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## Trimetallic WMoNi diesel ultra-deep hydrodesulfurization catalysts with enhanced synergism prepared from inorganic-organic hybrid nanocrystals



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## ABSTRACT

Supported WMoNi diesel ultra-deep hydrodesulfurization (HDS) catalysts with enhanced synergetic effects among metal species were prepared with W- and Mo-based hybrid inorganic-organic nanocrystals (HNCs) as the W/Mo precursors. The W- and Mo-based HNCs are monodispersed particles with similar structure. The thus-obtained supported WMoNi catalyst has superior hydrogenation and direct desulfurization activities for dibenzothiophene HDS and dramatically higher fluid catalytic cracking diesel HDS performance than WMoNi/Al<sub>2</sub>O<sub>3</sub> prepared by the impregnation method. This benefits from the bimetallic catalyst precursor WMo/Al<sub>2</sub>O<sub>3</sub>, which has highly dispersed W and Mo species and high sulfidability and thus generates a large number of metal sulfide slabs after sulfidation. The highly dispersed W/Mo sulfide slabs provide abundant edge sites for dispersing Ni species, facilitating both textural and chemical synergisms among the sulfide phases and yielding more synergetic NiWMoS active phases. The approach opens a novel route to optimizing the synergetic effects among metal species in supported WMoNi catalysts for diesel ultra-deep HDS.

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### 1. Introduction

Diesel ultra-deep hydrodesulfurization (HDS) has been a focus in the petroleum refining industry due to stringent regulations in countries all over the world [1-3]. The challenge to produce ultra-low sulfur diesel is highly efficient removal of dibenzothiophene (DBT)-type sulfur molecules [4,5]. Researchers reported that supported trimetallic WMoNi sulfide catalysts are more active than supported bimetallic W(Mo)Ni sulfide ones for the HDS of model sulfur-containing molecules and diesel fuels [6–10]. Through both density functional theory (DFT) calculations and experimental research, Thomazeau and Cervantes-Gaxiola et al. concluded that due to the synergetic effects between Ni sulfide species and the W<sub>0.5</sub>Mo<sub>0.5</sub>S<sub>2</sub> solid solution, the resultant NiWMoS phase is more active than NiMoS and NiWS ones [7,9]. The metal-sulfur (M-S) bond energy ( $\Delta E_{MS}$ ) descriptor (calculated at a DFT level) of metal sulfide catalysts enables the establishment of a volcano curve correlation between  $\Delta E_{MS}$  and HDS activity; based on the DFT-volcano curve concept, the synergetic effect signifies that the  $\Delta E_{MS}$  value of the NiWMoS phase (namely the Ni-promoted W<sub>0.5</sub>Mo<sub>0.5</sub>S<sub>2</sub> solid solution) was closer to the volcano curve's maximum than those of the NiMoS and NiWS phases, coincident with the Sabatier principle and supported by the catalytic results using the model compound thiophene or gas oil as the feedstock [9]. For metal sulfide HDS catalysts, two types of synergism are important: textural synergism and chemical synergism [11]. The textural synergism is a result of the increased number of active sites (tungsten (molybdenum) sulfide or/and nickel sulfide phases) upon mixing the individual sulfides. The chemical synergism is characterized by the generation of the NiW(Mo)S phase in which Ni preferentially exists as NiW(Mo)S instead of as a separate NiS<sub>x</sub> phase, since the NiW (Mo)S phase has a more stable structure than the bulk  $NiS_x$  phase based on DFT calculations [12]. The NiW(Mo)S phase can be considered to have the W(Mo)S<sub>2</sub> structure with Ni atoms coordinated with sulfur and located at its edges, leading to the change in selectivity [11,13]. From the above analysis, it is considered that the achievement of synergetic effects between  $NiS_x$  and the  $W_xMo_{1-x}S_2$ (0 < x < 1) structure requires that, on the one hand, W and Mo species are in intimate contact and highly dispersed on the support; and on the other hand, W and Mo species are highly reducible and highly sulfidable to generate more  $W_x Mo_{1-x}S_2$  structures capable of accommodating more nickel atoms to form NiWMoS phases. Therefore, effort is devoted to increasing the dispersion







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and improving the reducibility and sulfidability of W and Mo species, such as the use of alternative supports (e.g., Al-modified hexagonal mesoporous silica Al-HMS [14], Al-Ti-Mg mixed oxide, and SBA-15 [6,7]), the incorporation of phosphorus [10], the introduction of citric acid into the impregnation solution [15], and the development of the solution-based combustion method to prepare the WMoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst [16]. However, improved W/Mo dispersion and higher W/Mo reducibility and sulfidability cannot be simultaneously satisfied. Especially, the aforementioned approaches based on the conventional incipient impregnation (IM) method unavoidably lead to strong interaction between the metal (W/Mo) precursors and the support surface. This causes the formation of bulk metal oxides and thereby the lowly dispersed  $MS_2$  (M = W/Mo) slabs after sulfidation, unfavorable for the intimate contact of W and Mo species and for the accommodation of MS<sub>2</sub> slabs for Ni species on their edges [11,17].

In our previous work [18,19], we synthesized Mo- and W-based hybrid inorganic-organic nanocrystals (Mo- and W-HNCs) using cetyltrimethylammonium bromide (CTAB) and tetraethylammonium bromide (TEAB) as hybrid reagents to replace the conventional precursors of Mo-anions ( $Mo_7O_{24}^{6-}$ ) and W-anions ( $W_7O_{24}^{6-}$ ), respectively; then we prepared supported monometallic Mo/ $\gamma$ - $Al_2O_3$  and  $W/\gamma$ - $Al_2O_3$  catalyst precursors by the hydrothermal deposition method; and finally we obtained supported bimetallic NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiW/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts by impregnating Mo/ $\gamma$ - $Al_2O_3$  and  $W/\gamma$ - $Al_2O_3$  with a Ni(NO\_3)<sub>2</sub> solution. The resultant bimetallic catalysts exhibited superior HDS performance compared with their counterparts prepared by the IM method. More importantly, we found that the combined use of Mo- and W-based HNCs as precursors and the hydrothermal deposition method generated W/Mo species with high dispersion, high reducibility, and high sulfidability, fully in compliance with the essential prerequisites for achieving synergism effects in trimetallic WMoNi catalysts. Here we further show that both W- and Mo-HNCs can be synthesized with TEAB as the hybrid reagent and can be used as W/Mo precursors to prepare oxidic WMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which can be further impregnated with Ni(NO<sub>3</sub>)<sub>2</sub> to yield trimetallic WMoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts exhibiting superior synergetic effects among the metal species and thereby superior HDS activity.

