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Effect of pressure on the sulfidation behavior of NiW catalysts: A ^{182}W Mössbauer spectroscopy study

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ABSTRACT

The sulfidation of Al_2O_3- and ASA-supported NiW catalysts under conditions relevant to industrial practice was studied for the first time by ^{182}W Mössbauer spectroscopy. Only limited number of ^{182}W Mössbauer experiments have been performed previously, mainly due to the need of having specialized equipment for such measurements. ^{182}W MAS can clearly distinguish between WO_3- and WS_2-type phases encountered in the calcined and sulfided forms of W-based hydrotreating catalysts. NiW/Al_2O_3 catalysts are more difficult to sulfide than their Mo-based counterparts and, hence, intermediate stages of sulfidation can be studied as separate phases. At low sulfidation rates, an intermediate WS_3-type phase is identified at temperatures as high as 673 K. The presence of Ni atoms facilitates sulfidation and in this case the formation of an oxysulfidic intermediate is observed. Sulfidation at 673 K and 0.1 MPa leads to a poorly crystalline WS_2 phase, whereas subsequent sulfidation at 4.0 MPa results in the development of better-defined WS_2 structures. The merits of ^{182}W Mössbauer spectroscopy to study W-based hydrotreating catalysts are discussed.

1. Introduction

The metal combination used for hydrotreating catalysts mainly depends on the reaction and process requirements. In order to comply with the more stringent fuel specifications, the removal of alkylated dibenzothiophenes, the most abundant refractory sulfur compounds in gas oil, needs to be achieved, and consequently better performing hydrodesulfurization (HDS) catalysts are required. NiW/Al_2O_3 catalysts exhibit a higher hydrogenation activity than NiMo- and CoMo-based ones and are promising for the deep HDS of diesel [1].

In sulfided NiW catalysts, the active phase is thought to be similar to that in sulfided CoMo catalysts [2,3]. In analogy with the Co–Mo–S phase, the active phase in sulfided NiW catalysts consists of small Ni-sulfide particles adsorbed to the edges of WS_2 slabs. Type I and Type II Ni–W–S species were also distinguished in these catalysts [4,5], with a Type I phase being obtained after low temperature sulfidation with high hydrogenation (HYD) activity and a Type II phase with high HDS activity upon more complete sulfidation [5].

From a scientific point of view, the sulfidation of NiW/Al_2O_3 catalysts is interesting, since the transformation of the oxidic precursor to the active sulfided state is more difficult than for their Mo-based counterparts and, hence, intermediate stages of sulfidation can be studied as separate phases [6]. The sulfidation degree of the tungsten atoms, which depends on the preparation procedure and the sulfidation conditions, influences the catalytic performance of NiW catalysts strongly [7,8]. Therefore, these catalysts are often characterized by stepwise sulfidation to follow the formation of the active phase from the oxidic precursors.

High catalytic activity was reported for an amorphous silica-alumina (ASA) NiW in the HDS of dibenzothiophenes (DBTs), making it an interesting candidate for deep HDS applications [9]. The NiW/ASA catalysts are also excellent for first stage hydrocracking [27]. The ASA support usually contains, apart from the ASA proper, also a separate alumina phase (*e.g.*, as a binder), on which the tungstate preferentially adsorbs [10]. NiW/ASA is a better catalyst than NiW/Al_2O_3 for the HDS of substituted DBT because of its higher hydrogenation ability, and also its H_2S tolerance is much higher [11].

As the active sites of the catalysts are in a dynamic equilibrium with their environment, it is important to perform characterization studies under conditions (temperature, pressure) as close as possible to those of the catalyst in the working state [12]. Mössbauer spectroscopy is one of the few techniques that provide

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the possibility to perform characterization studies on such conditions. During the last three decades, Mössbauer spectroscopy has played an important role in the characterization of HDS catalysts [13]. Most of these investigations have been performed at ambient conditions, while in industrial practice sulfidation is carried out at elevated pressures. The use of Mössbauer spectroscopy for characterization of NiW catalysts was limited to the study of the sulfidation of Ni atoms by doping the NiW catalysts with ^{57}Co or ^{57}Fe [14].

Lee et al. [15] were the first to observe the Mössbauer effect in tungsten in 1959. Since then, only a limited number of ^{182}W Mössbauer experiments have been performed, mainly due to the special laboratory requirements for such measurements. Most notable is the high energy of the ^{182}W Mössbauer transition, which necessitates cooling both the source and the absorber to liquid helium temperature to obtain a measurable resonant absorption. Some ^{182}W Mössbauer absorption spectroscopy (MAS) experiments were carried out previously using standard absorbers like WSe_2 [16], WO_3 and other tungstates [17–19], WS_2 [17], WS_3, W_2C, and W_2N [20]. Here, the first ^{182}W Mössbauer study of supported NiW is presented. The objectives of this study were to find out whether ^{182}W Mössbauer spectroscopy is useful to elucidate the differences between low- and high-pressure sulfidation and whether it provides a clue to the enhanced hydrogenation activity of NiW on amorphous silica-alumina as compared to γ-alumina.

