

# Highly dispersed NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst prepared by hydrothermal deposition method

Hao Wang<sup>a</sup>, Yu Fan<sup>a,b</sup>, Gang Shi<sup>b</sup>, Zhihong Liu<sup>c</sup>, Haiyan Liu<sup>b</sup>, Xiaojun Bao<sup>a,b,\*</sup>

<sup>a</sup> State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, PR China

<sup>b</sup> The Key Laboratory of Catalysis, China National Petroleum Corp., China University of Petroleum, Beijing 102249, PR China

<sup>c</sup> Science & Technology Management Department, PetroChina Company Ltd., World Tower, 16 Andelu, Dongcheng District, Beijing 100011, PR China

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## Abstract

This article describes a novel hydrothermal deposition method for preparing highly dispersed NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and demonstrates its advantages over the conventional impregnation method. Via the hydrothermal precipitation reactions between sodium tungstate and hydrochloric acid and between nickel nitrate and urea, respectively, the active species W and Ni were deposited on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In the hydrothermal deposition of WO<sub>3</sub>, a surfactant hexadecyltrimethyl ammonium bromide (CTAB) was used to prevent the aggregation of WO<sub>3</sub>. The characterization results obtained by means of X-ray photoelectron spectroscopy (XPS), N<sub>2</sub> adsorption and high-resolution transmission electron microscopy (HRTEM) measurements showed that compared with the catalyst prepared by the conventional impregnation method, the catalyst with the same metal contents prepared by the hydrothermal deposition had much higher W and Ni dispersion, higher specific surface area, larger pore volume, the significantly decreased slab length and slightly increased stacking degree of sulfided W species, leading to the significantly enhanced dibenzothiophene (DBT) hydrodesulfurization (HDS) activity. The DBT HDS assessment results also revealed that the catalyst containing 17.7 wt% WO<sub>3</sub> and 2.4 wt% NiO prepared by the hydrothermal deposition method had the similar DBT HDS activity as a commercial NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst containing 23 wt% WO<sub>3</sub> and 2.6 wt% NiO, resulting in the greatly decreased amount of active metals for achieving the same HDS activity.

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## 1. Introduction

The ratio of the number of active metal atoms on the surface of a catalyst to the total number of active phase atoms in it is frequently defined as dispersion [1,2]. It is well known that decreasing the size of the active metal particles in a catalyst can increase the fraction of atoms exposed to the surface and lead to the enhanced dispersion, which is an effective approach to improving the catalytic activity of supported catalysts [3].

In preparing supported catalysts, impregnation and precipitation are commonly used methods. During an impregnation process, the deposition of active species often occurs due to the uncontrollable evaporation of the impregnating solution in

the drying step; in a precipitating process, a precipitator and a precursor to be precipitated often mix inhomogeneously. Both of the two methods may lead to the formation of larger active species crystallites on support surface, causing low dispersion of the active species [4–6].

For hydrodesulfurization (HDS) catalysts, a typical family of supported catalysts, it has been recognized that in addition to the dispersion of active species, the stacking degree of sulfided active species is also important. In terms of the Co–Mo–S active phase theory proposed by Topsøe and Topsøe [7], the highly stacked MoS<sub>2</sub> particles on alumina, often named as Type II active phase, are more active to the HDS of large sulfur-containing molecules such as dibenzothiophene (DBT) and its derivatives. According to the rim-edge model proposed by Daage and Chianelli [8], the stacking number of MoS<sub>2</sub> slabs also determines the selectivity of DBT HDS. However, increasing stacking degree also leads to the decreased dispersion of active species [9]. Obviously, there exists a compromise between dispersion and stacking degree for

\* Corresponding author at: China University of Petroleum, China National Petroleum Corp., No. 18 Fuxue Road, Changping, Beijing 102249, PR China. Tel.: +86 10 8973 4836; fax: +86 10 8973 4979.

E-mail address: [baoxj@cup.edu.cn](mailto:baoxj@cup.edu.cn) (X. Bao).

achieving the optimum catalyst performance. By strengthening the interaction between support and active species, some researchers had successfully reduced the size of active species [10–12], but this method had the double effects, the increase in dispersion and the decrease in the stacking degree of the active metal sulfide crystallites, the latter of which may be disadvantageous to the HDS of large sulfide molecules [7,9,13]. Reducing the lateral size of active species without strengthening the metal–support interaction can increase the amount of catalytically active sites and thus should endow the resulting catalyst with the compromised dispersion and stacking degree of the active species.

