

In Situ XAS of Ni-W Hydrocracking Catalysts

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Abstract. Ni-W based catalysts are very attractive in hydrotreating of heavy oil due to their high hydrogenation activity. In the present research, two catalyst samples, prepared by different methods, that exhibit significant differences in activity were sulfided in situ, and the local structure of the Ni and W were studied using X-ray absorption spectroscopy (XAS). The Ni XANES spectra were analyzed using a linear component fitting, and the EXAFS spectra of the WS₂ platelets in the sulfided catalysts were modeled. The Ni and W are fully sulfided in the higher activity sample, and there are both unsulfided Ni (~25%) and W (<10%) in the lower activity sample.

Keywords: EXAFS; Ni; W; hydrocracking catalyst; alumina; sulfiding

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INTRODUCTION

Ni-W based catalysts are very attractive in hydrotreating of heavy oil due to their high hydrogenation activity [1]. The method of catalyst preparation, the precursor materials, and the calcination temperature have been shown to affect the sulfidability of the W and Ni [2]. For these systems in situ XAFS has proven to be extremely valuable and widely used [3,4].

In the present research, we have developed an in situ sulfiding XAFS capability and used the procedure to study two Ni-W catalysts prepared by different methods. The sulfiding pathway and the overall degree of sulfiding both Ni and W are compared. The sheet size of the WS₂ platelets in the sulfided catalysts is estimated based on the model-fit of the EXAFS spectra, and the amount of unsulfided Ni and W are quantified. This work is part of a more detailed study of this system [5].

EXPERIMENTAL

The catalysts (denoted A and B) were prepared by two different methods. The weight percent of both the Ni and W, and the support material (USY zeolite, silica-alumina, and alumina), is identical in both samples.

The Ni K-edge and W L₃-edge EXAFS data were collected at 33BM at the Advanced Photon Source (APS), Argonne National Laboratory using a Si(111)

double crystal monochromator. The APS storage ring was operated at 7 GeV with a constant ring current of 105 mA. Harmonics were removed by two Rh-coated mirrors, with the first mirror also acting as a collimator.

In situ temperature-programmed sulfiding was carried out using a custom-designed in situ reactor [6]. The weight of each sample was calculated to have a total absorption length of ~2.0, and the fractional absorption by Ni or W was approximately 0.5. EXAFS data of the as-received oxidized samples were collected, then the samples were sulfided in situ by incremental heating in a flow of 10%H₂S/H₂ at 4°C/min to 410°C, followed by a dwell for one hour. The sample was cooled to room temperature and multiple EXAFS spectra were collected in order to improve the signal/noise ratio.

EXAFS data reduction and analysis were performed using Athena and Artemis [7], which are interfaces to IFEFFIT [8]. The background removal, normalization, and averaging of the χ -data were performed using standard procedures. The data were fit in R-space with theoretical models constructed from FEFF [9].

RESULTS AND DISCUSSION

Figure 1 shows the relative catalytic activity of samples A and B. The preparation method used for sample A results in a higher activity catalyst.

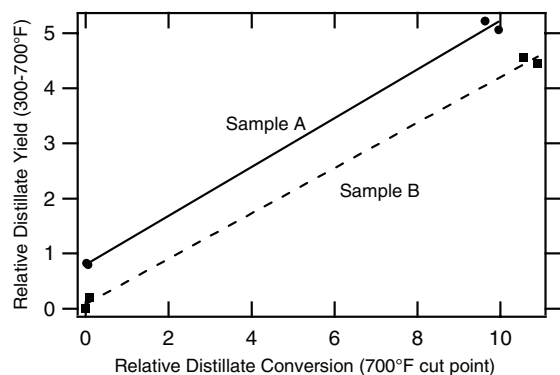


FIGURE 1. The relative catalytic activity of samples A and B. For a given conversion the distillate yield of Sample B is always lower than Sample A.

Figure 2 shows the comparison of the XANES of the Ni K-edge for both the oxidic and sulfided samples. Clearly, the white line of the oxidized samples is more intense than that of the sulfided samples. The white line of the Ni K-edge XANES is due to the ionic bonding between Ni and oxygen [10].

