the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst was prepared using CyDTA, which was accompanied with further increase of stacking degree and decrease of the basal plane size of the WS<sub>2</sub>-like slabs. Double-layered slabs were predominant in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst prepared with using CyDTA. This catalyst showed higher activity for both HYD of 4.6-DMDBT, and C-S bond cleavage of 4,6-DMDBT and THDMDBT. The HYD route and direct desulfurization (DDS) route were promoted simultaneously over this catalyst, leading to three times higher HDS activity than the Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst. These results suggest that the formation of the multi-layered Ni-W-S phase with the smaller basal plane size is crucial for promoting the HYD route in HDS of 4,6-DMDBT.

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#### 1. Introduction

Because of severe regulations for reducing emission from diesel vehicles, the production of ultra low sulfur diesel (ULSD) fuel has become one of most important issues at refineries. Further reducing sulfur content of ULSD fuel would be indispensable in near future to achieve near-zero emission of diesel vehicle [1]. Therefore, fundamental studies on effective hydrodesulfurization (HDS) of refractory sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) are still important.

So far, extensive efforts have been made to improve understanding of fundamental aspects of HDS of 4,6-DMDBT. Based on these studies, it has been suggested that HDS of 4,6-DMDBT proceeds in two parallel reaction routes, i.e. the direct desulfurization (DDS) and hydrogenation (HYD) routes [2–9]. Because the HYD route is much faster than the DDS route [6], promotion of the HYD route is a good strategy for effective HDS of 4,6-DMDBT [10].

NiW-based catalysts are well known to show higher activity for HYD of aromatic hydrocarbon than CoMo and NiMo-based catalysts [11]. Improvement in aromatic HYD activity of the NiW catalyst thus may be one of promising ways to achieve effective HDS of 4,6-DMDBT. However, much less attention has been paid to this catalyst compared with the CoMo and NiMo-based catalysts. In our previous studies, it was found that use of *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*',*N*'-tetraacetic acid (CyDTA) for preparation of the Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst improved activity for C–S bond cleavage of 4,6-DMDBT and tetrahydro-DMDBT (THDMDBT), leading to improvement in total HDS activity by a factor of 1.6 [12,13].

<sup>\*</sup> Corresponding author. Tel.: +81 022 795 7215; fax: +81 022 795 7215. *E-mail address:* koizumi@erec.che.tohoku.ac.jp (N. Koizumi).

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Chemical composition	of the catalysts prepared	in the present study.

Catalyst	Composition					
	WO <sub>3</sub> (mass%)	NiO (mass%)	Ni/W (mol mol <sup>-1</sup> )	CyDTA/W ( $mol mol^{-1}$ )	CyDTA/Ni (mol mol <sup>-1</sup> )	
W/Al <sub>2</sub> O <sub>3</sub>	15.0	0.0	0.0	0.0	-	
Ni/W/Al <sub>2</sub> O <sub>3</sub>	15.0	1.6	0.32	0.0	0.00	
CyDTA-Ni/W/Al <sub>2</sub> O <sub>3</sub>	15.0	1.6	0.32	0.6	1.88	
W/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	15.0	0.0	0.0	0.0	-	
Ni/W/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	15.0	1.6	0.32	0.0	0.00	
CyDTA-Ni/W/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	15.0	1.6	0.32	0.6	1.88	

In other words, preparation with using CyDTA promoted the DDS route. Quasi in situ XPS and in situ W L<sub>III</sub>-edge EXAFS measurement suggested that use of CyDTA retarded the sulfidation of Ni species through the formation of a stable complex with Ni<sup>2+</sup>, which facilitated coordination of Ni atoms on edge sites of WS<sub>2</sub>-like slabs, i.e. the formation of the Ni–W–S phase [14,15].

On the other hand, use of Al<sub>2</sub>O<sub>3</sub> support modified with boric acid (B-Al<sub>2</sub>O<sub>3</sub>) for the W and NiW catalysts improved activity for HYD of 4,6-DMDBT [12,13] into THDMDBT. Although this catalyst failed to promote the HYD route because of lower activity for C-S bond cleavage of THDMDBT, it was then found that use of B-Al<sub>2</sub>O<sub>3</sub> support in combination with CyDTA improved activity of the NiW catalyst not only for HYD of 4,6-DMDBT, but also for C-S bond cleavage of 4,6-DMDBT and THDMDBT. As a result, the HYD and DDS routes were promoted simultaneously. This catalyst showed 2.4 times higher activity for HDS of 4,6-DMDBT than the conventional Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst. Diffuse reflectance FTIR spectroscopy (DRIFTS) showed that strong basic Al-OH species on Al<sub>2</sub>O<sub>3</sub> surface was depleted by modification with boric acid, suggesting that use of B-Al<sub>2</sub>O<sub>3</sub> support for the NiW catalyst in combination with CyDTA affected morphology of the Ni-W-S phase that was effectively formed by the complex formation between Ni<sup>2+</sup> and CyDTA. In previous studies, several authors suggested importance of morphology of MoS<sub>2</sub> [16-20] and/or WS<sub>2</sub> [21]like slabs for promotion of the HYD route. However, these still exists apparent discrepancy among these studies. Furthermore, little information was obtained about structure of the promoter atoms, such as the formation of the coordinatively unsaturated sites (CUS) of the Co(Ni)-Mo-S and Ni-W-S phases in these previous studies.

Based on these studies, effect of novel SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on surface structure and HDS activity of the NiW catalyst prepared using CyDTA was investigated in this work by combination of quasi in situ TEM, DRIFTS coupled with NO adsorption and 4,6-DMDBT HDS activity measurements. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support used in the present study had unique surface acidic property, on which Al<sub>2</sub>O<sub>3</sub> surface was covered with small SiO<sub>2</sub> particles. Our attentions were paid to clarify surface structure of the catalyst that effectively promotes the HYD route in HDS of 4,6-DMDBT.