In recent years, the hydrothermal synthesis method via various precipitation reactions between metal salts and acid/base precipitators for preparing nanosize metal oxides has been well developed and has gained successful applications in manufacturing various nanosize metal oxides, such as Cd(OH)<sub>2</sub> [14], MoO<sub>3</sub> [15], ZnO [16], WO<sub>3</sub> [17–19] and NiO [20]. The advantages of the hydrothermal synthesis method lie in that it can produce materials with controllable particle size and high purity while using milder synthesis temperature and simpler process configuration. Furthermore, aqueous solutions under hydrothermal conditions have lower viscosities and lower resistances to mass transfer and thus can accelerate diffusion of the reacting species involved, leading to improved supersaturation distribution [6]. Naturally, it is conceived that the hydrothermal synthesis method can be considered as an effective way to prepare highly dispersed catalysts.

Very recently, we proposed a novel hydrothermal deposition method to prepare highly dispersed monometallic W/Al<sub>2</sub>O<sub>3</sub> hydrodenitrogenation catalyst without strengthening the metal–support interaction [21]. Starting from this point, we herein extend the hydrothermal deposition method to prepare highly dispersed bimetallic NiW/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. Two NiW/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the hydrothermal deposition method and the conventional impregnation method, respectively. The physicochemical properties of the catalysts were characterized by X-ray photoelectron spectroscopy (XPS), N<sub>2</sub> adsorption and high-resolution transmission electron microscopy (HRTEM) techniques, and their HDS performances were compared in a continuously flowing tubular fixed-bed microreactor using DBT as a sulfur-containing model compound.

## 2. Experimental

### 2.1. Catalyst preparation

γ-Al<sub>2</sub>O<sub>3</sub> particles (Sasol, specific surface area: 211.5 m<sup>2</sup>/g; pore volume: 0.52 cm<sup>3</sup>/g; average pore diameter: 8.1 nm; particle size: 20–40 meshes) are used as the support for preparing NiW/γ-Al<sub>2</sub>O<sub>3</sub> catalysts.

The hydrothermal deposition method is described as follows. Loading WO<sub>3</sub> onto the γ-Al<sub>2</sub>O<sub>3</sub> support involves the following steps: firstly, 5.0 g γ-Al<sub>2</sub>O<sub>3</sub> particles were suspended in a 47.77 mL sodium tungstate solution of 0.1 mol/L in an autoclave; secondly, a 3.98 mL HCl solution of 2.4 mol/L was dropwise added into the above suspension, and the addition of

0.87 g cation surfactant hexadecyltrimethyl ammonium bromide (CTAB, 99 wt%, Beijing Chemical Reagents Company, PR China) was followed, resulting in a mixture with WO<sub>4</sub><sup>2−</sup>:H<sup>+</sup>:CTAB molar ratio at 1:2:0.5; thirdly, the resulting suspension was stirred at 150 °C for 24 h for the precipitation and deposition of W species; finally, the mixture in the autoclave was naturally cooled down to room temperature, filtrated, washed with distilled water, dried at 110 °C for 2 h, and calcined at 550 °C for 4 h to obtain the monometallic catalyst precursor W/γ-Al<sub>2</sub>O<sub>3</sub>. The loading of NiO on W/γ-Al<sub>2</sub>O<sub>3</sub> was carried out by the following steps: firstly, a 33.50 mL solution of 0.06 mol/L nickel nitrate and 0.24 g urea were added into the autoclave containing W/γ-Al<sub>2</sub>O<sub>3</sub> to form a mixture with Ni<sup>2+</sup>:CO(NH<sub>2</sub>)<sub>2</sub> molar ratio at 1:2; then, the suspension was stirred at 90 °C for 8 h and 130 °C for 4 h, respectively; finally, the product was filtrated, washed, dried at 110 °C for 2 h, and calcined at 550 °C for 4 h to obtain the oxidic NiW/γ-Al<sub>2</sub>O<sub>3</sub> catalyst denoted as catalyst HD.