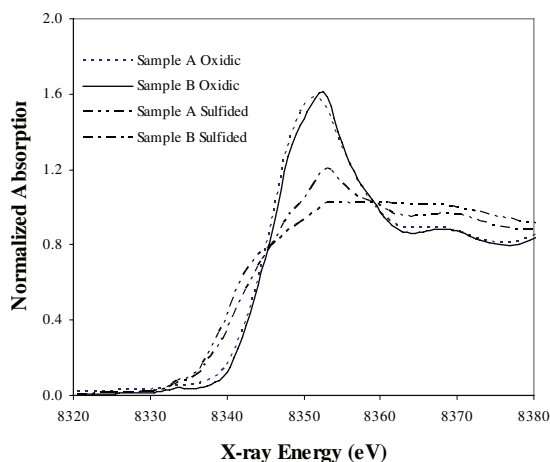


FIGURE 2. Ni K-edge XANES spectra of the oxidic and sulfided samples A and B.

As the oxygen atom is replaced by the sulfur atom, the white line intensity decreases due to the more covalent bond between Ni and sulfur.

The XANES spectra of A and B in the oxidic state are subtly different, indicating that the environment of the Ni is somewhat different in the two samples. After the sulfiding treatment, the spectrum of sample B has a much stronger white line than that of sample A, indicating that a larger percent of the Ni in sample B remains unsulfided. The degree of sulfiding of the Ni in both samples was quantified using a linear combination fitting of the spectra of the oxide sample and the fully sulfided sample spectrum. This showed that in sample A the Ni is essentially fully sulfided,

whereas in sample B $25 \pm 1\%$ of the Ni remains unsulfided.

The W L_3 -edge EXAFS spectra of the in situ sulfided samples are compared in Figure 3. The Fourier-transform (FT) uses the k -range of $2.6 \text{ \AA}^{-1}$ to $17.2 \text{ \AA}^{-1}$. Figure 3 shows that the amplitude of the EXAFS $\chi(k)$ spectra (Figure 3; top) from sample A is more intense than that of sample B. Similarly, the magnitude of the FT (Figure 3; bottom) shows larger peak heights from sample A as compared to B for both the first peak ($2.1 \text{ \AA}$ before phase correction) and the second peak ($3.4 \text{ \AA}$ before phase correction). These peaks correspond to S and W, respectively. These observations indicate larger and/or more uniform WS_2 sheets within sample A as compared to sample B. In order to quantify these observations, the W L_3 -edge EXAFS spectra of the sulfided samples were modeled with a WS_2 structure (Figure 4). The S_{0^2} (0.84 ± 0.02) was determined by fitting the spectrum of bulk WS_2 as a reference spectrum. The spectra from samples A and B were fit simultaneously in order to decrease the total number of parameters. The data k -range of $2.6 \text{ \AA}^{-1}$ to $17.2 \text{ \AA}^{-1}$ and the fit R -range of $1 \text{ \AA}$ to $6.2 \text{ \AA}$ corresponded to 48 independent points for each sample. The model was optimized to the measured spectra using a k -weighting of the FT of 1, 2, and 3.

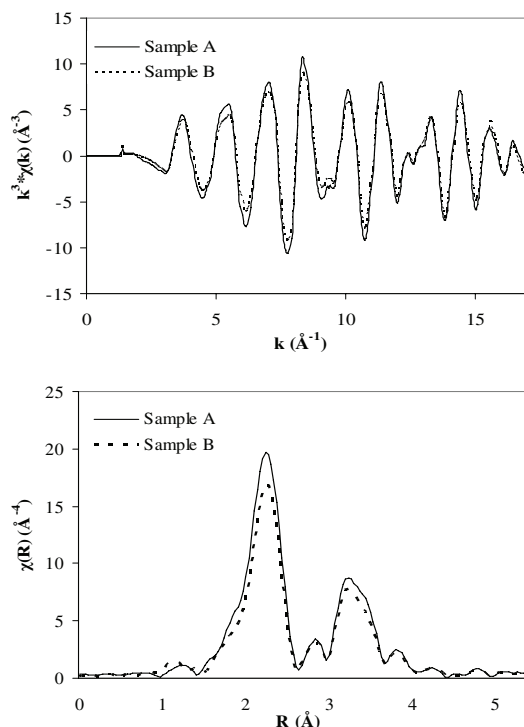


FIGURE 3. Comparison of $\chi(k)$ spectra (top) and the magnitude of FT (bottom) of the W L_3 edge EXAFS spectra of sulfided samples A and B.