2. Experimental

Seven alumina-supported catalysts (γ-Al_2O_3, Ketjen CK300, BET surface area 263 $m^2\,g^{-1}$, pore volume 0.66 $ml\,g^{-1}$, particle size 0.125–0.250 mm), prepared in earlier studies [8,14] were used as received. The catalysts were prepared by pore volume co-impregnation with aqueous solutions of nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$ (Aldrich p.a.) and ammonium metatungstate $(NH_4)_6W_{12}O_{39}{\cdot}xH_2O$ (Aldrich p.a.). The tungstate concentration was chosen such as to result in a final catalyst loading (L) of 15.2 wt.% W. All catalysts were dried in static air at 383 K overnight and subsequently calcined at 673 or 823 K for 2 h. The catalysts are denoted by (Ni)W(L)/Al_2O_3-T_c, where T_c refers to the calcination temperature. The Ni/W atomic ratio employed is also given in the catalyst denotation. Two ASA-supported samples calcined at 723 K, having 19 wt.% W and a Ni/W atomic ratio of about 0.6 at/at, were obtained from Shell (SRTCA, Amsterdam). One ASA support is a more acidic variation of the other and is denoted as ASA+.

The catalysts were sulfided in a flow of 60 $cm^3\,min^{-1}$ of 10% H_2S/H_2 mixture at pressures of 0.1 or 4 MPa in an *in situ* high-pressure Mössbauer cell. This state-of-the-art cell was designed and manufactured at the Reactor Institute Delft specifically to carry out ^{182}W MAS measurements. Catalyst samples can be sulfided at temperatures and pressures relevant to industrial operation, while subsequent MAS measurements can be carried out at cryogenic temperatures as low as 4.2 K. The samples were heated at a rate of 6 $K\,min^{-1}$ to the indicated temperature followed by an isothermal period of 2 h.

The ^{182}W MAS spectra were recorded at liquid helium temperature using a ^{182}Ta in Ta metal source, which was moved in a sinusoidal mode. The source was prepared at the Reactor Institute Delft by irradiating metallic Ta with thermal neutrons. The transmitted radiation was recorded with a high-purity Ge detector and stored in a 1024-channel analyzer. A metallic Fe foil was used for velocity calibration with a ^{57}Co:Rh source. The spectra were analyzed by least-squares fit methods with a proper set of Lorentzian-shape lines. For the ^{182}W MAS spectra a standard deviation of 0.2 and 0.4 $mm\,s^{-1}$ was found for the quadrupole splitting (Q.S.) and line widths (Γ), respectively. The absolute standard deviation of the spectral contribution (*A*) was about 15%.

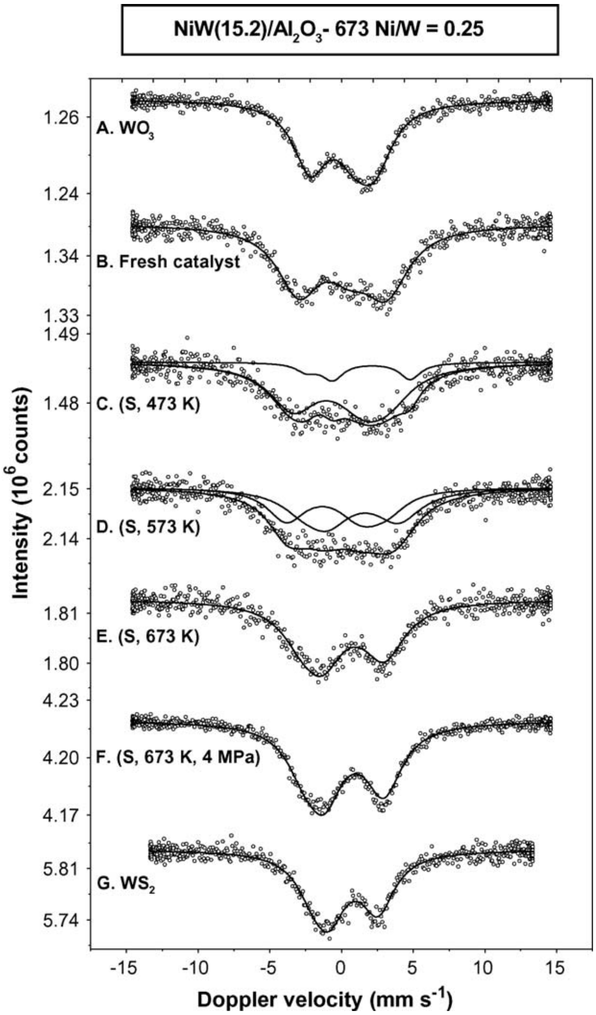

Fig. 1. ^{182}W Mössbauer spectra of WO_3, WS_2 and NiW(15.2)/Al_2O_3-673 Ni/W = 0.25 – after various successive sulfidation steps.