## 2. Experimental

## 2.1. Synthesis of Mo- and W-HNCs

The synthesis procedure of Mo-HNCs is the same as that of W-HNCs in our previous work [19], except that the sodium tungstate was replaced with sodium molybdate.

To prepare an oxidic WMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst precursor, a suspension of W- and Mo-HNCs was synthesized. First, a certain amount of a TEAB aqueous solution was mixed with an acidified sodium molybdate solution; second, a solution of polyoxotungstates, i.e., an acidified Na<sub>2</sub>WO<sub>4</sub> solution, was added to the above mixture; third, the pH value of the mixture was adjusted by a HCl solution to 3 under stirring, yielding suspension A containing W- and Mo-HNCs.

## 2.2. Preparation of alumina-supported oxidic bimetallic WMo and trimetallic WMoNi catalyst precursors

Two oxidic WMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> precursors, WMo-HHD and WMo-IM, were prepared by the hydrothermal deposition method with Wand Mo-HNCs as precursors, or HHD for short, and the IM method, respectively. The procedure of the HHD method is as follows: suspension A prepared above was transferred into a rotary autoclave containing 5.2 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles (20–40 mesh) and heated at 120 °C for 24 h; the resulting WMo-HNCs-Al<sub>2</sub>O<sub>3</sub> was filtered, washed with H<sub>2</sub>O, dried at 110 °C for 3 h, and calcined at 450 °C for 5 h, producing an oxidic catalyst precursor WMo-HHD. WMo-IM was prepared by impregnating  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles successively with aqueous solutions of (NH<sub>4</sub>)<sub>6</sub>W<sub>7</sub>O<sub>24</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (AHM); after each impregnation, the sample was dried at 110 °C for 3 h and calcined at 450 °C for 5 h. The WO<sub>3</sub> and MoO<sub>3</sub> loadings of WMo-HHD and WMo-IM are 13.7 and 8.5 wt.%, respectively. It should be emphasized that the W and Mo contents in WMo-HHD are repeatable and consistent with the feeding amount of the source materials.

Two oxidic trimetallic WMoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, WMoNi-HHD and WMoNi-IM, were prepared by impregnating WMo-HDD and WMo-IM with a Ni(NO<sub>3</sub>)<sub>2</sub> solution, drying at 100 °C for 3 h, and calcining at 450 °C for 5 h in air. The WO<sub>3</sub>, MoO<sub>3</sub>, and NiO loadings of WMoNi-HHD and WMoNi-IM are 13.1, 8.1, and 4.7 wt.%, respectively. Another oxidic trimetallic WMoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. WNi/MoNi-HHD, was obtained by mixing equivalent amounts of WNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (WNi-HHD) and MoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (MoNi-HHD) prepared by the HHD method. The procedures for preparing WNi-HHD and MoNi-HHD are the same as those used for WMoNi-HHD, except that a suspension containing only W-HNCs or Mo-HNCs at higher concentration was placed in the rotary autoclave containing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles. The WO<sub>3</sub> and NiO loadings of WNi-HHD are 26.2 and 4.7 wt.%, and the MoO<sub>3</sub> and NiO loadings of MoNi-HHD are 16.2 and 4.7 wt.%, so the WO3, MoO3 and NiO loadings of WNi/MoNi-HHD are 13.1, 8.1, and 4.7 wt.%, respectively.

#### 2.3. Characterization

The composition and structure determination of W(Mo)-HNCs and the confirmation of their deposition onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were obtained through the same methods as described elsewhere [18]. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterizations of the diluted suspension of Mo-HNCs were conducted on a Philips Tecnai G2 F20 instrument operated at 200 kV. Fourier transform infrared (FTIR) spectra were obtained on a MAGNA-IR 560 spectrometer. The transparent wafer was prepared with the mass ratio of the sample to KBr at 1:100. The Raman spectra were recorded on a Bruker RFS 100/S FT-Raman spectrometer (Germany), operated with a Nd-YAG laser at a wavelength of 532 nm. The laser spot size was approximately 1–2  $\mu$ m with a power level of 100 mW. Elemental analysis was performed with an inductively coupled plasma instrument (ICPE-9000) and a Perkin–Elmer 2400 II CHN element analyzer.

The oxidic WMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and WMoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were characterized by X-ray diffraction (XRD), N<sub>2</sub> physisorption, highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM), UV-vis diffuse reflectance spectroscopy (DRS UV-vis), and temperature-programmed reduction in hydrogen (H<sub>2</sub> TPR). The XRD patterns ( $2\theta = 10^{\circ} - 80^{\circ}$ ) were recorded with an X-ray diffractometer (Shimadzu XRD 6000) using CuKa radiation ( $\lambda$  = 1.5406 Å) and operated at a scanning rate of 4°/min. The N2 physisorption was performed at 77 K with a Micromeritics Tristar 3020 system. Specific surface areas were determined by the Bru nauer-Emmett-Teller (BET) method and pore volumes were estimated from N<sub>2</sub> adsorption-desorption isotherms. Mesopore diameters and size distributions were determined by the Barret-Joyner-Halenda (BJH) method. HAADF-STEM was performed on the above-mentioned Philips Tecnai G2 F20 instrument with a resolution of about 0.4 nm in STEM mode. The annular detector was adjusted to collect the electrons scattered between 60 and 120 mrad. The contrast in HAADF images is considered to be proportional to  $Z^{1.7}$  (Z is the atomic number of the scattering atom). DRS UV-vis spectra were obtained on a UV-vis spectrophotometer (Hitachi U-4100) installed with the integration sphere diffuse reflectance attachment in the wavelength range 200–800 nm. H<sub>2</sub> TPR was conducted on a conventional flow apparatus. 0.1 g of a sample were pretreated under Ar atmosphere at 450 °C for 2 h and subsequently cooled to 60 °C; afterward, a 10% H<sub>2</sub>/Ar flow (30 mL/min) was passed over the sample while the temperature was increased from 60 to 1050 °C at a ramp rate of 10 °C/min and maintained at 1050 °C for 0.5 h. The H<sub>2</sub> consumption signal was detected by a thermal conductivity detector (TCD).

The sulfided WMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and WMoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were characterized by X-ray photoelectron spectroscopy (XPS) and HRTEM. The sulfided samples were prepared by sulfiding the corresponding oxidic ones for 4 h with H<sub>2</sub> and 3 wt.% CS<sub>2</sub> in nheptane at 360 °C, 4 MPa, liquid hourly space velocity (LHSV) 1.5 h, and  $H_2/n$ -heptane 400 mL/mL. These samples were cooled to room temperature under N<sub>2</sub> atmosphere, ground, and kept in cvclohexane to prevent oxidation. XPS was performed on a VG ESCA Lab 250 spectrometer using Al K $\alpha$  radiation. Before XPS measurement, the sample was pressed onto a stainless steel sample holder in air, followed by mounting the holder on the XPS machine immediately. HRTEM was conducted on the above-mentioned instrument operated at 200 kV. Before HRTEM measurement, the ground sulfided sample was ultrasonically dispersed in ethanol, and the resultant suspension was dropped onto a carbon-coated Cu grid.

