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In situ EXAFS study on the chemical state of arsenic deposited on a NiMoP/Al_2O_3 hydrotreating catalyst

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The chemical state of arsenic deposited on a NiMoP/Al_2O_3 hydrotreating catalyst exposed to ppb levels of arsenic over several years in a refinery reactor has been studied by *in situ* EXAFS. In the as-received As-NiMoP catalyst, arsenic is exclusively coordinated to oxygen atoms. Upon sulfiding the sample in 2%H_2S/2%H_2/96%He, the As atoms become surrounded by approximately two sulfur atoms. No evidence was found for Ni–As bond formation. A possible model for the As local environment is suggested on the basis of combined EXAFS results, STM data and FEFF8.0 simulations (program for *ab initio* calculations on multiple scattering XAFS and XANES). The FEFF8.0 simulations of the proposed model are in accord with the experimental data measured at the As K edge. In this model, an As atom is located at the edge of a hexagonally truncated Ni-MoS_2 slab and is blocking the active NiMoS site.

KEY WORDS: arsenic; catalyst poisoning; catalyst deactivation; hydrotreating; Ni-Mo-S; EXAFS.

1. Introduction

The deactivation of CoMo and NiMo(P) hydrotreating catalysts used for desulfurization of hydrocarbon streams in refinery processes has been studied extensively for many years [1–6]. A detailed understanding of the deactivation phenomena and their consequences for the catalytic performance is important to optimize the process parameters in the refineries and to rationalize catalyst research. Hydrotreating catalyst deactivation has traditionally been classified into four categories [1]: (1) blocking of catalyst pores by coke formation, making the active centers unavailable for reactants; (2) sintering of MoS_2 slabs; (3) poisoning of active sites by strongly absorbing species, which are usually present as N-heterocyclic compounds in the middle and heavier feeds; (4) poisoning by deposition of metals, predominantly present in resid feeds, on the active sites. While poisoning of active sites by nitrogen compounds does not induce structural changes of the active sites and may be reversible by raising the process temperature, deposition of metals generally leads to irreversible deactivation. Ubiquitous metals in crude oil charges are vanadium and nickel. Investigations on the atomic detail of the deactivation processes following a deposition of these metals on the active centers of a hydrotreating catalyst have been reported [3,5,6]. Parallel to this, effective hydrodemetallation (HDM) catalysts have been developed to avoid a deposition of V and Ni on the hydrotreating catalyst surface.

A less-frequently studied metallic element present on a ppb or low-ppm level in many crude oil charges is arsenic [7]. Exposure of CoMo or NiMo(P) hydrotreating catalysts to arsenic containing feedstocks has been recognized to have a dramatic influence on the catalyst activity [8]. Owing to this problem, an "arsenic guard" material is installed in many hydrotreating reactors in order to prevent any arsenic coming in contact with the hydrotreating catalyst. This "arsenic guard" is usually a supported transition metal (Mo, Fe, Co, Ni, Cu) oxide/sulfide with a high tendency to chemisorb largely all the arsenic present in a hydrocarbon stream [9–11]. Recently, an investigation on an artificially poisoned As-Ni/Al_2O_3 catalyst was published, demonstrating a stepwise poisoning process by the initial formation of surface As adatoms, a migration of these into the Ni particle to form Ni_xAs_y intermetallic phases and the final formation of crystalline NiAs [12,13]. The formation of Ni_5As_2 and NiAs alloy phases on Ni-reforming catalysts has also been discussed by Nielsen and Villadsen [14]. However, the information currently available in the literature on the chemical state of arsenic after deposition on a NiMo(P)/Al_2O_3 hydrotreating catalyst is very scarce. Owing to the much lower amount of nickel atoms on the hydrotreating catalyst and the presence of the bimetallic Ni-Mo-S phase [2], the deactivation mechanism might be different, as for highly loaded Ni/Al_2O_3 catalysts studied in [12] and [13]. We have therefore performed an *in situ* extended X-ray absorption fine structure (EXAFS) study on a strongly deactivated NiMoP/Al_2O_3 hydrotreating catalyst exposed to a ppb level of arsenic over several years in a refinery reactor. By revealing the kind of interaction between arsenic and the catalytically

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active metals, we want to obtain information about the deactivation effect an arsenic deposition commits on a NiMoP hydrotreating catalyst. The catalyst has been studied under resulfiding conditions in order to mimic the active state of a NiMoP catalyst in the refinery reactor.