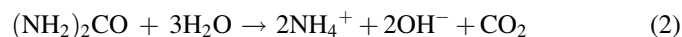
In the above preparation processes, tungstate reacts with HCl to form nanosize tungstic acid particles by the following hydrothermal route, i.e.:



The nanoparticles formed in the above reaction tend to aggregate. To resolve the problem, in the precipitation procedure of H<sub>2</sub>WO<sub>4</sub> we used the cation surfactant CTAB that can be anchored on the surface of tungstic acid particles to prevent their aggregation. The ammonium cations of CTAB interact with H<sub>2</sub>WO<sub>4</sub> colloids that absorb WO<sub>4</sub><sup>2−</sup> and exhibit negative charges in suspension to form a film covering on the colloidal particles, so the distances between the colloidal particles are increased and thus their aggregation is avoided [22].

The use of urea as precipitator in preparing nanosize NiO particles by homogeneous precipitation in conventional and hydrothermal solutions has been reported by many researchers [23,24]. It has been known that the simple addition by pouring all the precipitator agent into the solution of the precursor at one time cannot lead to homogeneous precipitation, because the resulting local concentration can exceed the supersolubility of the precipitated precursor in the bulk solution and thus give rise to the formation of nuclei in large amount and their quick growth into larger crystals. Separating the addition and reaction of a precipitating agent can minimize the local concentration differences and thus allow its gradual reaction with the precursor [4]. Because urea hydrolysis occurs and releases OH<sup>−</sup> at temperature higher than 90 °C, the nickel nitrate solution can mix with urea homogeneously at lower temperature, and then their precipitation reaction takes place fast at elevated temperature due to the increasing hydrolysis rate of urea. This process makes the mixing and the reaction of urea with the precursor in the solution separate as well as controllable, finally leading to the uniform precipitation of the active species on the support.

The hydrolysis and precipitation reactions can be described as:



It should be pointed out that the lower resistance to mass transfer of the solution under hydrothermal conditions can accelerate the diffusion of the solution inside the support because of its two-order lower viscosity than that of the solution at room temperature and pressure [25], which also contributes to the improved dispersion of the active species on the support [6].

The sequential pore volume impregnation method involves the following steps. W was impregnated by the pore volume impregnation method using ammonium metatungstate as precursor, and then Ni was impregnated by the same method using nickel nitrate hexahydrate as precursor. The solids obtained after each of the impregnation steps were dried and calcined under the same conditions as described above. The oxidic NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst prepared by the impregnation method was denoted as catalyst IM.

By the X-ray fluorescence spectroscopy (XRF) analyses taken on a ZSX 100e instrument (Rigaku), it was confirmed that the final catalysts prepared by the two methods contained 17.7 wt% WO<sub>3</sub> and 2.4 wt% NiO.

## 2.2. Catalyst characterizations

The XPS spectra of the samples were taken on an ESCA Lab 250 spectrometer (VG) using Al K $\alpha$  radiation. The binding energy was corrected by using the C1s peak at 285.0 eV as reference.

The specific surface areas, pore volumes of the support and the catalysts were measured on an ASAP 2020N instrument (Micromeritics) using nitrogen adsorption at  $-196^\circ\text{C}$ .

The HRTEM measurements of the sulfided catalysts were carried out on a Tecnai G2 F20 transmission electron microscope (Philips) operated at an accelerating voltage 200 kV. The catalysts were sulfided with a 3 wt% CS<sub>2</sub>/cyclohexane mixture at 300 °C for 4 h and placed in cyclohexane before measurement.

## 2.3. Catalyst activity assessment

The HDS reaction of DBT was used to assess the catalytic activity of the catalysts prepared. The reaction was carried out in a continuously flowing tubular fixed-bed microreactor of 16 mm in diameter and 500 mm in length. The catalysts (ca. 1 mL) were diluted with quartz particles before being loaded into the reactor. Both of the catalysts were sulfided for 4 h with a 3 wt% CS<sub>2</sub>/cyclohexane mixture at liquid hourly space velocity (LHSV) 8.0 h<sup>-1</sup>, 300 °C, 4.0 MPa, and H<sub>2</sub> to hydrocarbon (HC) volumetric ratio 300. The HDS activities of the catalysts were assessed with a 1 wt% DBT (99%, Acros)/cyclohexane mixture under the conditions of 300 °C, LHSV 8.0 h<sup>-1</sup>, 4.0 MPa, and H<sub>2</sub> to HC volumetric ratio 400. The sulfur contents in the reactant and the products were determined by a WK-2C microcoulometer (Jiangsu Jiangfen Electroanalytical Instrument Co. Ltd., PR China). The catalyst activity was expressed in terms of the conversion of DBT as

follows:

DBT conversion (%)

$$= \frac{\text{total sulfur content in feed (wt\%)} - \text{total sulfur content in product (wt\%)}}{\text{total sulfur content in feed (wt\%)}} \times 100$$

The product distribution of DBT HDS was analyzed off-line by a SSQ710 (Finnigan MAT) GC–MS equipped with a 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  HP-5MS capillary column. After the steady state was reached, the product was collected for GC–MS analysis.