## 2.4. Hydrodesulfurization performance assessment

The HDS performance of the sulfided WMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and WMoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was evaluated in a continuously flowing microreactor using a model compound (1.0 wt.% DBT in *n*-heptane) and a fluid catalytic cracking (FCC) diesel as the feedstocks. The FCC diesel was kindly supplied by a Chinese refinery. The FCC diesel had its boiling point in the range 205–380 °C, density 0.874 g/cm<sup>3</sup>, and sulfur and nitrogen content 3904 and 1088 µg/g, respectively. Before catalytic evaluation, the oxidic catalyst precursors were presulfided with H<sub>2</sub> and 3 wt.% CS<sub>2</sub> in *n*-heptane at 360 °C, total pressure 6.0 MPa, H<sub>2</sub>/*n*-heptane 500 mL/mL, and LHSV 1.5 h<sup>-1</sup> for 4 h [18]. DBT HDS was performed at 330 °C, 4.0 MPa, H<sub>2</sub>/hydrocarbon 600 mL/mL, and LHSV 45 h<sup>-1</sup> [20], and the FCC diesel HDS was performed at 360 °C, 6.5 MPa, H<sub>2</sub>/oil 500 mL/mL, and LHSV 1.5 h<sup>-1</sup>.

The DBT HDS products were analyzed using a Finnigan Trace GC–MS installed with a capillary column (60 m × 0.2 mm). The HDS rate constant  $k_{\rm HDS}$  (mol g<sup>-1</sup> s<sup>-1</sup>) was acquired from the equation

$$k_{\rm HDS} = \frac{F}{m} \ln\left(\frac{1}{1-\tau}\right),\tag{1}$$

where *F* is the DBT feeding rate (mol/s), m is the catalyst mass (gram), and  $\tau$  is the DBT conversion [20,21]. HDS turnover frequencies (TOF, s<sup>-1</sup>) of WMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and WMoNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, i.e., the numbers of reacted DBT molecules per second and per catalytic site (per W/Mo atom at the edge of per MS<sub>2</sub> slab), were also calculated [22]. The proportion of W/Mo atoms at the edges of MS<sub>2</sub> slabs (denoted as *f*<sub>M</sub>) was found from the equation [23,24]

$$f_{M} = \frac{M_{\text{edge}}}{M_{\text{total}}} = \frac{\sum_{i=1,\dots,t} (6n_{i} - 6)}{\sum_{i=1,\dots,t} (3n_{i}^{2} - 3n_{i} + 1)},$$
(2)

in which  $M_{edge}$  is the number of W/Mo atoms at the edges,  $M_{total}$  is the total number of W/Mo atoms,  $n_i$  is the number of W/Mo atoms along one edge of a MS<sub>2</sub> slab obtained from its length  $(L = 3.2(2n_i - 1) \text{ Å})$ , and t is the total number of MS<sub>2</sub> slabs. The total sulfur and nitrogen contents were analyzed using a sulfur and nitrogen analyzer (RPP-2000SN, Taizhou Central Analytical Instruments Co., Ltd., People's Republic of China).

#### 3. Results and discussion

#### 3.1. The structure of Mo-HNCs and the deposition of HNCs on alumina

As shown in Fig. 1a and the inset, the Mo-HNCs we have synthesized are distributed around 2.5 nm in size, and each HNC particle consists of an inorganic core with lattice fringes and an organic shell with low contrast (Fig. 1b). The ICP and CHN analysis results show that the Mo-HNCs have the chemical composition  $C_{1.40}H_{3.50}$ -N<sub>0.18</sub>Mo<sub>0.52</sub>O<sub>1.66</sub>, which can be rounded to  $(C_8H_{20}N)_2Mo_6O_{19}$ , which is supported by thermogravimetric analysis, as seen in Fig. S1 in the Supplementary Information.

Fig. 2a shows that the FTIR spectrum of Mo-HNCs has IR bands centered at 1383, 1487, 1454, and 2986  $cm^{-1}$  attributed to TEA<sup>+</sup> cations [19], and IR bands  $(964-500 \text{ cm}^{-1})$  assigned to Mo = O and O-Mo-O in inorganic cores [25]. Fig. 2b displays that the Raman spectrum of Mo-HNCs has a band at  $207 \text{ cm}^{-1}$  (vs. 222 cm<sup>-1</sup> for AHM) ascribed to the deformation vibration of Mo-O-Mo, bands at 285, 334, 364, and 421 cm<sup>-1</sup> (vs. 307, 335, 363, and 449 cm<sup>-1</sup> for AHM) assigned to the bending vibrations of Mo = 0, bands at 590 and  $833 \text{ cm}^{-1}$  (vs. 550 and  $860 \text{ cm}^{-1}$  for AHM) attributed to the vibrations of Mo-O-Mo, and bands at 907, 939, 964, and 994 cm<sup>-1</sup> (vs. 935 cm<sup>-1</sup> for AHM, no bands corresponding to 907, 939, and 994  $cm^{-1}$ ) ascribed to the stretching vibrations of Mo=O [26]. Importantly, the bands at 672, 907. 939, and 964 cm<sup>-1</sup> are characteristic of  $Mo_6O_{19}^{2-}$ , and those at 1072 and 1118 cm<sup>-1</sup> are likely ascribed to C–C and C–N in TEA<sup>+</sup> [27], while those at 882 and 935 cm<sup>-1</sup> are typical for  $Mo_7O_{24}^{6-}$  in AHM [26,28,29].

These results verify that highly dispersed Mo-HNCs with uniform size have been successfully obtained. Similarly to W-HNCs we reported previously [19], Mo-HNCs ((TEA)<sub>2</sub>Mo<sub>6</sub>O<sub>19</sub>) also have a core–shell structure. We must point out that, differently from CTAB used for synthesizing (CTA)<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub> [18], the hybridization reagent TEAB we here exploit can be used for synthesizing both W- and Mo-HNCs without causing precipitation when coming into contact with the acidified Na<sub>2</sub>WO<sub>4</sub> solution.