#### 2. Experimental

#### 2.1. Catalyst preparation

Preparation of the catalysts was carried out in accordance with the preparation method for the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts reported previously [15,22–24]. Briefly, aqueous solution containing (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·H<sub>2</sub>O (Aldrich, >99.99%) was firstly impregnated onto sieved SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (NK-31378, specific surface area = 320 m<sup>2</sup> g<sup>-1</sup>) powder followed by drying (383 K, 16 h) and calcination (673 K, 12 h). Aqueous solution containing Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Wako Pure Chemicals, purity > 99.9%) was then impregnated onto the thus prepared W catalysts followed by drying (383 K, 16 h) to

obtain the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiW catalysts. For preparation of the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst using CyDTA, aqueous solution containing both Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and CyDTA (Dojindo Chemicals, >99%) was used instead of aqueous Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution. Hereafter, the catalyst was denoted by, for example, CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, which means that the NiW catalyst was prepared by use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support in combination with CyDTA. The Al<sub>2</sub>O<sub>3</sub> supported catalysts were also prepared using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (NK-30129, specific surface area = 314 m<sup>2</sup> g<sup>-1</sup>) powder as references. Chemical compositions of the prepared catalysts are summarized in Table 1.

#### 2.2. Activity test

HDS of 4,6-DMDBT was carried out using a conventional highpressure flow reactor [25–27]. The reactor consisted of a stainless steel tube with internal diameter (Ø) of 8 mm in a four-zone electronic furnace. Four sets of temperature controllers and thermocouples regulated temperature in the catalyst bed within  $\pm 1$  K. The prepared catalyst was charged in the stainless steel reactor and then sulfided in a stream of 5% H<sub>2</sub>S/H<sub>2</sub> (>99.99995%) at 673 K and 1.1 MPa. After sulfiding pretreatment, temperature was cooled down to 573 K. A feed consisted of 0.3 mass% 4,6-DMDBT (Aldrich, 97%) diluted with decalin (Wako Pure Chemical Industry Ltd., 99%) was introduced into the reactor with high-pressure hydrogen flow. HDS of 4,6-DMDBT was performed at 573 K and 5.1 MPa (H<sub>2</sub> partial pressure). H<sub>2</sub> flow rate and H<sub>2</sub> to feed ratio were 300 mL (STP) min<sup>-1</sup> and 1000 mL mL<sup>-1</sup>, respectively. The time factor (*W*/*F*) was varied by changing catalyst weight charged.

Liquid products were collected from a product stream every 1 h, and analyzed with gas chromatographs (GC) equipped with flame ionization detector (Shimadzu, GC-17A), mass spectrometer (Shimadzu, QP5000) and/or an atomic emission detector (Agilent Technology, G2350A). Temperature-programmed GC analysis with a high-resolution capillary column (Supelco, Petrocol DH, length: 100 m, internal diameter: 0.25 mm) was used for separation of the product mixture.

#### 2.3. XRD measurement

XRD pattern of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support used for catalyst preparation was measured on a RINT diffractometer (Rigaku). Cu K<sub>\alpha</sub> radiation ( $\lambda$  = 1.54056 Å) was used as an X-ray source with an X-ray tube operating at 40 kV and 200 mA. Diffraction intensities were recorded at 0.02° s<sup>-1</sup> scan speed. Observed diffraction peaks were assigned by referring to JCPDS data.

#### 2.4. XPS measurement

XP spectra of support materials were measured with ESCA200 spectrometer (SIENTA). Monochromatized Mg  $K_{\alpha}$  line was used as an excited source. Charge shift was corrected using BN powder as an internal standard.

#### 2.5. Quasi in situ TEM measurement

Effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on morphology of WS<sub>2</sub>-like slabs (or the Ni-W-S phase) was investigated by quasi in situ TEM measurement. Before measurement, the catalyst was sulfided in a stream of 5% H<sub>2</sub>S/H<sub>2</sub> (>99.99995%) at 673 K and 1.1 MPa using a stainless steel reactor (Ø 4 mm). After sulfiding pretreatment, the catalyst was cooled down to room temperature in the 5% H<sub>2</sub>S/H<sub>2</sub> stream. The reactor was then flushed with a  $H_2$  (>99.999%) stream to remove residual H<sub>2</sub>S/H<sub>2</sub>, and transferred to a grove box filled with N<sub>2</sub> (O<sub>2</sub> content  $\leq$ 50 ppm) without contacting with the air in the grove box. The catalyst was taken from the reactor, crashed into fine powder using a motor and pestle, and then suspended into ethanol solution (> 99.5%) in the grove box. A few droplets of this suspension were dropped onto carbon-coated Cu grid followed by drying at ambient temperature. The sample was transferred into a vacuum chamber, and subjected to TEM measurment using an HF-2000 (Hitachi, Ltd.) with 200 kV accelerate voltage. 40-50 micrographs were taken for each sample. 730-830 WS<sub>2</sub>-like slabs (400–460 WS<sub>2</sub>-like clusters) were analyzed for each sample to calculate distribution of slab length and stacking number. Average slab length  $(\tilde{L})$  and stacking number  $(\tilde{N})$  were calculated using following equations.

$$\log \bar{L} = \frac{\sum n_i \log L_i}{\sum n_i} \tag{1}$$

$$\bar{N} = \frac{\sum n_i N_i}{\sum n_i} \tag{2}$$

#### 2.6. NH<sub>3</sub>-TPD measurement

Acidity of support was determined by temperatureprogrammed desorption of preadsorbed NH<sub>3</sub> (NH<sub>3</sub>-TPD). NH<sub>3</sub>-TPD profile of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder was compared with those of reference  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, conventional (amorphous) SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Fuji Silysia, Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> = 8.3/91.7 mass mass<sup>-1</sup>, surface area = 401 m<sup>2</sup> g<sup>-1</sup>) and SiO<sub>2</sub> (Fuji Silysia, surface area = 230 m<sup>2</sup> g<sup>-1</sup>) powder. The sample was pretreated at 773 K for 1 h in 60 mL min<sup>-1</sup> Ar flow, and then NH<sub>3</sub> was adsorbed at ambient temperature for 30 min in 60 mL min<sup>-1</sup> 10%NH<sub>3</sub>/90%He. After saturation of NH<sub>3</sub> adsorption, the sample was purged in 60 mL min<sup>-1</sup> Ar flow. NH<sub>3</sub>-TPD profiles were obtained by analyzing the desorbed species using quadrupole mass spectrometer (Q-MS) with heating from 373 K (or room temperature) to 973 K at a rate of 10 K min<sup>-1</sup>. The obtained profile was fitted with Gauss-Lorentz functions (Wave Metrics, Igor).