## 3. Results and discussion

### 3.1. XPS characterization

XPS characterization can be used to determine the chemical environment and the surface atom concentrations of the active metals loaded on the support. The XPS spectra of the W4f and Ni2p for the two oxidic NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts are displayed in Fig. 1a and b. The relevant electron-binding energies of W4f<sub>7/2</sub> and Ni2p<sub>3/2</sub> obtained from the XPS spectra are summarized in Table 1.

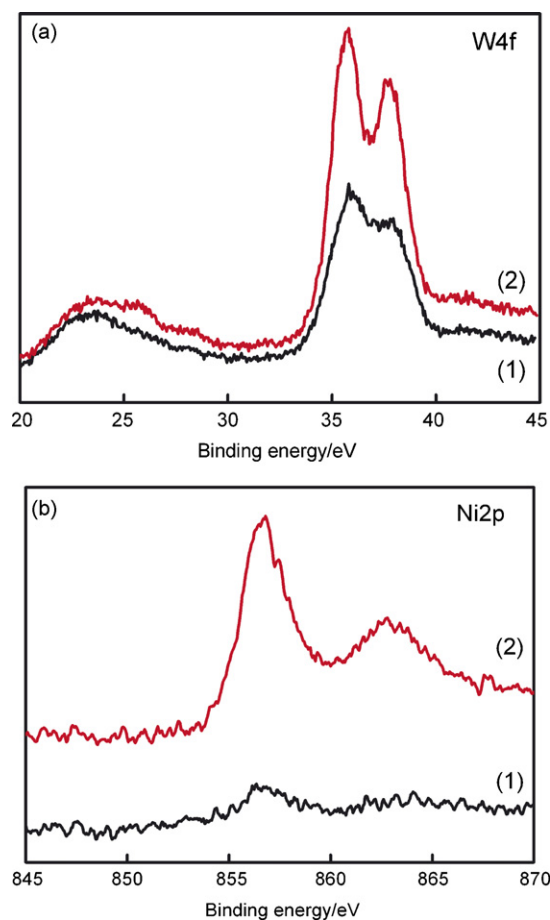


Fig. 1. XPS spectra of W4f (a) and Ni2p (b) in the two oxidic NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. (1) Catalyst IM; (2) catalyst HD.



Table 1  
Properties of the two NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

	Catalyst IM	Catalyst HD
W4f <sub>7/2</sub> (eV) <sup>a</sup>	35.8	35.8
Ni2p <sub>3/2</sub> (eV) <sup>a</sup>	856.3	856.7
W/Al <sup>b</sup>	0.060	0.121
Ni/Al <sup>b</sup>	0.015	0.066
BET surface area (m <sup>2</sup> /g)	165.6	210.5
Pore volume (cm <sup>3</sup> /g)	0.39	0.50
Average length (nm) <sup>c</sup>	4.75	3.46
Average layer number <sup>d</sup>	1.14	1.26

<sup>a</sup> XPS binding energies of the oxidic NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

<sup>b</sup> Surface atomic ratios of the oxidic NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts determined by XPS.

<sup>c</sup> Average lengths of WS<sub>2</sub> slabs on the sulfided NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

<sup>d</sup> Average stacking numbers of WS<sub>2</sub> slabs on the sulfided NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

As shown in Table 1, the binding energies of W4f<sub>7/2</sub> in the two oxidic catalysts IM and HD are both 35.8 eV, corresponding to oxidic W<sup>6+</sup> that has the binding energy W4f<sub>7/2</sub> = 35.7 ± 0.2 eV [26]; the binding energies of Ni2p<sub>3/2</sub> in the two oxidic catalysts IM and HD are 856.3 eV and 856.7 eV, respectively, ascribed to oxidic Ni<sup>2+</sup> that has the binding energy Ni2p<sub>3/2</sub> = 856.5 ± 0.2 eV [26]. These results indicate the similar chemical states of the active species W and Ni in the two oxidic catalysts.