3. Results and discussion

Fig. 1 shows the ^{182}W MAS spectra of NiW(15.2)/Al_2O_3-673 Ni:W = 0.25 upon stepwise sulfidation at atmospheric pressure, followed by sulfidation at high-pressure at the final temperature. The corresponding fit parameters are presented in Table 1. The ^{182}W MAS spectra of WO_3 (Aldrich p.a.) and WS_2 (Aldrich p.a.) are also presented. The tungsten atoms in WO_3 are in a distorted octahedral environment (ReO_3 type [16]), implying an irregular coordination of oxygen to the tungsten atoms reflected by the large Q.S. and the intermediate asymmetry parameter (η) [20]. The measured values are similar to the ones reported earlier [18,19]. Because of the relatively short lifetime of the 100 keV transition of ^{182}W, resulting in a broad natural line width ($\Gamma \sim 2.0\,mm\,s^{-1}$), accurate determination of isomer shifts is difficult [19].

The spectrum of the fresh catalyst resembles that of WO_3, indicating the presence of tungsten oxide phase. The large Q.S. and η values point to the existence of disordered tungsten oxide particles, which agrees with the accepted notion of small oxide clusters in strong interaction with the support [6]. In addition, the broad line width indicates a distribution in local surroundings of the tungsten atoms. Qualitatively, the spectra indicate that

Table 1
^{182}W Mössbauer parameters of (Ni)W(L)/Al_2O_3-T_c catalysts after sulfidation treatments.

Catalyst	T_s (K)	P (MPa)	Q.S.[a] (mm s^{-1})	Γ[b] (mm s^{-1})	η[c]	A (%)	Q.S. (mm s^{-1})	Γ (mm s^{-1})	η	A (%)
NiW(15.2)/Al_2O_3-673 Ni:W = 0.25			"W-oxide"				WS_2			
	WO_3		−8.4	2.6	0.5	100				
	Fresh		−11	3.3	0.8	100				
	673	0.1					10.5	3.2	0	100
	673	4					10.1	2.8	0	100
	WS_2						9.1	2.5	0	100
W(15.2)/Al_2O_3-673			"W-oxide"				WS_2			
	Fresh		−10.9	3.8	0.8	100			0	
			WS_3							
	673	0.1	−13.8	3.2[d]	0	61	10.4	3.2[d]	0	39
	673	4					9.8	3.0	0	100
NiW(15.2)/Al_2O_3-823 Ni:W = 0.25			"W-oxide"				WS_2			
	Fresh		−12.1	3.6	0.8	100				
	673	0.1					10.9	3.7	0	100
	673	4					10.4	3.0	0	100
W(15.2)/Al_2O_3-823			"W-oxide"				WS_2			
	Fresh		−11.8	3.6	0.8	100				
			WS_3							
	673	0.1	−13.5	3.2[d]	0	45	11.0	3.2[d]	0	55
	673	4					9.8	3.2	0	100
NiW(15.2)/Al_2O_3-383 Ni:W = 0.25			"W-oxide"				WS_2			
	Fresh		−7.7	3.2	0.9	100				
	673	0.1					10.0	3.0	0	100
	673	4					9.9	2.8	0	100
W(15.2)/Al_2O_3-383			"W-oxide"				WS_2			
	Fresh		−10.2	3.7	0.7	100				
	673	0.1					9.8	3.8	0	100
	673	4					9.6	3.2	0	100
NiW(15.2)/Al_2O_3-673 Ni:W = 0.60			"W-oxide"				WS_2			
	Fresh		−11.7	3.4	0.6	100				
	673	0.1					10.5	3.0	0	100
	673	4					10.1	2.5	0	100
NiW(19)/ASA-723 Ni:W = 0.6			"W-oxide"				WS_2			
	Fresh		−11.7	3.9	0.9	100				
	673	0.1					10.1	3.1	0	100
	673	4					10.1	2.9	0	100
NiW(19)/ASA+-723 Ni:W = 0.6			"W-oxide"				WS_2			
	Fresh		−11.4	3.8	0.8	100				
	673	0.1					10.2	2.9	0	100
	673	4					10.3	2.7	0	100

[a] Quadrupole splitting: Q.S. ± 0.2 mm s^{-1}.
[b] Line width: $\Gamma \pm 0.4$ mm s^{-1}.
[c] Asymmetry parameter: η.
[d] Fixed during fit.

tungsten sulfidation already starts after exposing the catalyst to the H_2S/H_2 gas mixture at 473 K and atmospheric pressure. The presence of partially sulfided W phases (WO_xS_y) with structural parameters of disordered WO_3 species and WS_3- and WS_2-type phases at the intermediate temperatures has been proposed before [21]. Because of the occurrence of such ill-defined WO_xS_y species with very large line widths, a quantitative analysis of the Mössbauer spectra obtained at 473 and 573 K (Fig. 1C and D) is not possible. For the same reason, only the spectra obtained after sulfidation at 673 K will be presented for the other catalysts.