#### 2.7. DRIFTS coupled with NO adsorption

DRIFTS coupled with NO adsorption was used to investigate effect of support on distribution of the CUS on W and Ni promoter. Apparatus used for measurement was reported previously [28–30]. Before NO adsorption, the catalyst was sulfided in following manners. The sample holder was filled with a finely powdered catalyst, and put in a high-pressure DRIFT chamber. The chamber was then connected with a high-pressure flow apparatus equipped with flow controllers and pressure regulators. 5% H<sub>2</sub>S/H<sub>2</sub> (>99.99995%) stream was fed into the chamber (30 mL min<sup>-1</sup>) at the pressure of 1.1 MPa, followed by heating the sample up to 673 K at a rate of 10 K min<sup>-1</sup>. After reaching 673 K, temperature was kept constant for 2 h. The catalyst was cooled down to room temperature followed by purging residual H<sub>2</sub>S/H<sub>2</sub> in the cell with He flow (>99.9995%).

After sulfidation pretreatment, NO adsorption was carried out by the pulse method. DRIFT spectrum of adsorbed NO was recorded on an FTS 575C FTIR spectrometer (Varian, Inc.) equipped with



Fig. 1. XRD pattern of Al<sub>2</sub>O<sub>3</sub> (a) SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (b) powder used for catalyst preparation.

Selector diffuse reflectance attachment (Specac) with 4 cm<sup>-1</sup> spectral resolution. The obtained spectrum was converted into a Kubelka–Munk function with a KBr spectrum recorded at room temperature followed by normalization to the spectrum of the catalyst before NO adsorption (also recorded at room temperature).

#### 3. Results

#### 3.1. Bulk and surface properties of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support

Specific surface area and pore volume of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder used in this work were almost the same as those of reference  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder. However, other physical and chemical properties of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder were not published by the manufacturer. Bulk and surface properties of this support material were thus investigated for better understanding of its support effect.

Fig. 1 depicts XRD patterns of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and reference  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder. Broad peaks of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase were observed at  $2\theta$  = 37.7°, 46.2° and 67.1° in the diffraction pattern of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder. These diffraction peaks were observed in the pattern of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder as well, whereas they were evidently weaker and broader. Furthermore, a much weaker and broader peak was observed in the diffraction pattern of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder in a range of 25–30°. This broader peak was related to the SiO<sub>2</sub> phase, suggesting that the SiO<sub>2</sub> phase was in a form of small particles or had amorphous nature. XPS measurement was also performed to calculate Si:Al atomic ratio of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder in sub-surface region. The thus calculated Si:Al atomic ratio was 20:80.

#### 3.2. Acidity of support

NH<sub>3</sub>-TPD and in situ DRIFT measurements were then performed to characterize acidity of these support materials. Fig. 2 summarizes NH<sub>3</sub>-TPD profile of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (a), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (b), conventional SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (c) and SiO<sub>2</sub> (d) powder. Five desorption peaks were observed in NH<sub>3</sub>-TPD profile of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder. According to the previous study [31], NH<sub>3</sub>-TPD profiles were arbitrarily divided into three regions (100–200, 200–350, 350–700 °C) to provide a measure of weak, medium and strong acid sites, respectively. In NH<sub>3</sub>-TPD profile of SiO<sub>2</sub> powder, a peak was observed only below 100 °C, indicating the formation of physisorbed NH<sub>3</sub>. On the other hand, four desorption peaks were observed at 161, 213, 292 and 681 °C in NH<sub>3</sub>-TPD profile of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder, showing the presence of weak, medium and strong acid sites in this support material. Comparison of NH<sub>3</sub>-TPD profile of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder with profile of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder indicated that the medium acid site increased at



Fig. 2. NH<sub>3</sub>-TPD profiles of Al<sub>2</sub>O<sub>3</sub> (a), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (b), amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (c), and SiO<sub>2</sub> (d) powder. Heating rate: 10 K min<sup>-1</sup>.

the expense of the weak acid site in  $SiO_2-Al_2O_3$  powder. The strong acid site was comparable between these materials. On the contrary, only two peaks related to the medium and strong acid sites were observed in profile of conventional  $SiO_2-Al_2O_3$  powder, showing that  $SiO_2-Al_2O_3$  powder has different acidity than conventional (amorphous)  $SiO_2-Al_2O_3$  powder.

Fig. 3 depicts in situ DRIFT spectrum of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder in the OH region in comparison with reference  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, conventional SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> powder. These spectra were recorded



**Fig. 3.** In situ DRIFT spectra of  $Al_2O_3$  (a),  $SiO_2-Al_2O_3$  (b), amorphous  $SiO_2-Al_2O_3$  (c), and  $SiO_2$  (d) powder in their OH region. The spectra were recorded in helium stream at ambient temperature after pretreatment in helium stream at 773 K (1 h).

at ambient temperature after drying pretreatment in a He stream at 773 K and 1 h. In the spectrum of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder, broad IR bands were observed at 3764, 3726, 3675 and  $3578 \text{ cm}^{-1}$ . All these bands were related to O-H stretching vibration of isolated and associated hydroxyl groups on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface [34]. On the other hand, an IR band was observed at 3743 cm<sup>-1</sup> in the spectrum of SiO<sub>2</sub> powder, showing the presence of the isolated hydroxyl group on the surface. In the spectrum of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder, IR bands were observed at 3738 and 3721 cm<sup>-1</sup>. Comparison with the reference spectra mentioned above indicated that the former band was related to stretching vibration of the isolated Si-OH group, whereas the latter band indicated the presence of some isolated Al–OH group. No IR bands were observed above 3750 cm<sup>-1</sup> in the spectrum of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder. The spectrum of conventional SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder provided the sharp band at 3743 cm<sup>-1</sup> similar to SiO<sub>2</sub> powder. Broad spectral feature was also observed in 3700–3500 cm<sup>-1</sup> region.

Based on these characterization results of the support materials, it was suggested that, on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> surface, small SiO<sub>2</sub> particles blocked up most of isolated and associated Al–OH species on the Al<sub>2</sub>O<sub>3</sub> surface. Especially, strong basic Al–OH species (3764 cm<sup>-1</sup>) [32] was totally absent from the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> surface. This will weaken W-support interaction by preventing the formation of W–O–Al bonds, and affect morphology of sulfide clusters and the formation of the CUS. This point was then investigated by quasi in situ TEM and DRIFTS coupled with NO adsorption.