XPS, because of its high surface sensitivity, has been considered as one of the best techniques for studying the dispersion of transition metal oxides on various supports [27]. Many researchers took XPS data, the surface atomic ratios of the active metal elements to aluminum element of the alumina support, as a measure of the dispersion of Ni(Co)–W(Mo) phases in hydrotreating catalysts [27–34]. Thus, the W/Al and Ni/Al ratios of the two oxidic catalysts were calculated from the XPS data and the results are listed in Table 1. It is interesting to note that the surface Ni/Al and W/Al atomic ratios of the oxidic catalyst HD are significantly higher than those of the oxidic catalyst IM, illustrating more exposed surface Ni and W atoms, or more exactly, the higher dispersion of the active species on the former catalyst.

### 3.2. N<sub>2</sub> adsorption characterization

The textural properties of the two oxidic catalysts are listed in Table 1. We can see that the specific surface area and pore volume of the oxidic catalyst HD are larger than those of the oxidic catalyst IM.

Vakros and coworkers [5,10] observed that the conventional impregnation method produced relatively larger crystallites of active species that might plug into the narrower pores of the alumina and cause the closing of some pore channels, resulting in considerable decrease in catalyst specific surface area. So, they developed the so-called equilibrium deposition filtration (EDF) technique to prepare CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts and found that this technique could form smaller particles of active species and thus the resulting catalyst had higher surface area, similar to the results obtained in the present investigation. The

scanning electron microscopy (SEM) images not cited here also show that the oxidic catalyst HD has more exposed pores on its external surface than the oxidic catalyst IM.

### 3.3. HRTEM characterization

Fig. 2a and b are the representative HRTEM images of the two sulfided NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The dark fringes in the images are WS<sub>2</sub> crystallites. The particles of the promoter Ni sulfide on the catalysts are too small to be visualized in the HRTEM images, because they are usually of the size of about 0.5 nm and lie in the WS<sub>2</sub> slabs [31,35].

To quantitatively compare the lengths and stacking numbers of the WS<sub>2</sub> slabs on the two catalysts, statistical analyses were