The deposition of W- and Mo-HNCs into the pores of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was proved by the FTIR and Raman characterizations of the resulting WMo-HNCs-Al<sub>2</sub>O<sub>3</sub> composite. Fig. 2c shows that, compared with that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the spectrum of WMo-HNCs-Al<sub>2</sub>O<sub>3</sub> has additional peaks at 1383, 1454, 2843, and 2919 cm<sup>-1</sup> attributed to TEA<sup>+</sup> in HNCs [19,30]; Fig. 2d displays that the Raman spectrum of WMo-HNCs-Al<sub>2</sub>O<sub>3</sub> has bands at 1120, 1071, 994, 953, and 674 cm<sup>-1</sup> associated with dried W- and Mo-HNCs (Fig. S2a in the Supplementary Information) [19,26]. These results demonstrate that W- and Mo-HNCs are successfully deposited into pores of alumina, which is also proved by the N<sub>2</sub> physisorption results (Table S1 and Fig. S2b and S2c in the Supplementary Information).

## 3.2. Hydrodesulfurization on sulfided WMo/Al<sub>2</sub>O<sub>3</sub> and WMoNi/Al<sub>2</sub>O<sub>3</sub> catalysts

The DBT HDS results over WMo-IM, WMo-HHD, WMoNi-IM, and WMoNi-HHD are displayed in Table 1. Compared with WMo-IM and WMo-HHD, both WMoNi-IM and WMoNi-HHD have higher values of  $k_{\text{HDS}}$  and TOF. To compare the synergetic effect between Ni and W/Mo species in WMoNi-IM and WMoNi-HHD, the synergetic factor (SF), defined by the ratio of  $k_{\text{HDS}}$ (NiWMoS) to  $k_{\text{HDS}}$ (WMoS), was calculated [31]. The SF value (7.5) of WMoNi-HHD is much larger than that (4.6) of WMoNi-IM, demonstrating the much stronger synergetic effect among Ni and W/Mo species in WMoNi-HHD.

Over metal sulfide HDS catalysts, DBT is converted via two paths: a direct desulfurization (DDS) path that produces biphenyl



Fig. 1. TEM (a) and HRTEM (b) images of Mo-HNCs in the highly diluted suspension.



Fig. 2. FTIR (a and c) and Raman (b and d) spectra of the different samples.

#### Table 1

HDS activity and product selectivity of the sulfided catalysts.

Catalyst	$k_{\rm HDS} (10^{-7} { m mol}{ m g}^{-1}{ m s}^{-1})$	$TOF (10^{-4} \text{ s}^{-1})^{a}$	SF <sup>b</sup>	Product selectivity (%) <sup>c</sup>			
				THDBT + HHDBT	BP	CHB	DDS/HYD ratio <sup>d</sup>
WMo-HHD	0.55	2.21	-	18.1	47.1	34.8	1.35
WMo-IM	0.12	0.66	-	54.6	26.9	18.5	1.45
WMoNi-HHD	4.13	8.94	7.5	3.4	52.7	43.9	1.20
WMoNi-IM	0.55	2.76	4.6	29.2	40.3	30.5	1.32

<sup>a</sup> Number of desulfurized DBT molecules per second per M (M = W/Mo) atom at the edge.

<sup>b</sup> Synergetic factor (SF) =  $k_{HDS}$ (WMoNiS)/ $k_{HDS}$ (WMoS).

<sup>c</sup> Achieved at about 50% of total DBT conversion by changing the liquid hourly space velocity.

 $^{\rm d}\,$  Obtained by dividing the BP selectivity by the CHB selectivity.

(BP), and a hydrogenation (HYD) path that yields the intermediates tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT), followed by desulfurization generating cyclohexylbenzene (CHB) [32]. The ratio of BP selectivity to CHB selectivity is used to evaluate the DDS/HYD ratio [20,33]. The selectivities to the different HDS products and the DDS/HYD ratios are also listed in Table 1. For WMo-IM, WMo-HHD, WMoNi-HHD, and WMoNi-IM, the preferential route for HDS is the DDS one.

WMo-HHD has higher selectivity to both BP and CHB than WMo-IM, indicating that the HHD method can effectively increase the DDS and HYD activity. Significantly, the incorporation of Ni enhances both BP and CHB selectivity and dramatically decreases the DDS/HYD ratios for both WMo-IM and WMo-HHD (Table 1), with WMoNi-HHD having a lower DDS/HYD ratio and higher BP and CHB selectivity than WMoNi-IM. These results show that there exists a chemical synergism between the Ni and W/Mo species, which increases the BP and CHB selectivity considering the negligible HDS activity of the NiS<sub>x</sub> phase [34]. Importantly, we found that the chemical synergism among W/Mo and Ni species in WMoNi-HHD is much stronger [35], as reflected by its greatly decreased DDS/HYD ratio compared with that of WMoNi-IM.

The FCC diesel HDS performance of WMoNi-IM and WMoNi-HHD was also evaluated. During the 456 h running, the HDS activity of the two trimetallic catalysts remained stable (Fig. S3 in the Supplementary Information), with WMoNi-HHD giving a lower S content and higher HDS ratio than WMoNi-IM (Table 2). Considering the inhibiting effect of nitrogen-containing compounds on HDS, the hydrodenitrogenation (HDN) results of WMoNi-IM and WMoNi-HHD are listed in Table 2, showing that WMoNi-HHD has a higher HDN ratio than WMoNi-IM and WNi/MoNi-HHD.

The above results raise the question of why the trimetallic WMoNi-HHD shows enhanced synergetic effects and thereby demonstrates higher HDS and HDN activity than its counterpart WMoNi-IM, despite their having the same W/Mo/Ni content. To answer this question, characterizations were conducted to investigate the morphology, reducibility, and sulfidability properties of the W/Mo/Ni species over the oxidic WMo and WMoNi catalysts and the morphology of  $MS_2$  (M = W/Mo) phases over the sulfided WMo and WMoNi catalysts.

### 3.3. Synergisms in the trimetallic catalysts

# 3.3.1. Morphology and reducibility of W/Mo/Ni species over the oxidic trimetallic catalysts

Fig. 3 shows that the XRD pattern of WMoNi-IM has peaks at  $2\theta = 12.8^{\circ}, 23.5^{\circ}, 27.4^{\circ}, \text{ and } 33.8^{\circ}, \text{ ascribed to the bulk MoO}_3 \text{ phase}$ (PDF No. 05-0506), indicating the existence of larger MoO<sub>3</sub> crystallites in the sample; meanwhile, the formation of bulk WO<sub>3</sub> crystallites is possible, since their characteristic peaks are at around 23.5° and 33.5° (PDF No. 43-1035). However, these peaks are absent in the XRD pattern of WMoNi-HHD, indicating higher W and Mo dispersion. To explore the W/Mo/Ni distribution in WMoNi-HHD and WMoNi-IM, a HAADF-STEM analysis was made and the results are presented in Fig. 4. The energy-dispersive X-ray (EDX) spectra of WMoNi-HHD and WMoNi-IM give similar WO<sub>3</sub> content (ca. 13.0 wt.%) and W/Mo (ca. 1.0) and Ni/(W + Mo) (ca. 0.53) molar ratios, coincident with the feeding atomic ratio of W, Mo, and Ni. The mapping images of W, Mo, and Ni show that, compared to those in WMoNi-IM (Fig. 4b), the metal (W/Mo/Ni) species in WMoNi-HHD (Fig. 4a) are more uniformly distributed on the alumina surface and more intimately contacted.