After treatment at 673 K the spectral shape is similar to that of WS_2 (Fig. 1E), but the large Q.S. and line width values indicate that only a poorly crystalline WS_2 phase is present after sulfidation at 0.1 MPa. The structure of WS_2 is similar to that of MoS_2 in which the Mo atoms are in the center of a regular trigonal prism, *i.e.* a structure in accordance with the observation of an axially symmetric electric field gradient ($\eta = 0$) [19]. Upon increasing the sulfidation pressure to 4 MPa at 673 K (Fig. 1F), the WS_2 slabs in NiW(15.2)/Al_2O_3-673 Ni:W = 0.25 catalyst become better crystallized, as follows from the decreasing line width. For this catalyst, an increased thiophene HDS activity has been observed upon increasing the sulfidation pressure from 0.1 to 1.5 MPa [8].

The Mössbauer spectra of the W(15.2)/Al_2O_3-673 catalyst sulfided at 0.1 and 4 MPa are presented in Fig. 2 and the resulting MES parameters are shown in Table 1. The spectrum of the fresh catalyst shows a very broad line width, pointing to the presence of less defined W-oxide species as compared to its Ni-containing counterpart. After treatment at 673 K, the presence of a quadrupole coupling of the same sign as WO_3 but with a zero asymmetry parameter is observed. This component is assigned to WS_3 [20]. The large Q.S. value indicates the presence of a very disordered WS_3-type structure. A proposal for intermediate WS_3 species in the sulfidation of NiW/Al_2O_3 and supported WO_3 has also been made earlier [9,22]. The partial formation of the poorly crystalline WS_2 phase is also observed at this point. After sulfidation at 673 K and 4 MPa, tungsten sulfidation is complete, although the WS_2 species are still ill-defined, as revealed by the large observed line width.

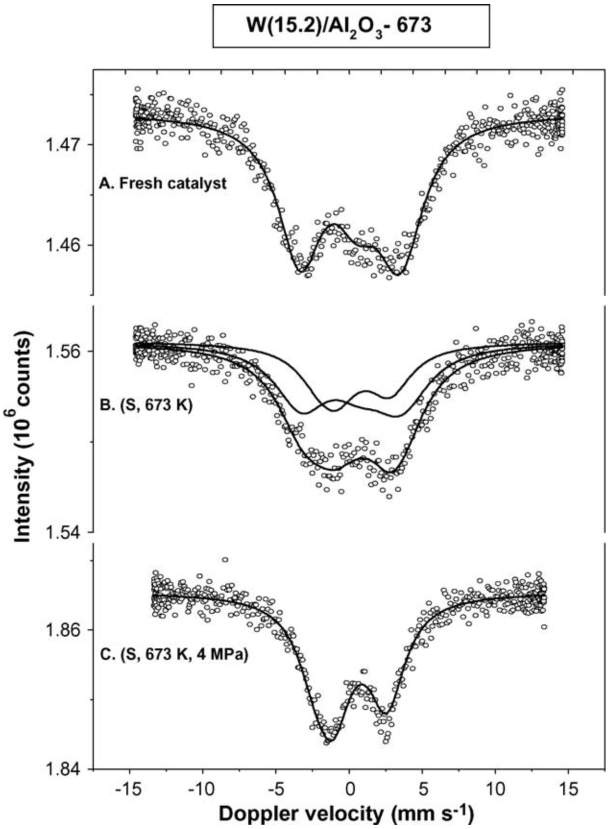

Fig. 2. ^{182}W Mössbauer spectra of W(15.2)/Al_2O_3-673 catalyst – after various successive sulfidation steps.

Fig. 3 shows the MAS spectra of NiW(15.2)/Al_2O_3-823 Ni:W = 0.25 sulfided at atmospheric pressure and subsequently at high-pressure. The corresponding fit parameters are presented in Table 1. The large Q.S. value for the oxidic tungsten phase in the fresh catalyst indicates a more irregular coordination of oxygen to the tungsten atoms. This can be understood in terms of a stronger W-support interaction, with more W–O–Al bonds as a result of calcination at higher temperature. The observed broad line width also confirms the presence of less crystallized W-oxide species in the fresh sample. Complete transition to poorly crystalline WS_2 phase takes place after sulfidation at 673 K and atmospheric pressure, the WS_2 crystallization degree being smaller compared to that of the sample calcined at 673 K sulfided under similar conditions. After sulfidation at 4.0 MPa (Fig. 3C), the WS_2 structures are better defined, but not to the same extent as observed for the high-pressure sulfided NiW(15.2)/Al_2O_3-673 Ni:W = 0.25 sample. Calcination at higher temperature is known to induce a more difficult sulfidation of tungsten atoms and this leads to lower thiophene HDS activities [8,23–25].