## 3.3. Morphology of WS<sub>2</sub>-like slabs on the $Al_2O_3$ and $SiO_2-Al_2O_3$ supported catalysts

#### 3.3.1. W catalyst

Quasi in situ TEM measurements were performed after sulfiding pretreatment at 673 K and 1.1 MPa. In these photographs, single-layered, ca. 4 nm-sized WS<sub>2</sub>-like slabs are mainly observed, and distributed homogeneously on both the catalysts. 730-830WS<sub>2</sub> slabs were analyzed for each catalyst to calculate distribution of their slab length (Fig. 4) and stacking number

Table 2	
Average slab length ( $\overline{L}$ ) and stacking number ( $\overline{N}$ ) of WS <sub>2</sub> -like slabs on the Al <sub>2</sub> O <sub>3</sub> and SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> supported catalysts calculated from	Eqs. (1) and (2).

	$W/Al_2O_3$	Ni/W/Al <sub>2</sub> O <sub>3</sub>	CyDTA-Ni/W/Al <sub>2</sub> O <sub>3</sub>	$W/SiO_2$ - $Al_2O_3$	$Ni/W/SiO_2-Al_2O_3$	CyDTA-Ni/W/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
Γ̄(nm)	4.6	3.9	3.7	4.0	3.3	3.3
Ñ	1.4	1.6	1.6	1.5	1.7	1.8



**Fig. 4.** Distribution of the length of WS<sub>2</sub>-like slabs on the  $Al_2O_3$  (a)  $SiO_2-Al_2O_3$  (b) supported catalysts calculated from quasi in situ TEM micrographs shown in Fig. 3 (730–830 WS<sub>2</sub> slabs were analyzed for each catalyst to obtain distribution).

(Fig. 5). Average slab length and stacking degree are tabulated in Table 2.

The length of  $WS_2$ -like slabs on the  $W/Al_2O_3$  catalyst was distributed from 1 to 15 nm with a maximum at around 4 nm. The



**Fig. 5.** Distribution of the stacking number of WS<sub>2</sub>-like slabs on the  $Al_2O_3$  (a)  $SiO_2-Al_2O_3$  (b) supported catalysts calculated from quasi in situ TEM micrographs shown in Fig. 3 (730–830 WS<sub>2</sub> slabs were analyzed for each catalyst to obtain distribution).

average slab length was 4.6 nm as tabulated in Table 2. Furthermore, the major fraction was present as single-layered slab on this catalyst (ca. 60%). The fraction of the slabs decreased exponentially with increasing stacking degree on this catalyst. Compared with the Al<sub>2</sub>O<sub>3</sub> supported catalyst, the fraction of the WS<sub>2</sub>-like slabs with 5-6 nm length was slightly lower on the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. The average slab length of the WS<sub>2</sub>-like slabs on the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was also slightly shorter compared with the Al<sub>2</sub>O<sub>3</sub> supported counterpart (4.0 vs. 4.6 nm, Table 2). More clear difference was observed in distribution of stacking degree of the WS<sub>2</sub>-like slabs between these catalysts (Fig. 5). The fraction of the single-layered slab was above 55% on the Al<sub>2</sub>O<sub>3</sub> supported catalyst. This fraction decreased to 45% on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalyst, whereas the fraction of the double-layered slabs increased to around 40% instead. Thus use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support slightly increased stacking degree of the WS<sub>2</sub>-like slabs.

#### 3.3.2. NiW catalyst

The NiW catalysts prepared with or without using CyDTA were also subjected to quasi in situ TEM measurement. Distribution of the  $WS_2$  slab length and stacking number are shown in Figs. 4 and 5. The average slab length and stacking number are tabulated in Table 2.

Distribution of the slab length (Fig. 4(a)) showed that the fraction of the WS<sub>2</sub>-like slabs with 5–6 nm length was slightly smaller on the Ni/W/Al<sub>2</sub>O<sub>3</sub> and CyDTA-Ni/W/Al<sub>2</sub>O<sub>3</sub> catalysts compared with the W/Al<sub>2</sub>O<sub>3</sub> catalyst. The average length of the WS<sub>2</sub>-like slabs on the former catalysts was also 0.7-0.9 nm shorter than those on the W/Al<sub>2</sub>O<sub>3</sub> catalyst (Table 2). Besides, the maximum shifted toward a shorter length in distribution of the slab length for the CyDTA-Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst compared with the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst, showing that preparation of the NiW/Al<sub>2</sub>O<sub>3</sub> catalyst using CyDTA decreased the length of the WS<sub>2</sub>-like slabs. Distribution of stacking degree of the slabs was slightly different among these catalysts as well (Fig. 5(a)). The addition of Ni to the W/Al<sub>2</sub>O<sub>3</sub> catalyst increased the fraction of the doublelayered slabs at the expense of the single-layered slab. Preparation using CyDTA enhanced this trend. However, the single-layered slabs were still major slabs in the CyDTA-Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst.

The length and stacking degree of the WS<sub>2</sub>-like slabs changed in similar ways on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalysts. The average length of the WS<sub>2</sub>-like slabs was 0.7-0.9 nm shorter on the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts compared with the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. The maximum shifted toward a shorter length in distribution of the slab length for the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst compared with the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. This indicated that preparation of the NiW/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst with using CyDTA decreased the length of the slabs as well, although the average lengths of the slabs on the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were identical. The fraction of the single-layered slabs decreased in following order; W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

Compared with the  $Al_2O_3$  supported catalysts, the length of the slabs was shorter for the  $SiO_2-Al_2O_3$  supported catalysts. Furthermore, the fraction of the single-layered slab was always smaller on the  $SiO_2-Al_2O_3$  supported catalysts. Most important difference was that the double-layered slab was major species in the CyDTA-Ni/W/SiO\_2-Al\_2O\_3 catalyst, whereas the major fraction is present



**Fig. 6.** Effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on distribution of the CUS on the NiW catalyst prepared using CyDTA investigated by in situ DRIFTS coupled with NO adsorption; CyDTA-Ni/W/Al<sub>2</sub>O<sub>3</sub> (a), Ni/W/Al<sub>2</sub>O<sub>3</sub> (b), CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (c), Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (c), Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (d), W/Al<sub>2</sub>O<sub>3</sub> (e), Ni/Al<sub>2</sub>O<sub>3</sub> (f) Sulfiding pretreatment: 5% H<sub>2</sub>S/H<sub>2</sub>, 673 K, 1.1 MPa (2 h) NO pulse adsorption: 10% NO/He, ambient temperature.

as the single-layered slab in the  $Al_2O_3$  supported counterparts (Fig. 5(b)).