The H<sub>2</sub>-TPR profiles (Fig. 5) of the two oxidic WMoNi catalysts have the low- and high-temperature peaks associated with the first-step reduction (from M<sup>6+</sup> to M<sup>4+</sup>, M = W/Mo) of polymeric  $MO_x$  and the deep metal reduction (from M<sup>6+</sup> or M<sup>4+</sup> to M<sup>0</sup>, M = W/Mo), respectively [18,20,36–38]. Compared with those of WMo-IM and WMo-HHD, both the low- and high-temperature peaks of WMoNi-IM and WMoNi-HHD shift to lower temperatures, indicating promoted W/Mo reduction by Ni incorporation [19]. The larger difference in the high-temperature peaks (31 vs. 16 °C) of WMoNi-HHD and WMo-HHD than of WMoNi-IM and WMo-IM indicates the more pronounced W/Mo reduction of Ni incorpora-

Table 2		
FCC diesel HDS	HDN results of the sulfided catalyst	s.



Fig. 3. XRD patterns of the different samples: (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) WMo-IM, (c) WMo-HHD, (d) WMoNi-IM, and (e) WMoNi-HHD.

tion on WMo-HHD than on WMo-IM. Moreover, compared with WMoNi-IM, WMoNi-HHD has higher  $H_2$  consumption in the high-temperature region, which implies its higher  $WO_x$  and  $MOO_x$  content with higher reducibility, including octahedral ( $O_h$ ) Mo and W species [22,39]. Worthy of mention is that in the low-temperature region, compared with WMoNi-HHD, WMoNi-IM has a lower reduction temperature and a higher  $H_2$  consumption. There are two possible reasons for this phenomenon. One is that the poorly dispersed and segregated Ni species in WMoNi-IM (supported by the lower Ni/Al ratio in the XPS results below) have higher reducibility [19,40]; the other is that WMoNi-IM has a larger number of poorly dispersed octahedrally coordinated polymetalates originated from the polymerized nature of W/Mo precursors and metal oxide crystallites with distorted  $O_h$  coordination, which were detected by XRD and possess higher reducibility [38].

These results demonstrate that, in WMoNi-HHD, W, Mo and Ni species are highly dispersed and in intimate contact, and can generate highly dispersed W/Mo/Ni oxide species with high reducibility and sulfidability and thereby induce both textural and chemical synergisms among the resultant sulfide species.

#### 3.3.2. Textural synergism

Fig. 6 shows the W4f and Mo3d XPS spectra of sulfided WMoNi-IM and WMoNi-HHD. The binding energies of different levels  $(W4f_{7/2}, W4f_{5/2}, Mo3d_{5/2}, and Mo3d_{3/2})$  for M<sup>4+</sup> (MS<sub>2</sub>), M<sup>5+</sup> (MO<sub>x</sub>S<sub>y</sub>), and M<sup>6+</sup> (MO<sub>3</sub>) (M = W/Mo) have been listed in the literature [19,22,37]. The metal sulfidation degrees (M<sub>sulfidation</sub> (M = W/Mo)) are the ratios of M<sup>4+</sup> to the sum of M<sup>4+</sup>, M<sup>5+</sup> and M<sup>6+</sup>, i.e., M<sub>sulfidation</sub> = M<sup>4+</sup>/(M<sup>4+</sup> + M<sup>5+</sup> + M<sup>6+</sup>) [22]. The values of W<sub>sulfidation</sub> and Mo<sub>sulfidation</sub> of oxidic WMo/Al<sub>2</sub>O<sub>3</sub> and WMoNi/Al<sub>2</sub>O<sub>3</sub>, and the surface W/Al, Mo/Al and Ni/Al atomic ratios of W<sub>sulfidation</sub> and WMoNi-HHD are displayed in Table 3. The values of W<sub>sulfidation</sub>

Catalyst	Content in feedstock (µg/g)		Content in product (µg/g)		Ratio (%)	
	S	Ν	S	N	HDS	HDN
WMoNi-HHD	2004	1000	18.0	96.3	99.5	91.2
WMONI-IM WNi/MoNi-HHD	3904	1088	98.7 32.9	143.2 106.4	97.5 99.2	86.8 90.2



**Fig. 4.** HAADF-STEM images of WMoNi-HHD (a) and WMoNi-IM (b). The insets are the EDX spectra and the element mapping images of Al (orange), O (red), W (orchid), Mo (green), and Ni (yellow), illustrating the element distributions for the areas highlighted by the red squares. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. TPR profiles of alumina-supported WMo and WMoNi catalysts.

and Mo<sub>sulfidation</sub> (44.5% and 58.3% and 34.3% and 53.5%) of WMoNi-HHD and WMoNi-IM are much higher than those of WMo-HHD and WMo-IM, with WMoNi-HHD having higher values of W<sub>sulfidation</sub> and Mo<sub>sulfidation</sub> than WMoNi-IM; moreover, WMoNi-HHD has higher surface W/Al, Mo/Al, and Ni/Al atomic ratios than WMoNi-IM despite their having the same W/Mo/Ni content, suggesting that WMoNi-HHD has higher W/Mo/Ni dispersion. This demonstrates the textural synergism among the metal sulfide phases, since the Ni incorporation increases the amount of  $MS_2$  phases, and more  $MS_2$  phases lead to an increased number of  $NiS_x$  species dispersed on the edges of the  $MS_2$  slabs [11].

The lengths ( $\overline{L}$ ) of the MS<sub>2</sub> slabs over the sulfided WMo and WMoNi catalysts were acquired from statistical analyses of about 30 representative micrographs containing 300–500 MS<sub>2</sub> slabs [24]. Compared with WMo-HHD, WMoNi-HHD has a shorter  $\overline{L}$  (decreased by 20.8%) and a higher  $f_M$  (increased by 40.0%); compared with WMo-IM, WMoNi-IM also has a shorter  $\overline{L}$  (decreased by 6.1%) and a higher  $f_M$  (increased by 6.7%) (Table 3). This indicates that the influences of Ni incorporation in increasing the amount of W<sub>x</sub>Mo<sub>1-x</sub>S<sub>2</sub> phases and the number of edge sites are much stronger for WMo-HHD than for WMo-IM. Taking the sulfidability properties and surface metal ratios of WMoNi-IM and WMoNi-HHD into account, WMoNi-HHD has more conspicuous textural synergism among W, Mo, and Ni species than WMoNi-IM [35].