The model included two W-S paths and three W-W paths, as well as the multiple scattering paths of the W

shells. In the EXAFS model, the bond lengths (R) and the mean-square displacement terms (σ^2) were constrained to be the same for the two samples, and only the coordination numbers (CNs) were independently refined parameters. In addition to the W-S and W-W contributions, a short W-O contribution was also included in the model to retrieve the information of the unsulfided W.

The fit results of the first W-S path, the W-O path, and first two W-W paths are listed in Table 1. In agreement with the qualitative observation, sample A has larger CNs for both W-S and W-W than sample B, indicating a larger sheet size of the WS₂ platelets. Moreover, sample B has a significant W-O CN indicating that sample B has more residual unsulfided W species.

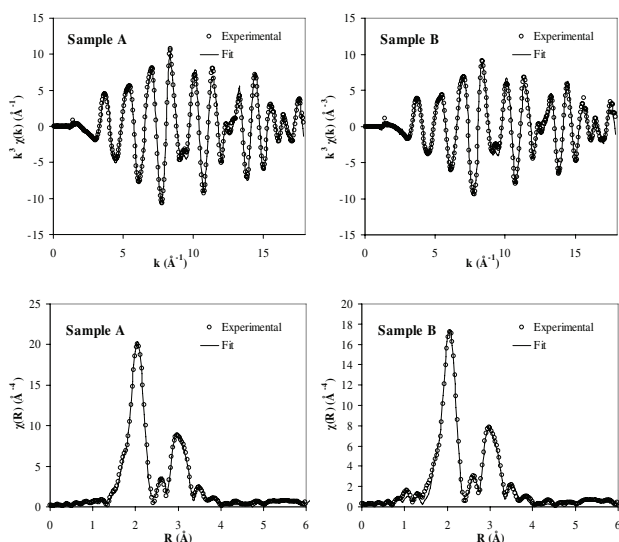


FIGURE 4. Comparison of $\chi(k)$ plots and the magnitude of FT of the W L₃-edge EXAFS spectra and fits for the sulfided samples A and B.

TABLE 1. The results of the fits to the W EXAFS data of samples A and B.

Sample		A	B
E0		$6.6 \pm 0.2(\text{eV})$	
W-S1	C.N	5.5 ± 0.1	4.6 ± 0.1
	R	2.406 ± 0.001	
	σ^2	0.0028 ± 0.0001	
W-W1	C.N	3.8 ± 0.3	3.1 ± 0.3
	R	3.159 ± 0.002	
	σ^2	0.0041 ± 0.0002	
W-S2	C.N	3.5 ± 0.6	3.6 ± 0.6
	R	3.965 ± 0.005	
	σ^2	0.007 ± 0.001	
W-O1	C.N	0.1 ± 0.1	0.4 ± 0.1
	R	1.807 ± 0.006	
	σ^2	0.002 ± 0.001	

Based on the EXAFS CNs, the sheet size of the WS₂ platelets can be estimated: the lateral extent of the platelets in sample A is $\sim 20\text{\AA}$ while in sample B is $\sim 10\text{\AA}$. TEM characterization is planned to confirm the average WS₂ sheet size in the samples. The lower activity of sample B could be due to the smaller lateral extent of the WS₂ sheets, or due to the lower amount of sulfided Ni and W, there is a correspondingly lower amount of the “Ni-W-S” structure, which is the active phase in the catalyst [11].

CONCLUSION

The sulfidability of the W and Ni in two hydrocracking catalysts prepared using two different methods are compared using in situ XAFS. The Ni and W in sample A have a much better sulfidability than in sample B. The Ni and W in sample A are essentially sulfided whereas in sample B, a significant amount of the metal oxide remains. The relative catalytic activity of the samples correlates with the extent of sulfiding.

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