The Mössbauer spectra of W(15.2)/Al_2O_3-823 catalyst sulfided at 673 K are presented in Fig. 4 and the resulting MAS parameters are shown in Table 1. The spectrum of the fresh catalyst was fitted with the same large Q.S. contribution as observed for its Ni-containing counterpart, confirming the presence of very disordered W-oxide species upon calcination at 823 K. After atmospheric-pressure sulfidation at 673 K, the formation of the disordered WS_3-type species is found. The low sulfidation rate of supported WO_3 materials allows the observation of WS_3, even for the relatively high sulfidation temperature. This suggests that the presence of Ni modifies to some extent the sulfidation mechanism. Tentatively, the Ni-sulfide species in NiW/Al_2O_3 catalysts stabilize intermediate W species. Nevertheless, the

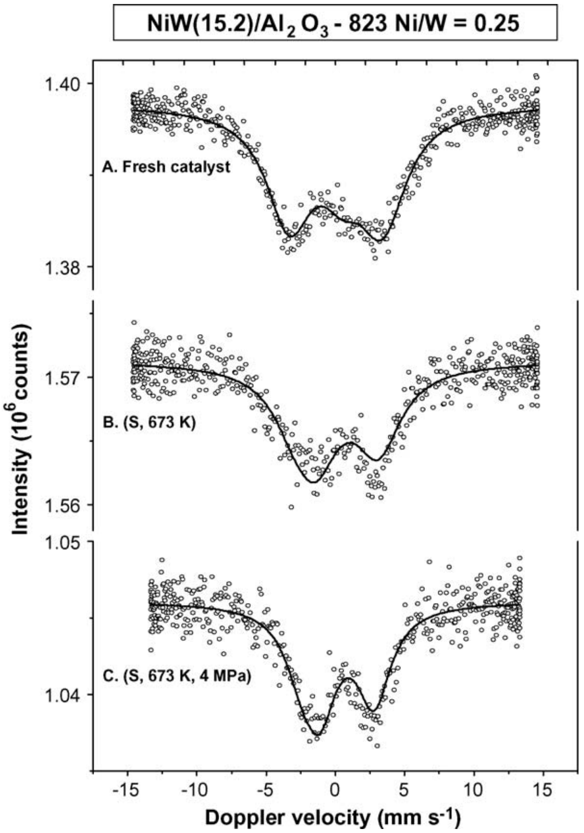

Fig. 3. ^{182}W Mössbauer spectra of NiW(15.2)/Al_2O_3-823 Ni/W = 0.25 – after various successive sulfidation steps.

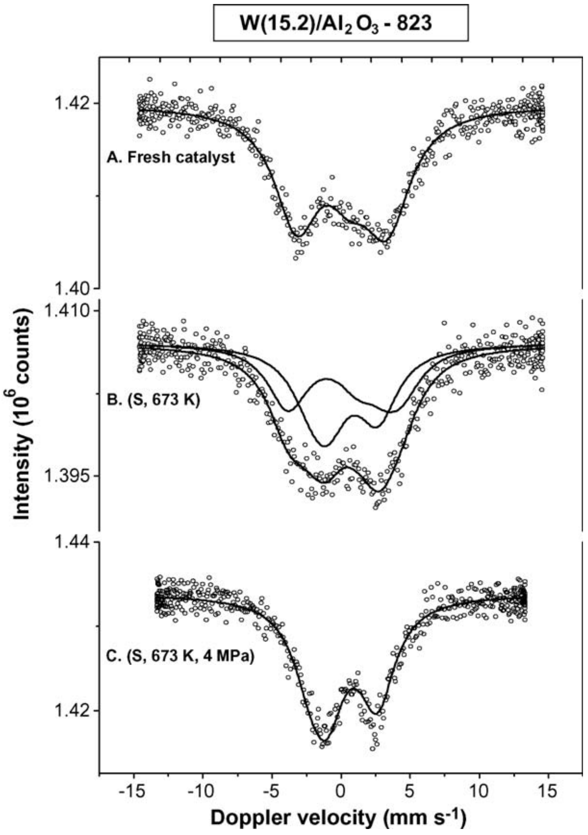

Fig. 4. ^{182}W Mössbauer spectra of W(15.2)/Al_2O_3-823 – after various successive sulfidation steps.

transformation into WS_2 is complete for the Ni-containing sample. Upon treatment at 673 K and 4 MPa, this is also the case for the W(15.2)/Al_2O_3-823 catalyst, although the formed WS_2 species are again poorly crystallized.