## 3.3.3. Chemical synergism

According to Nair et al. [41], for alumina-supported oxidic WO<sub>3</sub>/ MoO<sub>3</sub> catalysts, when the surface W/Mo concentration was higher than 2 atoms/nm<sup>2</sup>, the molecularly and electronically mixed  $WO_x/$ MoO<sub>x</sub> phase was formed on the alumina surface. WMoNi-HHD has a surface metal (W and Mo) concentration of 2.9 atoms/nm<sup>2</sup>, signifying the possibility of chemical (electronic) interaction between W and Mo; combining the HAADF-STEM results, it is suggested that after sulfidation the Ni-W-Mo-O species existing in WMoNi-HHD could generate NiWMoS phases with chemical synergism between  $W_x Mo_{1-x}S_2$  and nickel sulfide [42]. As demonstrated in Section 3.2, the possible existence of chemical synergism among W/Mo species and Ni can be well corroborated by comparing BP and CHB selectivity and DDS/HYD ratios of the WMo and WMoNi catalysts. It is known that the chemical synergism among W/Mo species and Ni signifies the formation of a NiWS, NiMoS, or NiWMoS phase over the supported WMoNi catalysts, whereas the higher HDS activity of WMoNi-HHD than of WNi/MoNi-HHD with the same W/Mo/Ni content indicates that in WMoNi-HHD there exist NiWMoS phases having  $\Delta E_{MS}$  closer to the volcano curve's maximum [9,42]. Compared with WMoNi-IM, WMoNi-HHD has much higher selectivity to BP and CHB but much lower selectivity to THDBT and HHDBT, thus giving a lower DDS/HYD ratio (Table 1). This indicates that the active phases over the two trimetallic catalysts have guite different structures and thus show quite different reaction paths for DBT HDS. Moreover, as seen in Fig. 7, the MS<sub>2</sub> slab lengths of WNi/MoNi-HHD obtained by mechanically mixing WNi-HHD and MoNi-HHD are broadly distributed between 3 and 8 nm; in contrast, the MS<sub>2</sub> slabs on WMoNi-HHD are finely dispersed with a narrower length distribution (3–5 nm). This agrees with the results of Thomazeau et al., who made a comparison between alumina-supported trimetallic NiWMoS phases and alumina-supported bi-metallic NiWS and NiMoS phases [8], further suggesting that most MS<sub>2</sub> phases on WMoNi-HHD are NiWMoS ones [42]. For WMoNi-IM, although it has the same surface W/Mo concentration as WMoNi-HHD, the poor W/Mo dispersion and sulfidability of WMo-IM result in fewer MS<sub>2</sub> slabs with fewer edge sites for accommodating Ni (Fig. 7 and Table 3), which is unfavorable for chemical synergism among W, Mo, and Ni. It should be noticed that the metal sulfide slabs over both WMoNi-HHD and WMoNi-IM are highly stacked (Fig. 7), possessing the same average stacking layer number (2.3). These results demonstrate that the superior HDS performance of WMoNi-HHD originates from stronger textural and chemical synergisms.



Fig. 6. Mo3d and W4f XPS spectra of the sulfided catalysts: (a) WMoNi-IM, and (b) WMoNi-HHD.

## Table 3 XPS and HRTEM characterization results of the sulfided catalysts.

Sample	Surface atomic ratio and sulfidation degree					MS <sub>2</sub> morphology parameter	
	W/Al <sup>a</sup>	Mo/Al <sup>a</sup>	Ni/Al <sup>a</sup>	$Mo_{sulfidation}/\%$	W <sub>sulfidation</sub> /%	$\overline{L}^{\mathrm{b}}$	$f_{M}{}^{c}$
WMo-HHD	0.040	0.036	-	49.2	30.5	5.3	0.20
WMo-IM	0.026	0.024	-	44.7	25.3	6.6	0.15
WMoNi-HHD	0.045	0.035	0.043	58.3	44.5	4.2	0.28
WMoNi-IM	0.033	0.021	0.030	53.5	34.3	6.2	0.16
WMONI-HHD WMoNi-IM	0.045	0.035	0.043	58.3 53.5	44.5 34.3	4.2 6.2	0.28 0.16

<sup>a</sup> Surface atomic ratio of the catalysts.

<sup>b</sup> Mean length (nm) of MS<sub>2</sub> (M = W/Mo) on the catalysts.

<sup>c</sup> Proportion of M atoms at the edge.

#### 3.4. Origin of the synergisms in the trimetallic WMoNi catalysts

WMoNi-IM and WMoNi-HHD have the same W/Mo/Ni content, and Ni in them is incorporated by the same method (IM); the only difference lies in the use of different W/Mo precursors and different loading methods—WMoNi-IM is derived from WMo-IM prepared using  $(NH_4)_6W_7O_{24}\cdot 6H_2O$  and  $(NH_4)_6MO_7O_{24}\cdot 4H_2O$  as the W and Mo precursors and the IM method, while WMoNi-HHD is derived from WMo-HHD prepared using W- and Mo-HNCs as the W/Mo precursors and the HHD method. To understand the origin of the synergisms in the trimetallic WMoNi catalysts, the properties of WMo-IM and WMo-HHD are characterized.

Similar to that of WMoNi-IM, the XRD pattern of WMo-IM (Fig. 3) has peaks ascribed to the bulk MoO<sub>3</sub> (WO<sub>3</sub>) phase, whereas these peaks are absent in that of WMo-HHD, indicating higher W and Mo dispersion in WMo-HHD. The N<sub>2</sub> physisorption results also show that, compared with WMo-IM, WMo-HHD has a larger surface area (198.2 vs. 173.7 m<sup>2</sup>/g) and a larger pore volume (0.46 vs. 0.43 mL/g) (Table S1 in the Supplementary Information). The DRS UV–vis results (Fig. S4 in the Supplementary Information) show that WMo-HHD has a higher band-gap energy ( $E_g$ ) (3.6 vs. 3.4 eV) than WMo-HHD [15].