2. Experimental

The spent As-NiMoP/Al_2O_3 catalyst was investigated as received from the refinery. Prior to the analysis, the remaining oil was removed by Soxhlet extraction. The metal loadings analyzed by inductively coupled plasma (ICP) were 0.26 wt% As, 1.42 wt% Ni and 6.33 wt% Mo.

The *in situ* EXAFS experiments were performed at the X1 beamline at HASYLAB (Hamburg, Germany). The catalyst (sieved particle fraction 75–125 μm) was sulfided *in situ*, with 2%H_2S/2%H_2/96%He in a reaction cell [15]. The gas composition was monitored by a mass spectrometer (Balzers Thermostar) connected to the outlet of the reactor. The experiments were carried out in transmission geometry around the As, Ni and Mo K-edges. Double Si(311) and Si(111) crystals were used to monochromatize the X rays. A slight detuning of the monochromator was used to minimize the presence of higher harmonics. Three ionization chambers were used to record the intensity of the incident and transmitted X rays. A reference sample situated between the second and third ionization chambers was used to calibrate the energy of the EXAFS spectra. Each sample was sulfided at room temperature until no further structural changes could be probed by EXAFS. Then the temperature was raised to 450 °C at a rate of 5 °C/min. EXAFS spectra were recorded at RT before reaction, at 450 °C and at room temperature after reaction in the reaction mixture. Quick EXAFS (QEXAFS) scans were recorded while heating to 450 °C in the reaction mixture. EXAFS spectra were recorded on pellets of As_2O_3, As_2O_5 (both Aldrich), As_2S_3 (Strem Chemicals), NiAs, $NiAs_2$ (both Alfa Chemicals), MoS_2, MoO_2, MoO_3, NiO, Ni_3S_2, Mo_2As_3 [16] and $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ni\}_2(\mu\text{-}C_4H_8S_2)][pts]_2$ [Cp' = methylcyclopentadienyl; pts = *p*-toluenesulfonate, $C_4H_8S_2$ = 1,4-dithiane] [17] in order to be used as model samples in the data processing.

Standard data analyses including deglitching, pre-edge subtraction, background subtraction, normalization and Fourier transformation were performed. Fourier transformation was applied on the k^1-weighted $\chi(k)$ functions in the interval $k = 2.2$–15, 3–15 and 3–15 Å^{-1} for the As, Mo and Ni K-edges respectively. The first peak in the Fourier-transformed function was filtered and then inversely Fourier transformed back into k-space. The backscattering amplitudes and phase shifts of the first neighbor contributions were taken from the experimental spectra of the model samples.

3. Results and discussion

3.1. In situ EXAFS measurements

The EXAFS experiments focussed in the first stage on the identification of the arsenic coordination sphere in the as-received As-NiMoP/Al_2O_3 sample. Possible reference samples were chosen among several metal arsenides (NiAs, $NiAs_2$, Mo_2As_3) as well as arsenic oxides and sulfides (As_2O_3, As_2O_5, As_2S_3). Figure 1 shows the X-ray absorption near-edge spectroscopy (XANES) region of the As K-edge absorption spectra and the Fourier-transformed data of the as-received and sulfided As-NiMoP catalyst and the reference samples As_2O_5, As_2S_3 and NiAs. In the as-received catalyst, the features and position of the As K absorption edge and the nearest-neighbor distance are closely resembled by the reference spectrum and the As–O bond distance of the As_2O_5 model sample. The fit of the recorded data with the As_2O_5 model sample functions [18] indicated that the As atoms in the as-received As-NiMoP catalyst are surrounded by, on average, 4.5 oxygen atoms at an average distance of 1.78 ± 0.02 Å. The NiAs and Mo_2As_3 bulk-model compounds have As-Ni and As-Mo [16] at average distances of 2.54 and 2.46 Å respectively, which are much larger than the observed distances in both the as-received and re-sulfided As-NiMoP/Al_2O_3 compound. The oxidation of arsenic is presumably caused by the exposure of the spent, but still-warm catalyst to air during the removal from the hydrotreating reactor.