## 3.4. Formation of CUS on the $Al_2O_3$ and $SiO_2$ - $Al_2O_3$ supported catalysts

Distribution of the CUS on the Ni and W catalysts was then investigated by DRIFTS coupled with NO adsorption. Fig. 6 shows DRIFT spectra of NO adsorbed on the Ni/W/Al<sub>2</sub>O<sub>3</sub> and CyDTA-Ni/W/Al<sub>2</sub>O<sub>3</sub> catalysts, in comparison with those of NO adsorbed on the W/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. This figure also includes spectra of the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalysts. In the spectrum of NO adsorbed on W/Al<sub>2</sub>O<sub>3</sub> catalyst, doublet bands were observed at 1761 and 1694 cm<sup>-1</sup>. These doublet bands were similar to those reported for Mo/Al<sub>2</sub>O<sub>3</sub> catalysts [33-36], and thus assigned to symmetric and anti-symmetric vibration of dnitrosyl species adsorbed on the CUS of W sulfide species. In contrast, an asymmetric band was observed at 1842 cm<sup>-1</sup> in the spectrum of NO adsorbed on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. This band could be assigned to symmetric vibration of dinitrosyl species adsorbed on the CUS of Ni species, with anti-symmetric vibration of this species overlapped in a lower frequency region [34]. Similar band was observed in the spectrum of NO on the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst, whereas the intensity of this band is much weaker compared with Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Furthermore, a weak shoulder band was observed at around 1760 cm<sup>-1</sup> in this spectrum. By comparison with the spectrum of NO on the W/Al<sub>2</sub>O<sub>3</sub> catalyst, this shoulder band was assigned to symmetric vibration of dinitrosyl species on the CUS of W sulfide species. In our previous paper [37], the DRIFT spectrum of NO adsorbed on physical mixture of the W/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts was reported. Compared with the spectrum of NO on this physical mixture, the relative intensity of the band of symmetric vibration of dinitrosyl species on Ni species was much stronger for the spectrum of NO on the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst. In other words, the CUS was more selectively formed on Ni species on the Ni/W/Al<sub>2</sub>O<sub>3</sub> cat-



**Fig. 7.** Promoting effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on 4,6-DMDBT HDS activity of the NiW catalyst prepared using CyDTA. Sulfiding pretreatment: 5% H<sub>2</sub>S/H<sub>2</sub>, 673 K, 1.1 MPa (2 h) HDS of 4,6-DMDBT: 0.3 mass% 4,6-DMDBT/decalin, 573 K, 5.1 MPa (H<sub>2</sub>),  $W/F = 1.3 g_{cat} h g_{4,6-DMDBT}^{-1}$ .

alyst. This suggests the formation of the Ni–W–S phase in which Ni atoms block up the W atoms at the edge sites of the WS<sub>2</sub>-like slabs. The Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst showed a similar DRIFT spectrum. However, the band at around 1760 cm<sup>-1</sup> was stronger compared with the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst, suggesting that the formation of the Ni–W–S phase was suppressed on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support compared with Al<sub>2</sub>O<sub>3</sub> counterpart.

When the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalysts was prepared using CyDTA, the bands at around 1760 cm<sup>-1</sup> almost disappeared. This suggested that the Ni–W–S phase was effectively formed on this catalyst as suggested by quasi in situ XPS and in situ W L<sub>III</sub>-edge EXAFS measurement on the catalyst sulfided at high-pressure in our previous study [15]. CyDTA has a similar effect on the DRIFT spectra of NO adsorbed on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported counterpart. Therefore, it was suggested that use of CyDTA promoted the formation of the Ni–W–S phase in the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst as well.

#### 3.5. Effect of support on HDS activity and selectivity

#### 3.5.1. 4,6-DMDBT HDS activity

In HDS of 4,6-DMDBT with the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalysts, dimethylbiphenyl (DMBPh), dimethylcyclohexylbenzene (DMCHB), and dimethyl-bicyclohexyl (DMBCH) were obtained as HDS products. HYD products, tetrahydrodimethyldibenzothiophene (THDMDBT) and hexahydrodimethyldibenzo-thiophene (HHDMDBT), were also detected in their products. Fig. 7 compares the yield of these products normalized to total metal (Ni + W) content of the catalysts (W/F = 1.3 g<sub>cat</sub> h g<sub>4,6-DMDBT</sub><sup>-1</sup>). HDS (HYD) activity was defined as the total yield of the HDS (HYD) products normalized to total metal content of the catalysts.

Effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on HDS and HYD activity of the monometal sulfide catalysts were investigated first. In HDS of 4,6-DMDBT with the W/Al<sub>2</sub>O<sub>3</sub> catalyst, THDMDBT and HHDMDBT were main products. Only small amount of DMCHB was obtained with this catalyst, whereas DMBPh was not detected in the product. On the other hand, the DMCHB yield obtained with the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was 10 times greater than that with the Al<sub>2</sub>O<sub>3</sub> supported counterpart. Small amount of DMBPh was also detected in the product obtained with this catalyst. Furthermore, the THDMDBT and HHDMDBT yields were also higher for the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. Therefore, the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst showed higher HDS and HYD activity than the Al<sub>2</sub>O<sub>3</sub> supported counterpart. For the Ni catalyst, higher HDS and HYD activity was obtained with the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalyst as well.