The H<sub>2</sub> TPR profiles of the oxidic WMo catalysts (Fig. 5) show that WMo-HHD has a lower high- temperature peak (956 vs. 970 °C) than WMo-IM, indicating higher W/Mo reducibility in WMo-HHD due to the separating effect of TEA<sup>+</sup>s between the Mo<sub>6</sub>- $O_{19}^2/W_6O_{19}^2$  and the support; a small shoulder peak starting from 830 °C in the TPR profile of WMo-HHD implies the existence of O<sub>h</sub> tungsten species [39]; and the increased peak area (H<sub>2</sub> consumption) of WMo-HHD than of WMo-IM in the hightemperature region demonstrates the formation of more highly reducible W/Mo species in the former. The W4*f* and Mo3*d* XPS spectra of sulfided WMo-IM and WMo-HHD are displayed in Fig. S5 in the Supplementary Information. Both W<sub>sulfidation</sub> and Mo<sub>sulfidation</sub> (30.5% and 49.2%) of WMo-HHD are higher than those of WMo-IM (25.3% and 44.7%) (Table 3), which results from the higher W/Mo reducibility of WMo-HHD, as described above. WMo-HHD has higher W/Al and Mo/Al atomic ratios than WMo-IM despite their having the same W/Mo content (Table 3), suggesting that WMo-HHD has higher metal (W and Mo) dispersion. The HRTEM micrographs (Fig. S6 in the Supplementary Information) and the statistical results (Table 3) of sulfided WMo-IM and WMo-HHD show that, in comparison to WMo-IM, WMo-HHD possesses a higher  $f_M$  (0.20 vs. 0.15) and a smaller average MS<sub>2</sub> length  $\overline{L}$  (5.3 vs. 6.6 nm) with a narrower distribution (Fig. S6 in the Supplementary Information), indicating that WMo-HHD has more W<sub>x</sub>-Mo<sub>1-x</sub>S<sub>2</sub> phases and edge sites [22].

Therefore, the superior synergetic effects among W, Mo, and Ni species in WMoNi-HHD benefit from two aspects: (1) the exploitation of W- and Mo-HNCs as W/Mo precursors in which TEA<sup>+</sup> cations exert a separating effect and decrease the interaction between  $W_6O_{19}^{2}/Mo_6O_{19}^{2}$  and the alumina surface; and (2) the use of hydrothermal deposition, which leads to the uniform distribution of W- and Mo-HNCs. These two aspects result in the superior W/Mo dispersion and high W/Mo reducibility and sulfidability in the resultant oxidic WMo-HHD catalyst and thereby provide the prerequisites for generating both textural and chemical synergisms in the resulting trimetallic WMoNi-HHD catalyst [7,16,18,20].

The different structures of active phases in the above WMo and WMoNi catalysts are schematically illustrated in Fig. 8. For WMo-IM (Fig. 8a), the strong interaction between the polyoxometalate anions and the alumina surface causes lower W/Mo dispersion and poorer sulfidability and thereby the formation of oxysulfidic  $MO_xS_y$  (M = W/Mo) and poorly dispersed sulfide slabs with large size. For WMoNi-IM (Fig. 8c), which is prepared by incorporating Ni into WMo-IM, the poorly dispersed W and Mo species with low sulfidability in WMo-IM cannot provide edge sites enough to accommodate Ni species to form a NiWMoS phase with desirable synergetic effects. Conversely, for WMo-HHD (Fig. 8b), the simulta-



Fig. 7. HRTEM images and length distributions of MS<sub>2</sub> (M = W/Mo) slabs on sulfided WMoNi-IM (a1 and a2), WMoNi-HHD (b1 and b2), and WNi/MoNi-HHD (c1 and c2).



Fig. 8. Schematic representation of the composition and structure of the active phases over WMo-IM (a), WMo-HHD (b), WMoNi-IM (c), and WMoNi-HHD (d).

neous deposition of W- and Mo-HNCs onto the  $Al_2O_3$  surface through the hydrothermal treatment generates intimately contacting W and Mo species with fine dispersion and high sulfidability, resulting in more  $W_xMo_{1-x}S_2$  phases in WMo-HHD. For WMoNi-HHD (Fig. 8d), which is prepared by incorporating Ni into WMo-HHD, the intimately contacting W and Mo species with fine W/Mo dispersion and sulfidability in WMo-HHD provide adequate edge sites to accommodate Ni species [8,9,43], generating NiWMoS phases with both textural and chemical synergisms in the resulting WMoNi-HHD catalyst [7,16]. Worthy of mention is that the superior HYD and HDN activities of the synergetic NiWMoS phases would attenuate the inhibiting effect of nitrogen-containing compounds on HDS and favor the removal of DBT-type molecules and thus ultra-deep HDS performance [37,42,44].

As stated in the Introduction, many researches have attempted to enhance the HDS performance of WMoNi/Al<sub>2</sub>O<sub>3</sub> catalysts by

improving the W/Mo dispersion and/or sulfidability. However, due to the strong interaction between the conventional W/Mo precursors (polyoxomolybdates or polyoxotungstates) and the alumina surface, W/Mo species with poor dispersion or sulfidability are formed, which is unfavorable for the textural and chemical synergisms between  $W_x Mo_{1-x}S_2$  and NiS<sub>x</sub>. In this work, TEAB are used for synthesizing a suspension containing both W- and Mo-HNCs, and the resultant HNCs are simultaneously deposited onto alumina to prepare trimetallic WMoNi/Al<sub>2</sub>O<sub>3</sub> catalysts. The superior dispersion and sulfidability of intimately contacted W and Mo species in WMoNi-HHD are fully in compliance with the prerequisites for inducing synergetic effects among the sulfide phases, resulting in the superior performance of the trimetallic WMoNi-HHD catalyst.

### 4. Conclusions

W- and Mo-HNCs with  $W_6O_{19}^{2-}/Mo_6O_{19}^{2-}$  and TEA<sup>+</sup>s as the core and shell, respectively, have been obtained with TEAB as the hybrid reagent and are used as the W/Mo precursors for preparing a trimetallic WMoNi/Al<sub>2</sub>O<sub>3</sub> catalyst. Both textural and chemical synergisms exist in the HHD-derived WMoNi-HHD, which benefits from the exploitation of the HNC precursors that decrease the interaction between  $W_6O_{19}^{2-}/Mo_6O_{19}^{2-}$  and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface and the use of the hydrothermal deposition that brings about the uniform distribution of HNCs. The resultant catalyst precursor WMo-HHD has highly dispersed, highly reducible, and highly sulfidable W/Mo species and thus more W<sub>x</sub>Mo<sub>1-x</sub>S<sub>2</sub> phases with increased capability for accommodating NiS<sub>x</sub> at the edges of sulfide slabs, which provides the prerequisites for generating both textural and chemical synergisms in the resultant trimetallic WMoNi/Al<sub>2</sub>O<sub>3</sub> catalvst. This work opens a novel route for enhancing the synergetic effect among W, Mo, and Ni species in supported WMoNi catalysts with dramatically improved ultra-deep HDS performance.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.09.019.

#### References

136.

- [1] P. Castillo-Villalón, J. Ramirez, J.A. Vargas-Luciano, J. Catal. 320 (2014) 127-
- [2] N.-Q. Bui, C. Geantet, G. Berhault, J. Catal. 330 (2015) 374-386.