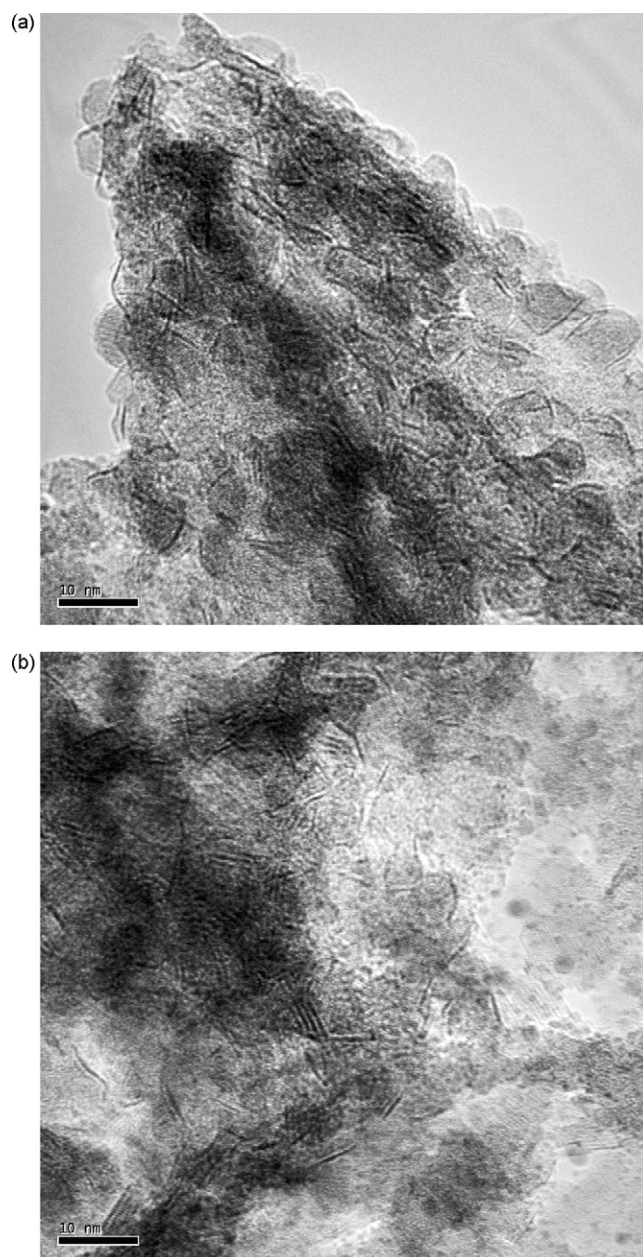


Fig. 2. HRTEM images of the two sulfided NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. (a) Catalyst IM; (b) catalyst HD.

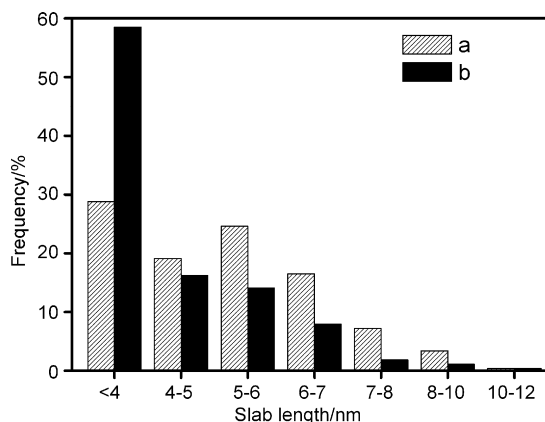


Fig. 3. Slab length distribution of the  $\text{WS}_2$  slabs on the sulfided  $\text{NiW}/\gamma\text{-Al}_2\text{O}_3$  catalysts. (a) Catalyst IM; (b) catalyst HD.

made based on at least 20 images including 230–280 slabs taken from the different parts of each catalyst and the results are presented in Figs. 3 and 4.

On the catalyst HD, the fraction of the  $\text{WS}_2$  slabs shorter than 4 nm takes a share of about 58.5%, about 20.9% of the  $\text{WS}_2$  slabs are presented in two to three layers and 79.1% in single layer. For the catalyst IM, the fraction of the  $\text{WS}_2$  slabs shorter than 4 nm takes a share of only 28.8%, and 14.4% and 85.6% of the  $\text{WS}_2$  slabs exist in the form of two to three layers and in the form of single layer, respectively. The average stacking layers and the average lengths of the  $\text{WS}_2$  slabs of the two catalysts are listed in Table 1. It can be seen that compared with the catalyst IM, the catalyst HD has the higher average stacking layer number (1.26 for HD and 1.14 for IM) and the shorter average length of  $\text{WS}_2$  slabs (3.46 nm for HD and 4.75 nm for IM).

### 3.4. DBT HDS activity

Fig. 5 shows the conversion of DBT on IM, HD and a commercial  $\text{NiW}/\gamma\text{-Al}_2\text{O}_3$  catalyst with time on stream.

It can be seen that the DBT HDS conversion of the catalyst HD is about 20% points higher than that of the catalyst IM,

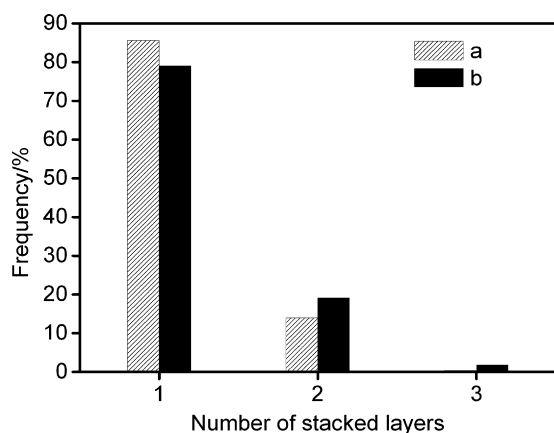


Fig. 4. Stacking layer number distributions of  $\text{WS}_2$  slabs on the sulfided  $\text{NiW}/\gamma\text{-Al}_2\text{O}_3$  catalysts. (a) Catalyst IM; (b) catalyst HD.