Upon sulfiding the As-NiMoP/Al_2O_3 catalyst, the As absorption edge shifts toward lower energy and the height of the As white line decreases slightly (figure 1(a)). The Fourier transform of the EXAFS spectra (figure 1(b)) shows that the nearest-neighbor distance increases significantly upon reaction, revealing extensive sulfidation and removal of the oxygen atoms from the coordination sphere of the As atoms. The XAFS spectra and the corresponding Fourier transform of the sulfided As-NiMoP/Al_2O_3 catalyst show a strong resemblance with the As_2S_3 model sample. The fit of the sulfided As-NiMoP data with the As_2S_3 model sample data ($N_{\text{As-S}} = 3$, $d_{\text{As-S}} = 2.28$ Å [19]) reveals that the average sulfur coordination and As-S distance in the sulfided As-NiMoP catalyst are $N_{\text{As-S}} = 1.8 \pm 0.5$ (Å) and $d_{\text{As-S}} = 2.22 \pm 0.02$ Å respectively (see table 1). No direct bonding of the As atoms to the Ni-promoter atoms was found.

The EXAFS spectra collected at the Ni K edge do not show any evidence of Ni-As interactions. Figure 2 shows the normalized absorption spectra for the Ni K edge and the Fourier-transformed data before and after sulfiding the catalyst. In the as-received As-NiMoP/Al_2O_3 catalyst, the Ni atoms are surrounded by oxygen. This is evidenced by the presence of a large white line in the XANES region of the absorption spectra (figure 2(a)) characteristic of NiO_x species [20]. Upon sulfiding, the white line decreases and the energy position of the

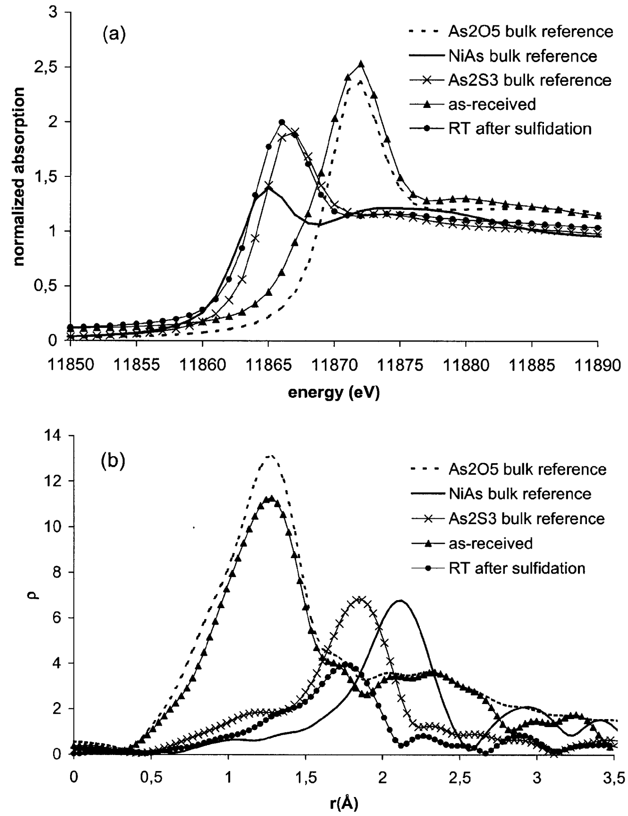

Figure 1. (a) Normalized absorption spectra at the As K edge and (b) magnitude of the Fourier-transformed data of the as-received and sulfided As-NiMoP/Al$_2$O$_3$ catalyst as well as relevant bulk references (As$_2$O$_5$, As$_2$S$_3$ and NiAs).