- [3] H. Wu, A. Duan, Z. Zhao, T. Li, R. Prins, X. Zhou, J. Catal. 317 (2014) 303-317.
- [4] H. Song, J. Wang, Z. Wang, H. Song, F. Li, Z. Jin, J. Catal. 311 (2014) 257-265.
- [5] L. Yang, X. Li, A. Wang, R. Prins, Y. Chen, X. Duan, J. Catal. 330 (2015) 330-343.
- [6] J.A. Mendoza-Nieto, O. Vera-Vallejo, L. Escobar-Alarcón, D. Solís-Casados, T. Klimova, Fuel 110 (2013) 268-277.
- [7] M.E. Cervantes-Gaxiola, M. Arroyo-Albiter, A. Pérez-Larios, P.B. Balbuena, J. Espino-Valencia, Fuel 113 (2013) 733-743.
- C. Thomazeau, C. Geantet, M. Lacroix, M. Danot, V. Harle, Oil Gas Sci. Technol. [8] 60 (2005) 781-790.
- [9] C. Thomazeau, C. Geantet, M. Lacroix, M. Danot, V. Harlé, P. Raybaud, Appl. Catal. A Gen. 322 (2007) 92-97.
- [10] S. Sigurdson, V. Sundaramurthy, A.K. Dalai, J. Adjaye, J. Mol. Catal. A Chem. 291 (2008) 30-37.
- [11] M. Zdražil, Catal. Today 3 (1988) 269-365.
- [12] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, J. Catal. 187 (1999) 109-122.
- 13] H. Topsøe, B.S. Clausen, Catal. Rev. 26 (1984) 395-420.
- [14] R. Huirache-Acuña, B. Pawelec, C.V. Loricera, E.M. Rivera-Muñoz, R. Nava, B. Torres, J.L.G. Fierro, Appl. Catal. B Environ. 125 (2012) 473-485
- [15] J.A. Mendoza-Nieto, F. Robles-Méndez, T.E. Klimova, Catal. Today 250 (2015) 47-59.
- [16] S.L. González-Cortés, S. Rugmini, T. Xiao, M.L.H. Green, S.M. Rodulfo-Baechler, F.E. Imbert, Appl. Catal. A Gen. 475 (2014) 270–281.
- [17] T. Alphazan, A. Bonduelle-Skrzypczak, C. Legens, Z. Boudene, A.-L. Taleb, A.-S. Gay, O. Ersen, C. Copéret, P. Raybaud, J. Catal. 340 (2016) 60-65.
- [18] W. Han, P. Yuan, Y. Fan, G. Shi, H. Liu, D. Bai, X. Bao, J. Mater. Chem. 22 (2012) 25340-25353.
- [19] S. Shan, P. Yuan, W. Han, G. Shi, X. Bao, J. Catal. 330 (2015) 288-301.
- [20] Y. Fan, H. Xiao, G. Shi, H. Liu, X. Bao, Energy Environ. Sci. 4 (2011) 572–582.
- [21] D. Laurenti, B. Phung-Ngoc, C. Roukoss, E. Devers, K. Marchand, L. Massin, L. Lemaitre, C. Legens, A.A. Quoineaud, M. Vrinat, J. Catal. 297 (2013) 165-175.
- [22] A. Duan, T. Li, Z. Zhao, B. Liu, X. Zhou, G. Jiang, J. Liu, Y. Wei, H. Pan, Appl. Catal. B Environ. 165 (2015) 763-773.
- [23] A. Romero-Galarza, A. Gutiérrez-Alejandre, J. Ramírez, J. Catal. 280 (2011) 230-238.
- [24] E.J.M. Hensen, P.J. Kooyman, Y. van der Meer, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen, R.A. van Santen, J. Catal. 199 (2001) 224-235.
- [25] X. Wang, Y. Guo, Y. Li, E. Wang, C. Hu, N. Hu, Inorg. Chem. 42 (2003) 4135-4140.
- [26] G. Mestl, T.K.K. Srinivasan, Catal. Rev. 40 (1998) 451-570.
- [27] B. Ingham, S.V. Chong, J.L. Tallon, J. Phys. Chem. B 109 (2005) 4936–4940.
- [28] G. Davidson, Spectrosc. Prop. Inorg. Organomet. Compounds 38 (2006) 241-283.
- [29] I. Shiyanovskaya, H. Ratajczak, J. Baran, M. Marchewka, J. Mol. Struct. 348 (1995) 99 - 102
- [30] K.-H. Schnabel, G. Finger, J. Kornatowski, E. Löffler, C. Peuker, W. Pilz, Micropor. Mater. 11 (1997) 293-302.
- [31] T.K.T. Ninh, L. Massin, D. Laurenti, M. Vrinat, Appl. Catal. A Gen. 407 (2011) 29-39
- [32] M. Egorova, R. Prins, J. Catal. 225 (2004) 417-427.
- [33] P.A. Nikulshin, D.I. Ishutenko, A.A. Mozhaev, K.I. Maslakov, A.A. Pimerzin, J. Catal. 312 (2014) 152-169.
- [34] M.V. Landau, L. Vradman, M. Herskowitz, Y. Koltypin, A. Gedanken, I. Catal, 201 (2001) 22-36.
- [35] M. Zdrazil, Bull. Soc. Chim. Belg. 100 (1991) 769-780.
- [36] B. Scheffer, P. Molhoek, J.A. Moulijn, Appl. Catal. 46 (1989) 11-30. [37] Y. Fan, H. Xiao, G. Shi, H. Liu, Y. Qian, T. Wang, G. Gong, X. Bao, J. Catal. 279
- (2011) 27-35. [38] D.C. Vermaire, P.C. van Berge, J. Catal. 116 (1989) 309-317.
- [39] C. Martín, G. Solana, P. Malet, V. Rives, Catal. Today 78 (2003) 365-376. [40] A.V. Mozhaev, P.A. Nikulshin, A.A. Pimerzin, K.I. Maslakov, A.A. Pimerzin, Catal.
- Today 271 (2016) 80-90. [41] H. Nair, M.J. Liszka, J.E. Gatt, C.D. Baertsch, J. Phys. Chem. C 112 (2008) 1612-
- 1620. [42] L. van Haandel, M. Bremmer, P.J. Kooyman, J.A.R. van Veen, T. Weber, E.J.M. Hensen, ACS Catal, 5 (2015) 7276-7287.
- [43] T.E. Klimova, D. Valencia, J.A. Mendoza-Nieto, P. Hernández-Hipólito, J. Catal. 304 (2013) 29-46
- [44] I. Wang, R.C. Chang, J. Catal. 117 (1989) 266-274.