XAFS characterization of industrial catalysts: *in situ* study of phase transformation of nickel sulfide

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Abstract. The online sulfiding process for nickel-contained catalyst often ends up with a nickel sulfide mixture in refinery plant. To elucidate the local environment of nickel and its corresponding sulfur species, a model catalyst (nickel sulfide) and model thermal process were employed to explore the possibilities for characterization of real catalysts in industrial conditions. The present investigation shows effectiveness of *in situ* XANES and EXAFS measurements for studying the phase stability and phase composition in these systems, which could be used to simulate real sulfiding process in industrial reactions, such as hydrodesulfurizations of oil.

1. Introduction

Nickel sulfide materials have a wide industrial application in petrochemical and refinery processes for catalyst [1-5]. Generally, nickel sulfide catalyst is obtained by an *in situ* sulfiding procedure [6] using nickel oxide precursor with mixed gas stream of H_2 and H_2S at certain temperature and pressure. The catalyst activity and selectivity for these processes are a function of sulfiding procedure because nickel-contained catalyst can form a variety of nickel sulfides with various phase compositions (Ni_3S_2, Ni_6S_5, Ni_7S_6, NiS, NiS_2) [7-13]. However, both the structure and chemical composition of the final nickel and sulfur species are generally not known due to the complexity of nickel-sulfur compounds existing in the real catalyst system during and after sulfurization process. Another open question is the extent of stability of nickel sulfur species subjected to hydrogen atmosphere at reaction temperatures due to the occurrence of phase transformation [14] and the sequential loss of sulfur [15].

It is difficult to elucidate the structure of nickel sulfides during the sulfiding process by means of the conventional in-house characterization. For example, X-ray diffraction is a conventional method to study phase transformations but it is limited in this case due to the unavoidable contamination of the expensive *in situ* cell of the diffractometer, and the difficulty to identify, quantify or even isolate the diffraction pattern of nickel sulfide catalyst from that of the support materials. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies are quite useful for studies of local atomic environments [16]. The sensitivity of XANES spectra to the electronic structure, oxidation state, and geometry of the absorbing site is well known. A combination of the XANES and EXAFS analyses of nickel K-edge is expected to enable determination of the

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chemical state and detailed local environment of nickel but their use for industrial catalysts is scarce and not well documented, to the best of our knowledge.

In this investigation, a well characterized nickel sulfide mixture (a reference compound, from a commercial supplier, consisting of 70 wt.% α-Ni_3S_2 and 30 wt.% α-Ni_7S_6) was used as a starting material for exploring the local structure changes and phase composition of nickel sulfide by XANES and EXAFS data analysis during the phase transformation of α-Ni_7S_6 to α-Ni_3S_2 under hydrogen atmosphere. These results could facilitate characterizations in the sulfiding process of nickel catalyst or nickel sulfide catalysts itself in hydrodesulfurization reaction.

2. Experimental

2.1. Sample preparation
A commercial nickel (II) sulfide (Alfa Aesar) was used as a starting material (denoted as NiS_x). It was analyzed to be made up of 70 wt.% of α-Ni_3S_2 and 30 wt.% of α-Ni_7S_6 by chemical analysis. Sample NiS_x was reduced at different temperatures (T) with the pure hydrogen at a flowrate of 50 ml/min for 240 min at most. Finally, the reduced sample was characterized to be pure α-Ni_3S_2 by XRD (Bruker AXS D8 Advance), chemical analysis (ICP-AES, Varian 725 ES) and X-ray Absorption Spectroscopy.

2.2. X-ray absorption measurements
Sample NiS_x for the nickel K-edge measurements were conducted on the beamline of NSLS X19A at National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, New York, USA. A pellet made by mixing ground NiS_x and alumina in the mass ratio of 1:3 was prepared for *in situ* nickel K-edge measurements. The sample was mounted in an *in situ* XAS cell (the Nashner-Adler cell) [17] and reduced in 5 vol.% H_2 in He at 450°C for 4 h. EXAFS scans before and after reduction were recorded at room temperature, denoted as NiS_x and NiS_x-R. The pure α-Ni_3S_2 for nickel K-edge measured at room temperature was also measured. Composition of sample NiS_x-R was analyzed by chemical analysis, which consisted of 80 wt.% of α-Ni_3S_2 and 20 wt.% of α-Ni_7S_6.

2.3. Data Analysis
Data processing and analysis were performed using the IFEFFIT package [18, 19]. The relative amount of α-Ni_7S_6 and α-Ni_3S_2 in the sample NiS_x-R was analyzed by linear combination analysis (LCA) on k^2-weighted EXAFS spectra using Athena software.

3. Results

3.1. Phase transformation of α-Ni_7S_6 to α-Ni_3S_2 evidenced by XRD
Figure 1 presents the XRD patterns of NiS_x to a pure α-Ni_3S_2 measured at room temperature after reduction at different temperature and time. By identification of the structure in the PDF database, the crystal phase for NiS_x shows a mixed phase of α-Ni_7S_6 (JCPDF#24-1021) and α-Ni_3S_2 (JCPDF#44-1418). According to the chemical analysis by ICP-AES, the major phase in the raw nickel sulfide material is α-Ni_3S_2 with a content of 70.0 wt.%, the minor phase for α-Ni_7S_6 is 30.0 wt.%. XRD analysis demonstrated that α-Ni_7S_6 could be transformed to α-Ni_3S_2 when heating sample NiS_x in hydrogen.