Fig. 5 shows the ^{182}W MAS spectra obtained with NiW(15.2)/Al_2O_3-383 Ni:W = 0.25 catalyst sulfided at 0.1 and 4 MPa and the corresponding fit parameters are collected in Table 1. The spectrum of the fresh catalyst shows the presence of a contribution with an unexpectedly low Q.S. value, which may point to a Ni-W-O interaction phase. The sulfidation of W atoms is already complete after treatment at 673 K and 0.1 MPa, the resulting WS_2 structures being better defined as compared to those present in the similar sample calcined at 673 K and sulfided in the same conditions. After treatment at 673 K and 4 MPa, better-crystallized WS_2 species are formed.

The Mössbauer spectra of the W(15.2)/Al_2O_3-383 sample sulfided at 673 K are presented in Fig. 6 and the resulting MAS parameters are shown in Table 1. The spectrum of the fresh catalyst shows the presence of a somewhat more regular W-oxide structure as compared with the previous samples. Upon treatment at 673 K under both atmospheric and high-pressure conditions, the sulfidation of the W(15.2)/Al_2O_3-383 samples appears to be complete, but the resulting WS_2 slabs are clearly poorly crystallized, as deduced from the large line widths measured.

Fig. 7 shows the ^{182}W MAS spectra obtained with NiW(15.2)/Al_2O_3-673 Ni:W = 0.6 catalyst sulfided at 673 K and the corresponding fit parameters are collected in Table 1. The sulfidation pattern of the W atoms is similar for NiW(15.2)/Al_2O_3-673 Ni:W = 0.6 and NiW(15.2)/Al_2O_3-673 Ni:W = 0.25 catalysts after activation at both 0.1 and 4 MPa. However, the WS_2 species are less crystallized in the high promoter-loading catalyst after the 0.1 MPa treatment, leading to a higher thiophene HDS activity compared to

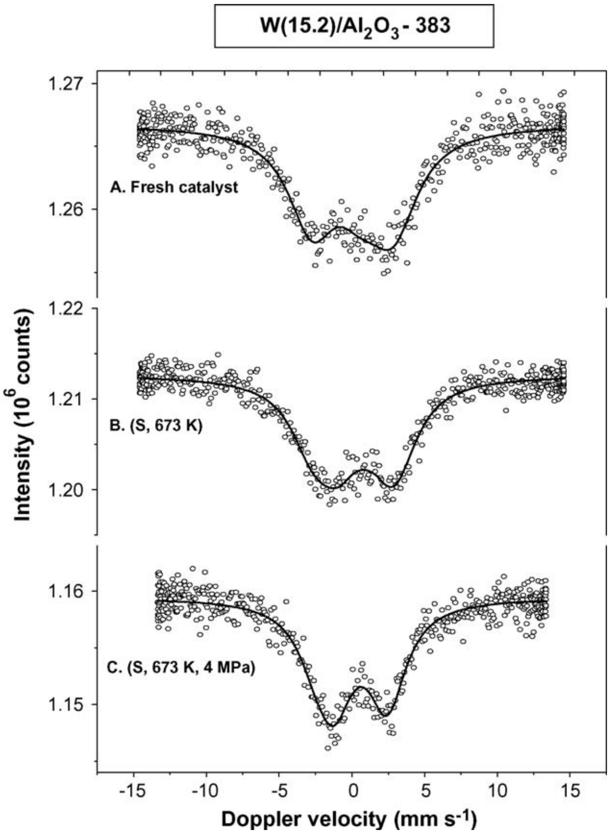

Fig. 6. ^{182}W Mössbauer spectra of W(15.2)/Al_2O_3-383 – after various successive sulfidation steps.