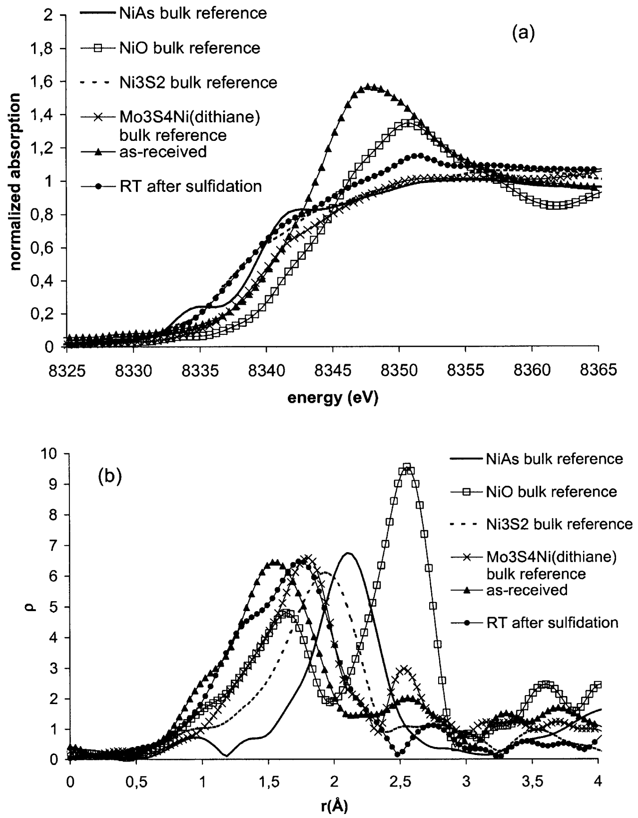

Figure 2. (a) Normalized absorption spectra at the Ni K edge and (b) magnitude of the Fourier-transformed data of the As-NiMoP/Al$_2$O$_3$ catalyst before and after sulfiding, respectively, as well as bulk-reference samples of NiO, Ni$_2$S$_3$, NiAs and the Mo$_3$S$_4$Ni(dithiane) cluster.

absorption edge shifts to lower energy. The Fourier-transformed data (figure 2(b)) show a shift of the nearest-neighbor peak toward larger bond distances as a consequence of the exchange of oxygen atoms by the larger sulfur atoms. As a model, samples for the Ni K edge were chosen: Ni$_3$S$_2$ and a heterobimetallic cluster compound, $[\{(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4\text{Ni}\}_2(\mu\text{-C}_4\text{H}_8\text{S}_2)][\text{pts}]_2$ [17] with four sulfur atoms around Ni in the first coordination sphere and three Mo atoms in the second coordination sphere. The positions of the nearest peak of the As-NiMoP/Al$_2$O$_3$ catalyst and the Mo$_3$S$_4$Ni(dithiane) bulk-model sample agree well (figure 2(b)), whereas the nearest-neighbor (Ni-As) peak of the NiAs model sample is located at larger bond distances than the nearest-neighbor peak of the sulfided As-NiMoP/Al$_2$O$_3$ sample. No complete sulfiding of the sample is achievable at 450 °C as evidenced in figure 2(a) by the presence of a slight white line on the As-NiMoP/Al$_2$O$_3$ sulfided catalyst-absorption spectra as well as a shoulder at the position of the Ni–S bond in figure 2(b). The fit of the first coordination shell of the Fourier-transformed EXAFS spectra with the Mo$_3$S$_4$Ni(dithiane) bulk-model sample functions indicates that the Ni atoms are, on average, surrounded by 4.4 ± 0.5 S atoms at a distance of 2.21 ± 0.02 Å. These

Table 1
Summary of structural data for the sulfided As-NiMoP/Al$_2$O$_3$ catalyst

	Model sample	Atoms	Coordination number	Distance (Å)
As K edge	As$_2$S$_3$	As-S	1.8 ± 0.5	2.22 ± 0.02
Ni K edge[a]	Mo$_3$S$_4$Ni(dithiane)	Ni-S	4.4 ± 0.5	2.21 ± 0.02
Mo K edge	MoS$_2$	Mo-S	7.4 ± 1.0	2.41 ± 0.02
		Mo-Mo	3.8 ± 1.0	3.15 ± 0.02

[a] Note that the absorption spectra at the Ni K edge showed an incomplete sulfidation of the Ni atoms. This may affect the results of the fit. However, the results agree with those obtained in [22] for a Ni-Mo-S catalyst.