In HDS of 4,6-DMDBT with the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst, the HDS products (DMBPh, DMCHB and DMBCH) were main products. Small



**Fig. 8.** Product selectivity over the Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst as a function of the 4,6-DMDBT conversion; DMBPh ( $\triangle$ ), DMCHB ( $\square$ ), DMBCH ( $\Diamond$ ), THDMDBT ( $\bigcirc$ ), HHDMDBT ( $\times$ ).

amounts of the HYD products (THDMDBT and HHDMDBT) were also detected in the products. The HDS product yield obtained with the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was only 60% of that with the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst. On the other hand, the HYD product yield with the former catalyst was evidently higher compared with the latter. Therefore, the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst showed lower HDS activity, but higher HYD activity than the Al<sub>2</sub>O<sub>3</sub> supported counterpart. As a result, total activity (total product yield normalized to total metal content) was comparable between the Ni/W/Al<sub>2</sub>O<sub>3</sub> and Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts. Fig. 7 also shows that the addition of Ni to the W/Al<sub>2</sub>O<sub>3</sub> catalyst improved HDS activity by a factor of 69. This large activity enhancement is well known as the promoting effect of Ni. However, when Ni was added to the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, HDS activity enhancement was no more than 6. In other words, the promoting effect of Ni was significantly suppressed by use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support. This is consistent with the results from DRIFTS coupled with NO adsorption which showed that the formation of the Ni–W–S phase was suppressed on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support.

#### 3.5.2. Selectivity

Fig. 7 suggested that use of  $SiO_2-Al_2O_3$  support instead of  $Al_2O_3$  support affected HDS and HYD selectivity of the NiW catalyst. To investigate this point in detail, HDS of 4,6-DMDBT was conducted with the Ni/W/Al\_2O\_3 and Ni/W/SiO\_2-Al\_2O\_3 catalysts at various *W/F*. Product selectivity of these catalysts was compared in wide conversion range.

Fig. 8 depicts selectivity for each product obtained with the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst as an example. At the low conversion (10 mol%), THDMDBT was a main product. Small amounts of DMBPh, DMCHB and HHDMDBT were also detected at this conversion. Selectivity for DMBPh, THDMDBT and HHDMDBT decreased with the conversion of 4,6-DMDBT, whereas DMCHB and DMBCH selectivity increased. DMCHB was a main product at a higher conversion range ( $\leq$ 80 mol%). This conversion-selectivity profile was well consistent with previous results which suggested that HDS of 4,6-DMDBT proceeds in two parallel routes, i.e. direct desulfurization (DDS) and HYD routes [38-40]. In addition to these products, small amounts of DMCHB, DMBPh and DMBCH isomers were detected in the products obtained with the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst when the conversion was higher than 40 mol%. Because these isomers were not observed at lower conversions, it is reasonable to assume that they are formed from DMCHB, DMBPh and/or DMBCH, but not from 4,6-DMDBT isomers. Therefore, selectivity of the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst for DMCHB, DMBPh and DMBCH

mentioned below included selectivity for the corresponding isomers. It is also worthy to note that material (carbon) balance was 70% or less for the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst when the conversion was higher than 60 mol%. No cracking products were detected in the products. Besides, carbon balance was always 90% or higher irrespective of the conversion for the Al<sub>2</sub>O<sub>3</sub> supported catalysts. It was suggested that carbon deposition occurred on acidic sites of the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> surface during HDS of 4,6-DMDBT.

Fig. 9 compares DMBPh, DMCHB and THDMDBT selectivity of the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Ni/W/Al<sub>2</sub>O<sub>3</sub> catalysts. DMBPh selectivity of these catalysts was almost the same in the whole conversion range. On the other hand, the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst showed lower selectivity for DMCHB than the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst. In stead, THD-MDBT selectivity of the former catalyst was higher. These results suggested that use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support promoted HYD of 4,6-DMDBT into THDMDBT and/or HHDMDBT, whereas it suppressed C–S bond cleavage of THDMDBT. Such the effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support will be related with the differences in morphology of WS<sub>2</sub> slabs and distribution of the CUS as described previously.

#### 3.6. Effect of CyDTA on HDS activity and selectivity

#### 3.6.1. 4,6-DMDBT HDS activity

Fig. 7 also depicts effect of CyDTA on the yield of the products obtained with the Ni/W/Al<sub>2</sub>O<sub>3</sub> and Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts ( $W/F = 1.3 \text{ g}_{cat} \text{ h} \text{ g}_{4,6-DMDBT}^{-1}$ ). As reported previously [12,13], higher yields of DMBPh and DMCHB were obtained with the CyDTA-Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst compared with the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst. Use of CyDTA improved HDS activity of the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst by a factor of 1.6. On the other hand, use of CyDTA for the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst improved the yields of DMBPh and DMCHB by factors of 3 and 5, respectively. DMBCH was also detected in the products with the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. This catalyst showed three times higher HDS activity than the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst. It should be also noted that HDS activity of the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared using CyDTA reported previously [12,13].

#### 3.6.2. Product selectivity

To investigate effect of CyDTA on product selectivity, HDS of 4,6-DMDBT was conducted with the Ni/W/Al<sub>2</sub>O<sub>3</sub> and CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts at various W/F. DMBPh, DMCHB and THDMDBT selectivity of these catalysts was depicted in Fig. 10 as a function of the conversion of 4,6-DMDBT. Similar to the reaction with the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, DMCHB, DMBPh and DMBCH isomers were detected in the products with the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst when the conversion was higher than 65 mol%. DMCHB, DMBPh and DMBCH selectivity depicted in Fig. 10 included the corresponding isomers. From this figure, one can easily understand that product selectivity of the Ni/W/Al<sub>2</sub>O<sub>3</sub> and CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts are almost identical. On the other hand, the yields of the HDS products, DMBPh, DMCHB and DMBCH. obtained with the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst were evidently higher than those with the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst. These results suggest that both the DDS and HYD routes are promoted on the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst at the same rate compared with the Ni/W/Al<sub>2</sub>O<sub>3</sub> catalyst. Such simultaneous promotion is a reason for higher 4,6-DMDBT HDS activity of the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

#### 4. Discussion

In the present study, novel SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support with the unique acidic property was used for preparation of the NiW catalyst in combination with CyDTA. In this section, obtained results were discussed in terms of effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on morphology of



Fig. 9. Effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on DMBPh, DMCHB and THDMDBT selectivity over the NiW catalyst; Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (closed symbol), Ni/W/Al<sub>2</sub>O<sub>3</sub> (open symbol).



Fig. 10. Effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support in combination with CyDTA on DMBPh, DMCHB THDMDBT selectivity over the NiW catalyst; CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (closed symbol), Ni/W/Al<sub>2</sub>O<sub>3</sub> (open symbol) catalyst.

the WS<sub>2</sub>-like slabs and the formation of the CUS on the Ni promoter. Relationship with 4,6-DMDBT HDS activity and selectivity was also discussed here.