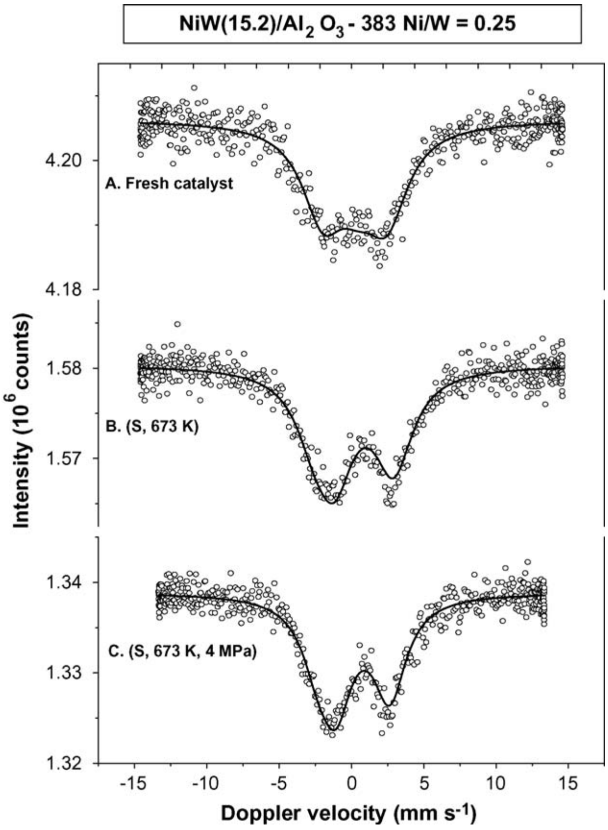

Fig. 5. ^{182}W Mössbauer spectra of NiW(15.2)/Al_2O_3-383 Ni/W = 0.25 – after various successive sulfidation steps.

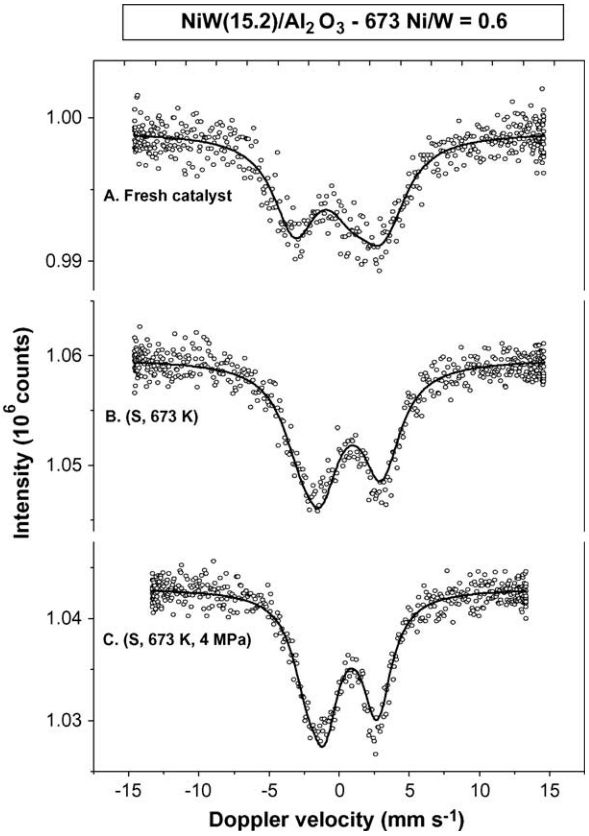

Fig. 7. ^{182}W Mössbauer spectra of NiW(15.2)/Al_2O_3-673 Ni/W = 0.6 – after various successive sulfidation steps.

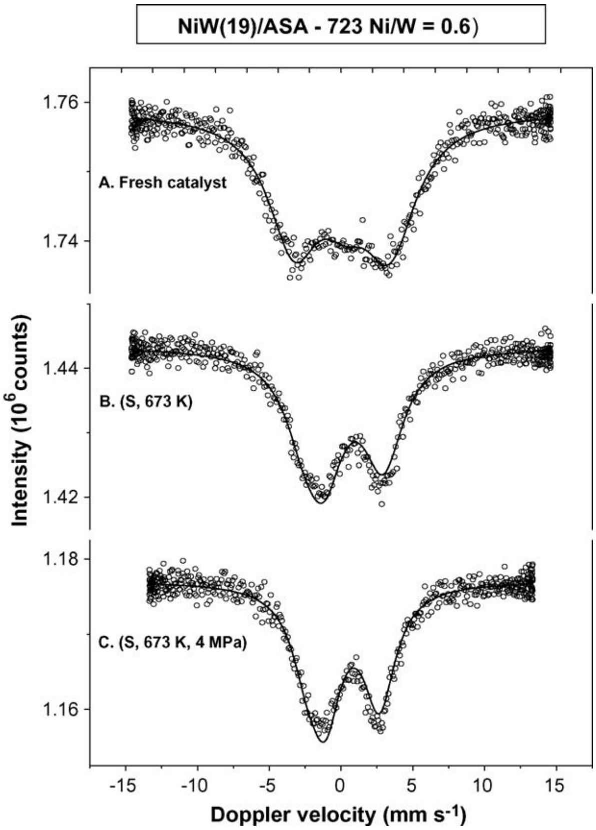

Fig. 8. ^{182}W Mössbauer spectra of NiW(19)/ASA-723 Ni:W = 0.6 – after various successive sulfidation steps.