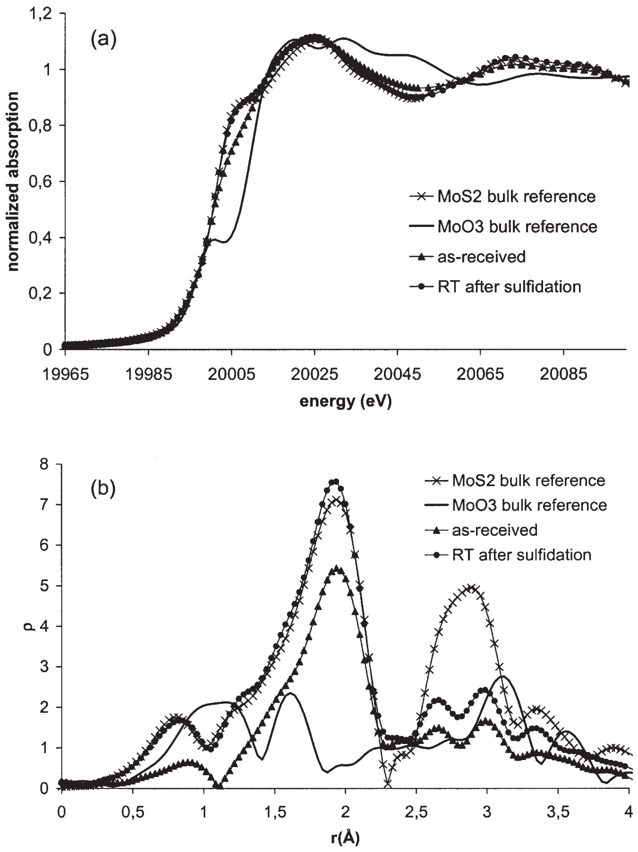

Figure 3. (a) Normalized absorption spectra at the Mo K edge and (b) magnitude of the Fourier-transformed data of the As-NiMoP/Al_2O_3 catalyst before and after sulfiding, respectively, as well as the reference samples MoO_3 and MoS_2.

results are in agreement with previously reported EXAFS results on Ni-Mo-S catalyst systems [20].

The Mo atoms of the as-received As-NiMoP/Al_2O_3 catalyst were coordinated by sulfur and oxygen atoms. The real and imaginary part of the Fourier-transformed as-received As-NiMoP/Al_2O_3 absorption spectra were best fitted with a combination of 65% of MoS_2 and 35% of MoO_3 model sample curves. Figure 3 shows the Mo K-edge absorption spectra and the corresponding k^1-weighted magnitude of the Fourier-transformed data before and after sulfiding. Upon sulfidation, slight changes occur in the XANES region. A complete agreement at the Mo K edge between the MoS_2 model sample and the sulfided As-NiMoP/Al_2O_3 sample is reached upon sulfiding up to 450 °C. A perfect fit is obtained for the first and second shell peaks with the functions of the MoS_2 model sample. An increase in the height of the Mo–S peak in the Fourier-transformed EXAFS spectra is clearly seen in figure 3(b). In a previous EXAFS study on NiMoP/Al_2O_3 catalysts [20], it was observed that the number of sulfur atoms around Mo increases upon sulfiding as a consequence of the filling of sulfur vacancies at the edges of the MoS_2 slabs. In the first coordination shell around Mo, we obtained an average sulfur coordination number of 7.4 ± 1 at a distance of 2.41 ± 0.02 Å. The second coordination shell of Mo atoms is located at 3.15 ± 0.02 Å (Mo–Mo coordination number 3.8 ± 1). Very similar values for Mo–S and Mo–Mo distances have been obtained previously for MoS_2/Al_2O_3 catalysts [21].