#### 4.1. Effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on morphology of WS<sub>2</sub>-like slabs

Effect of support on morphology of WS<sub>2</sub>-like slabs has been investigated by several authors. Sun et al. [21] investigated effect of modification of  $Al_2O_3$  support with ammonium fluoride (F- $Al_2O_3$ ) on morphology of the WS<sub>2</sub>-like slabs in the W and NiW catalysts prepared using ammonium metatungstate (AMT) and ammonium tetrathiotungstate (ATT) by means of high-resolution TEM. They found that, irrespective of the type of W source, modification with ammonium fluoride increased stacking degree of the WS<sub>2</sub>-like slabs in the W and NiW catalysts. Major fractions were present as doublelayered slabs on the F-Al<sub>2</sub>O<sub>3</sub> supported catalysts prepared using ATT. On the other hand, modification with ammonium fluoride hardly affected the basal plane sizes of the slabs on the ATT derived catalysts. ver Meer et al. [41] reported inhomogeneous distribution of the WS<sub>2</sub>-like slabs on the amorphous silica-alumina (ASA) supported NiW catalyst. The slabs were preferentially distributed over the alumina part of ASA support. Single-layered slabs predominated in these catalysts.

Quasi in situ TEM observation in the present study showed that the WS<sub>2</sub>-like slabs were homogeneously distributed on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support as well as on Al<sub>2</sub>O<sub>3</sub> support. Stacking degree of the WS<sub>2</sub>like slabs in the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts was higher compared with the Al<sub>2</sub>O<sub>3</sub> supported counterparts. Furthermore, the WS<sub>2</sub>-like slabs on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalysts had smaller basal plane sizes compared with the Al<sub>2</sub>O<sub>3</sub> supported counterparts. Distribution of stacking number of the WS<sub>2</sub>-like slabs in these SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalysts was similar to those on the F-Al<sub>2</sub>O<sub>3</sub> supported catalysts prepared using ATT [21], whereas it was reported that use of F-Al<sub>2</sub>O<sub>3</sub> support hardly affected the basal plane sizes of the slabs. DRIFT measurement on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support after drying in He showed that strong basic Al-OH species was absent from the surface of this support material, indicating that weak W-support interaction leads to the formation of the WS<sub>2</sub>-like slabs with higher stacking degree, but smaller basal plane sizes. Different effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and F-Al<sub>2</sub>O<sub>3</sub> support on the basal plane sizes of the WS<sub>2</sub>-like slabs suggests that W-support interaction is weaker for SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support.

Use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support for the NiW catalyst in combination with CyDTA further increased stacking degree of the WS<sub>2</sub>-like slabs. The double-layered WS<sub>2</sub>-like slabs became predominant over this catalyst. It also decreased the basal plane size of the slabs. CyDTA showed similar effect for the Al<sub>2</sub>O<sub>3</sub> supported catalyst. Obviously, CyDTA enhanced the morphological changes of the WS<sub>2</sub>-like slabs induced by Ni addition. It is then stressed that these morphological changes induced by CyDTA and/or Ni addition were similar to those observed for the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalysts in comparison with the Al<sub>2</sub>O<sub>3</sub> supported counterparts. Thus their effect could be explained in terms of W-support interaction; In our previous study, in situ W  $L_{\rm III}\text{-}edge$  EXAFS measurement of the W/Al\_2O\_3 and Ni/W/Al<sub>2</sub>O<sub>3</sub> catalysts sulfided at high-pressure showed that the addition of the Ni promoter to the W/Al2O3 catalyst increased sulfiding degree of the WS<sub>2</sub>-like slabs [15]. Higher sulfiding degree of the WS<sub>2</sub>-like slabs on the promoted catalyst would be brought by breaking of some W–O–Al bonds during sulfiding pretreatment, due to higher ability for H<sub>2</sub> dissociation of the Ni atoms. Breaking of some W-O-Al bonds results in weaker W-support interaction, leading to the formation of the WS<sub>2</sub>-like slabs with higher stacking degree, but smaller basal plane sizes after sulfiding pretreatment. This mechanism would effectively work when the Ni atoms are located near WS<sub>2</sub>-like slabs, i.e. during the formation of the Ni-Mo-S phase. Thus, CyDTA enhanced morphological changes by Ni addition through the effective formation of the Ni–W–S phase as suggested by DRIFTS coupled with NO adsorption.

#### 4.2. Effect of $SiO_2$ - $Al_2O_3$ support on the formation of the CUS

In situ DRIFT coupled with NO adsorption further revealed that use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support for preparation of the NiW catalyst also affected distribution of the CUS; the CUS was less selectively formed on Ni in the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst compared with the Al<sub>2</sub>O<sub>3</sub> supported counterpart. This suggested that the formation of the Ni-W-S phase was suppressed on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> surface. The reason for this is not so clear. Ni<sup>2+</sup> may be trapped by some kinds of cation-exchange sites on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> surface during the catalyst preparation steps like zeolite [42], which could not be involved in the formation of the Ni-W-S phase during sulfiding pretreatment. When the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst is prepared using CyDTA, the formation of such Ni<sup>2+</sup> species will be prevented because CyDTA forms the stable complex with Ni<sup>2+</sup>. Thus, the formation of the Ni-W-S phase was promoted by use of CyDTA on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> surface as well as on Al<sub>2</sub>O<sub>3</sub> surface. Combining with the results from quasi in situ TEM measurement, it was suggested that the multi-layered Ni-W-S phase with the smaller basal plane size was effectively formed by use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support in combination with CyDTA.

#### 4.3. 4,6-DMDBT HDS activity and selectivity

So far, extensive efforts have been made to improve understanding of fundamental aspects of HDS of 4,6-DMDBT. Based on these studies, it has been suggested that HDS of 4,6-DMDBT proceeds in the DDS HYD routes [2–9]. Because the HYD route is much faster than the DDS route [6], promotion of the HYD route is a good strategy for effective HDS of 4,6-DMDBT.