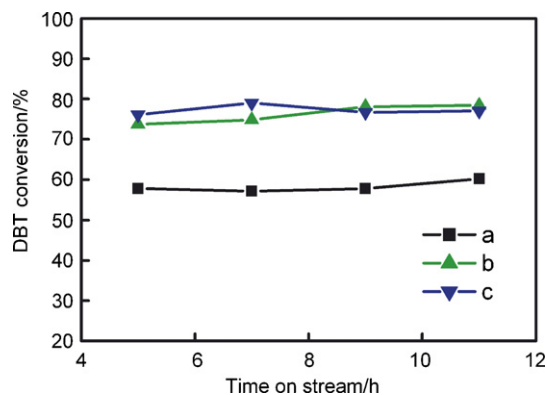


Fig. 5. DBT conversion on the three  $\text{NiW}/\gamma\text{-Al}_2\text{O}_3$  catalysts. (a) Catalyst IM; (b) catalyst HD; (c) the commercial catalyst.

although they have the identical loadings of the active species W and Ni and use the same alumina support. The difference in their activities should be attributed to the different surface characteristics related to the different preparation techniques. In addition, it is also noted that the DBT HDS activity of the catalyst loaded with 17.7 wt%  $\text{WO}_3$  and 2.4 wt% NiO prepared by the hydrothermal deposition method is close to that of the commercial catalyst loaded with 23 wt%  $\text{WO}_3$  and 2.6 wt% NiO, suggesting that the hydrothermal deposition method can greatly decrease the loadings of the active species for achieving the identical HDS activity.

It is well known that DBT has two HDS reaction pathways: (i) direct desulfurization (DDS), which leads to the formation of biphenyl (BP); (ii) hydrogenation (HYD) yielding tetrahydro-intermediates followed by desulfurization to cyclohexylbenzene (CHB) [8,36]. HYD and DDS selectivity can be calculated by dividing the total DBT conversion into CHB and BP yields, respectively [37,38]. Table 2 shows the conversions of DBT via the DDS pathway to form BP and the HYD pathway to form CHB as well as the ratios of HYD/DDS for the catalysts HD and IM. Compared with the catalyst IM, the catalyst HD can increase both the conversions via the HYD and DDS routes, in agreement with the results obtained by Hensen et al. [13]. Moreover, the HYD/DDS ratio of the catalyst HD is slightly lower than that of the catalyst IM, signifying that the catalyst HD increases the selectivity of the DDS pathway. In terms of the rim-edge model [8], the catalyst HD with more stacked  $\text{WS}_2$  slabs, as confirmed by the HRTEM observations, has the increased proportion of the edge sites to the total active sites and thus has the improved selectivity of DDS pathway of DBT HDS. From the results introduced above, we can conclude that compared with the conventional impregnation method, the hydrothermal deposition method can enhance the dispersions of

Table 2  
DBT HDS product distributions and selectivity of the two  $\text{NiW}/\gamma\text{-Al}_2\text{O}_3$  catalysts

	DBT conversion (%)	CHB (%)	BP (%)	HYD/DDS
Catalyst IM	58.0	27.9	30.1	0.93
Catalyst HD	78.0	37.2	40.8	0.91

Ni and W species, decrease the length and increase the stacking degree of WS<sub>2</sub> slabs, and thus can produce more active sites that confer the resulting catalyst with the significantly improved HDS activity.

#### 4. Conclusions

In the present investigation, the hydrothermal deposition method developed in the previous work was extended to prepare the highly dispersed NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and compared with the conventional sequential pore volume impregnation method. The two catalysts prepared by the two methods were characterized and their catalytic performances for DBT HDS were tested. The results showed that the catalyst prepared by the hydrothermal deposition method had higher W and Ni dispersions, larger specific surface area and pore volume, and the decreased length and increased stacking degree of WS<sub>2</sub> slabs compared with the catalyst prepared by the conventional impregnation method. Consequently, the DBT HDS activity of the catalyst prepared by the hydrothermal deposition method was about 20% points higher than that of the catalyst prepared by the conventional impregnation method, although they had the same active metal loadings (WO<sub>3</sub> 17.7 wt% and NiO 2.4 wt%). Moreover, the results also showed that the former catalyst had almost the similar activity for DBT HDS as a commercial NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst loaded with 23 wt% WO<sub>3</sub> and 2.6 wt% NiO. The above results demonstrate that the hydrothermal deposition method can produce supported catalysts with the compromised dispersion and stacking degree of active metal species and thus can be taken as a promising approach to preparing high-performance supported hydrotreating catalysts.

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