3.2. *Creation of a model for the As-poisoned NiMoP catalyst*

It is generally accepted that the NiMo(P)/Al_2O_3 catalysts are constituted of MoS_2 slabs, where Ni is substituting for Mo positions at the edges of the slabs [22,23]. In the case of As-poisoned catalysts, As may be occupying a new position at the edge of the slab. A model was created taking into account the bond distances and coordination numbers obtained by EXAFS. Simulations by the FEFF8.0 program package (program for *ab initio* calculations on multiple scattering XAFS and XANES [24]) at the As, Ni and Mo K-edges were performed with SCF potentials and averaging overall the atoms of the same type in the cluster. A cluster of the same size and shape as observed by scanning tunneling microscopy (STM) for a single-layer Co-Mo-S slab an Au(111) surface [25] was used. This is in good agreement with the element ratios obtained from the chemical analysis of the As-NiMoP/Al_2O_3 catalyst: Ni/As = 7, Mo/Ni = 2.7, Mo/As = 19 (in the model, the ratios are Ni/As = 9, Mo/Ni = 3, Mo/As = 27). The model is shown in figure 4. Two perpendicular mirror planes are passing through the arsenic atom. The metal–metal distances at the As-containing Ni edge are slightly larger than those at the As-free Ni edges. In the simulations, the same Debye–Waller factor has been given to all atoms of the same element type and therefore the disorder is underestimated. Another simplification of our model is that only one cluster size has been considered, though it is

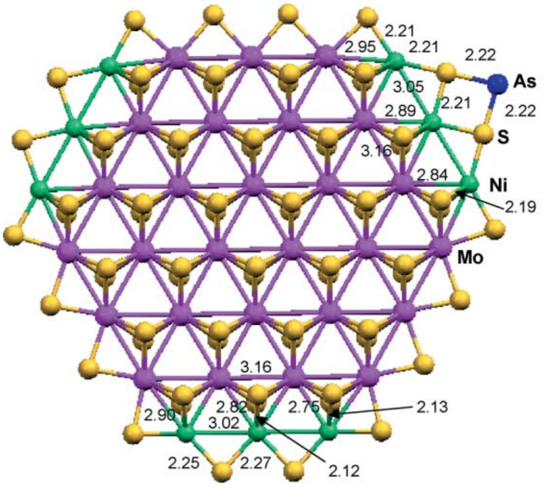

Figure 4. Structural model of the hexagonally truncated Ni-MoS_2 slab with an As atom coordinated at one edge. Relevant atomic distances are given in Å.