From this point of view, several authors investigated effects of additives such as boric acid and ammonium fluoride on the reaction routes in HDS of DBT and 4,6-DMDBT on NiMo and CoMo catalysts. Among these studies, the addition of boric acid to Al<sub>2</sub>O<sub>3</sub> support was reported to promote the HYD route in HDS of DBT and 4,6-DMDBT on NiMo catalyst [16-19]. Based on Mo K-edge EXAFS and XPS measurement, Li et al. [16] suggested that the formation of single-layered MoS<sub>2</sub>-like slabs was responsible for the promotion of the HYD route. On the contrary, Kagami et al. [19] found that preparation of NiMo/Al<sub>2</sub>O<sub>3</sub> using NTA improved 4,6-DMDBT HDS activity by a factor of 2. They suggested that the formation of MoS<sub>2</sub>-like slabs with higher stacking degree was effective for promoting the HYD route, leading to higher HDS activity. For CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst, Kwak et al. [20] reported that the addition of ammonium fluoride to Al<sub>2</sub>O<sub>3</sub> support promoted the HDY route, leading to improvement in 4,6-DMDBT HDS activity by a factor of 1.6. Based on temperature-programmed sulfidation measurement, they suggested that ammonium fluoride addition improved the dispersion of the MoS<sub>2</sub> slabs, which was responsible for the promotion of the HYD route. All these studies suggested the importance of morphology of the MoS<sub>2</sub>-like slabs for promotion of the HYD route, although apparent discrepancies exist among them. One should also remind that different types of catalytic functions, i.e. HYD of the aromatic ring and subsequent C-S bond cleavage of hydrogenated 4,6-DMDBT, are required to promote the HYD route. The higher ability for C-S bond cleavage of 4,6-DMDBT and hydrogenated DMDBT is suggested being brought by Co and/or Ni addition [8,43,40]. Therefore, surface structure of these promoters should be also taken into consideration to establish the structureactivity relationship for the HYD route in HDS of 4,6-DMDBT.

It was found in the present study that the CyDTA-Ni/W/SiO<sub>2</sub>- $Al_2O_3$  catalyst showed three times higher 4,6-DMDBT HDS activity than the Ni/W/Al\_2O\_3 catalyst. This activity enhancement was

greater than the difference in NO adsorption capability of these two catalysts. It is also noted that 4,6-DMDBT HDS activity of the CyDTA-Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was still higher than that of the B-Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst prepared using CyDTA reported previously [12,13]. The activity enhancement by use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support in combination with CyDTA was greater than those reported previously (also see above).

It was also found that use of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support promoted HYD of 4,6-DMDBT to THDMDBT and/or HHDMDBT over the W catalyst. Taking the quasi in situ TEM results into consideration, it was suggested that the formation of the WS<sub>2</sub>-like slabs with higher stacking degree, but the smaller basal plane size was effective for promoting HYD of 4,6-DMDBT. Higher stacking degree of the WS<sub>2</sub>like slabs is effective for HYD of 4,6-DMDBT, probably because the slabs with higher stacking degree will reduce steric hindrance for  $\pi$ -adsorption of 4,6-DMDBT onto their coordinatively unsaturated edge and corner sites. On the other hand, the smaller basal plane size increases the fraction of the corner sites, which will also reduce steric hindrance for  $\pi$ -adsorption of 4,6-DMDBT. It is noted, however, that the W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst showed higher HDS activity than the  $W/Al_2O_3$  catalyst. Thus, the  $WS_{2-}$  like slabs with the above morphology also have weak activity for C-S bond cleavage of 4,6-DMDBT and/or THDMDBT. This structure-activity relationship will also hold true for higher activity for HYD of 4,6-DMDBT over the Ni/W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst

On the other hand, activity for C–S breaking of 4,6-DMDBT and THDMDBT was suppressed by use of  $SiO_2-Al_2O_3$  support for the NiW catalyst. This was apparently related with the fact that the formation of the Ni–W–S phase was suppressed on the  $SiO_2-Al_2O_3$  surface as suggested by DRIFTS coupled with NO adsorption. When the  $SiO_2-Al_2O_3$  supported NiW catalyst was prepared using CyDTA, the formation of the Ni–W–S phase was promoted, which was accompanied with further increase of stacking degree and decrease of the basal plane size of the WS<sub>2</sub>-like slabs. Such sulfide structure is effective for both HYD of 4,6-DMDBT, and C–S bond cleavage of 4,6-DMDBT and THDMDBT. The HYD and DDS routes were thus promoted simultaneously on this catalyst, leading to higher HDS activity. Our results suggest that the formation of the multi-layered Ni–W–S phase with the smaller basal plane size is crucial for promoting the HYD route in HDS of 4,6-DMDBT.

#### 5. Conclusions

Effect of novel SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support on surface structure and HDS activity of the NiW catalyst prepared using CyDTA was investigated by combination of quasi in situ TEM, DRIFTS coupled with NO adsorption and 4,6-DMDBT HDS activity measurements. Important results obtained are summarized as follows.

- In situ DRIFT measurement on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support showed that strong Al–OH species was absent from the surface of this support material.
- (2) Without using the chelating agent, quasi in situ TEM measurement showed that the WS<sub>2</sub>-like slabs on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported W and NiW catalysts had higher stacking degree, but smaller basal plane sizes compared with the Al<sub>2</sub>O<sub>3</sub> supported counterparts. On the other hand, the formation of the Ni–W–S phase was suppressed when SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support was used for the NiW catalyst instead of Al<sub>2</sub>O<sub>3</sub> support.
- (3) The SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst showed higher activity for HYD of 4,6-DMDBT into THDMDBT than the Al<sub>2</sub>O<sub>3</sub> supported counterpart. However, because of lower activity for C–S bond cleavage of THDMDBT, this catalyst failed to promote the HYD route, and showed lower HDS activity than the Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst.

- (4) The formation of the Ni–W–S phase was effectively promoted when the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst was prepared using CyDTA, which was accompanied with further increase of stacking degree and decreased the basal plane size of the WS<sub>2</sub>-like slabs.
- (5) This catalyst showed higher activity for both HYD of 4,6-DMDBT, and C–S bond cleavage of 4,6-DMDBT and THDMDBT. The HYD and DDS routes in HDS of 4,6-DMDBT were promoted simultaneously on this catalyst, leading to three times higher HDS activity than the Al<sub>2</sub>O<sub>3</sub> supported NiW catalyst. These results suggested that the formation of the multi-layered Ni–W–S phase with smaller basal plane sizes is crucial for promoting the HYD route in HDS of 4,6-DMDBT.

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