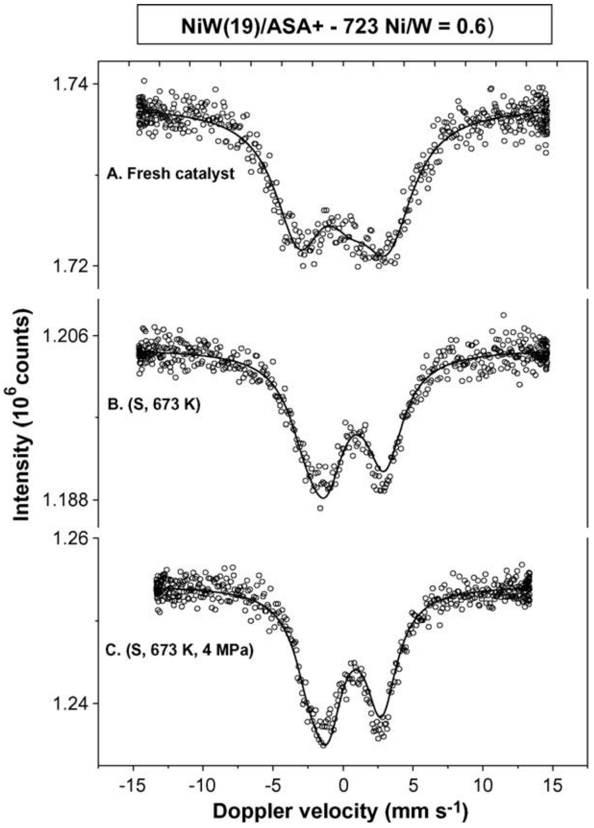

Fig. 9. ^{182}W Mössbauer spectra of NiW(19)/ASA+-723 Ni:W = 0.6 – after various successive sulfidation steps.

the catalyst with a Ni:W ratio of 0.25 [14,28]. Complete crystallization of the WS_2 slabs is observed for the NiW(15.2)/Al_2O_3-673 Ni:W = 0.6 catalyst upon sulfidation at 673 K and 4 MPa, the measured line width being similar to that of bulk WS_2. The more crystalline WS_2 slabs present low dispersion and low intrinsic activities [8].

The Mössbauer spectra of the NiW(19)/ASA-723 Ni:W = 0.6 and NiW(19)/ASA+-723 Ni:W = 0.6 catalysts sulfided at 0.1 and 4 MPa are presented in Figs. 8 and 9 and the corresponding fit parameters are collected in Table 1. The sulfidation behavior of the ASA-supported NiW catalysts is very similar to the alumina-supported ones, but the WS_2 crystallization degree appears to be higher for the NiW(19)/ASA+-723 Ni:W = 0.6 catalyst after activation at both 0.1 and 4 MPa. However, no clear indication of any electronic effect has emerged. Trendwise, there is not much difference in spectral parameters with the alumina-supported ones (Fig. 7) and this is no doubt due to the preference of tungsten to be located on the alumina part of the ASA support. The higher DBT HDS activities obtained with NiW catalysts supported on ASA+ were previously related to an increased hydrogenation activity [11]. The HYD rate is believed to increase with an increasing stacking degree because of a more favorable planar adsorption geometry of reactants on multilayered Mo(W)S_2 [26]. Nevertheless, from the Mössbauer data alone no reason can be deduced for the NiW hydrogenation function to become more powerful in the series $Al_2O_3 < ASA < ASA+$.

4. Conclusions

The sulfidation of Al_2O_3- and ASA-supported NiW catalysts under conditions relevant to industrial practice was studied by ^{182}W Mössbauer spectroscopy. This is the first study of its kind employing ^{182}W Mössbauer absorption spectroscopy for characterization of catalysts.

^{182}W MAS of supported tungsten catalysts can distinguish between WO_3- and WS_2-type phases as encountered in the calcined and sulfided forms of W-based hydrotreating catalysts. In general, the line widths are substantially broadened compared to crystalline WO_3 and WS_2 reference compounds because small, disordered particles interacting with the support are present in such catalysts. Some indications for the presence of oxysulfidic W or WS_3 intermediates have been found. It is typically observed that enhanced support interaction through increased calcination temperatures leads to more difficult sulfidation of W. In cases where the sulfidation rate is lowest, an intermediate WS_3-type phase is identified at temperatures as high as 673 K. Ni facilitates sulfidation and in this case sulfidation occurs via an oxysulfidic intermediate. A general conclusion is that sulfidation at 673 K and 0.1 MPa leads to a poorly crystalline WS_2 phase. Subsequent sulfidation at 4.0 MPa increases the crystallinity of the catalysts as evidenced by the approach of the spectral parameters to those of WS_2. There are no salient differences between the behaviors of NiW/ASA and NiW/Al_2O_3 catalysts.

In all, however, ^{182}W MAS does not appear to be about to displace X-ray absorption spectroscopy as the method of choice to structurally characterize NiW-based catalysts and, in any case, transmission electron microscopy and catalytic activity studies will be needed as well, in order to study the difficult issue of Type I/II behavior [1] in hydrotreating catalysts.

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