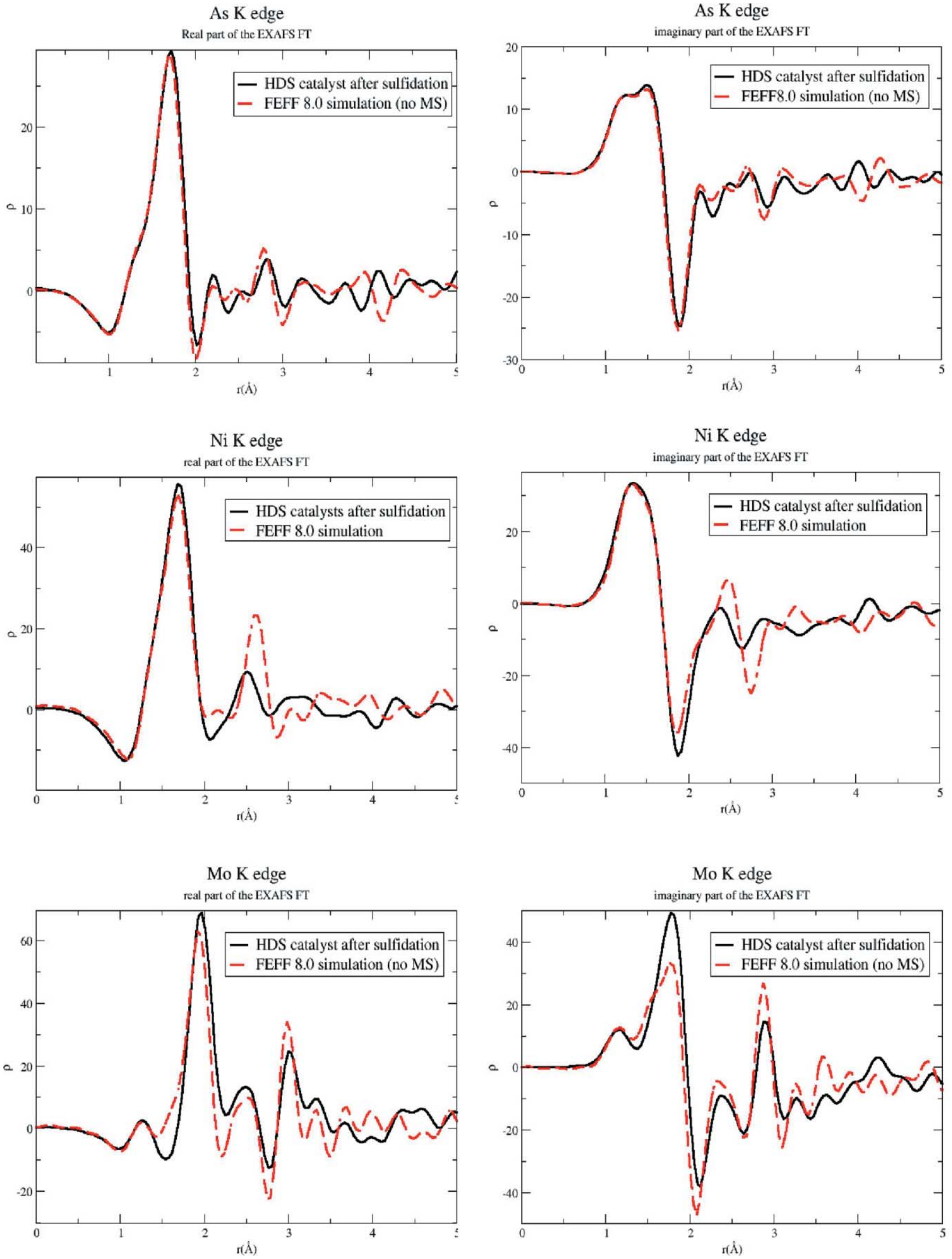

Figure 5. Measured and simulated magnitude of FT EXAFS spectra at the As, Ni, and Mo K edge, respectively (left column: real parts; right column: imaginary parts).

probable that the sample contains clusters of different sizes. Figure 5 shows the real and imaginary parts of the measured and simulated FT EXAFS spectra at the As, Ni and Mo K-edges, respectively. The agreement between the measured and simulated data, especially at the As K edge, is very high. However, in the simulations at the As K edge, a better agreement was obtained without consideration of multiple scattering, which indicates a high level of disorder in the structure.

The present structural model constitutes a simplified view of how arsenic affects the catalytic activity of hexagonally truncated Ni-MoS$_2$ slabs by blocking the active Ni sites at the cluster edges. Improvements of the model might be achieved by performance of Monte Carlo simulations to obtain the best position for each atom in the model. These optimizations, however, were beyond the scope of this investigation. Nevertheless, in view of the good agreement between measured and simulated EXAFS data, the structural pattern leading to arsenic poisoning of this specific NiMoP/Al$_2$O$_3$ catalyst seems to be established. Future EXAFS investigations on As-poisoned NiMo and CoMo catalysts with different metal ratios will have to show if this model may be generalized for other types of As-poisoned hydrotreating catalysts.

4. Conclusion

In the as-received As-NiMoP/Al$_2$O$_3$ catalyst, arsenic was found to be coordinated to oxygen. The reoxidation of As is presumably caused by the exposure of the spent catalyst to air. The Ni atoms are also in oxidic surroundings, whereas Mo is only partially oxidized. After resulfiding the sample, and thus under realistic working conditions, As, Ni and Mo were found to be bonded to sulfur in the nearest coordination sphere. An average As–S coordination number close to 2 was calculated by fitting the experimental data to the structural data for As$_2$S$_3$. There is no evidence for the formation of As–Ni bonds. It is tempting to associate the As-induced deactivation of this NiMoP/Al$_2$O$_3$ hydrotreating catalyst to the formation of stable Ni–S–As bonds at the edges of Ni-Mo-S slabs involving the blocking of Ni sites.

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