3.2. Electronic structure changes and phase composition of NiS_x during in situ XAS
Figure 2 compares the experimental Ni K-edge spectra of NiS_x, NiS_x-R and α-Ni_3S_2 in E-space, K-space and R-space measured at 25°C. It can be seen that a slightly shift to higher energy occurred in Figure 2a with the loss of sulfur from NiS_x to α-Ni_3S_2 via NiS_x-R, which means the loss of sulfur could be perceptive from XANES shift. However, it is impossible to find the phase composition of NiS_x-R from XANES analysis by linear combination method because the features do not change too

significantly, and the contrast is weak. EXAFS fitting is also impossible to use for this purpose because of the very disordered structure of $\alpha\text{-}Ni_7S_6$.
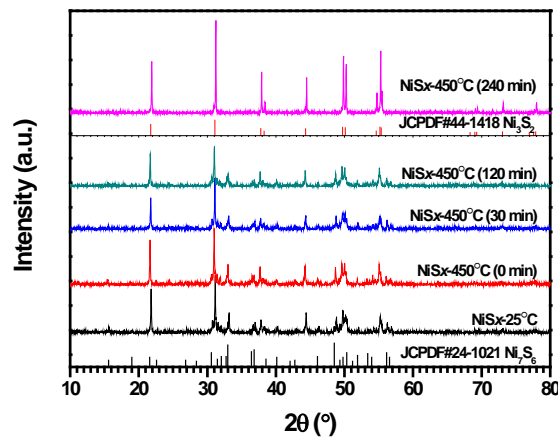

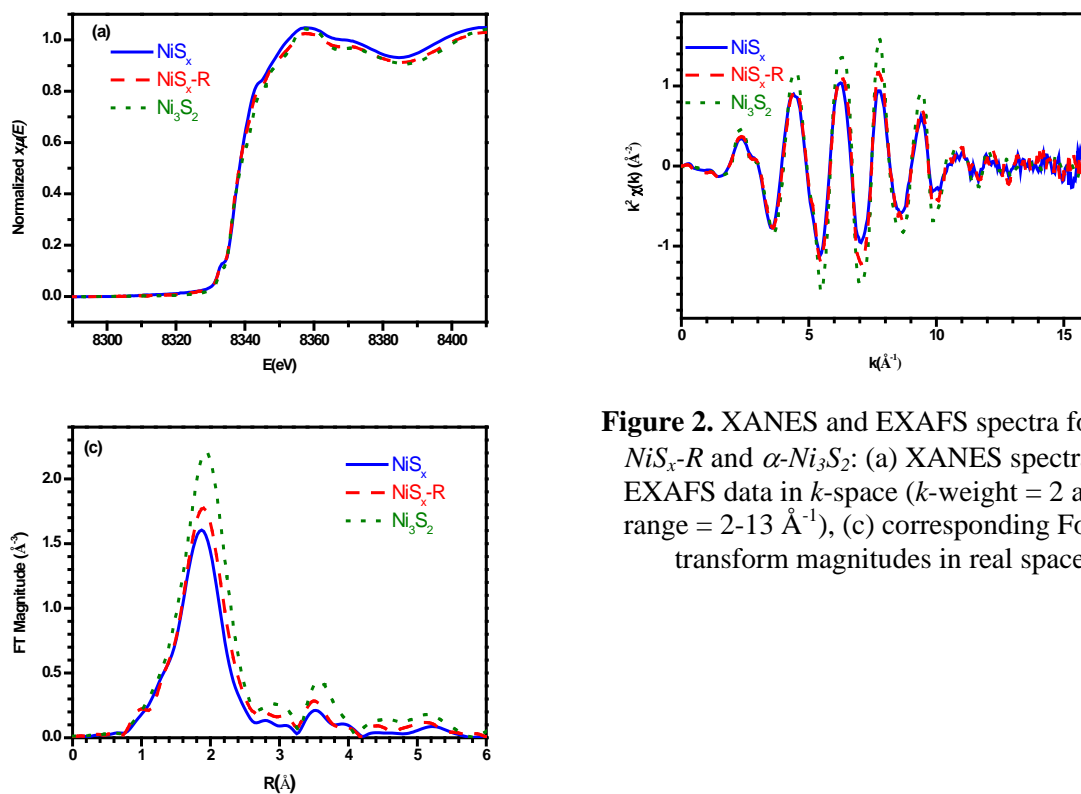**Figure 1.** XRD patterns of NiS_x measured at room temperature after reduction at different temperatures and durations.

Figure 2. XANES and EXAFS spectra for NiS_x, $NiS_x\text{-}R$ and $\alpha\text{-}Ni_3S_2$: (a) XANES spectra, (b) EXAFS data in k-space (k-weight = 2 and k-range = 2-13 Å^{-1}), (c) corresponding Fourier transform magnitudes in real space.

However, EXAFS data do change significantly between the starting sample and the final sample (Figures 2b,c). The changes show presence of isosbestic points in k-space, hence, the unknown composition is a two-phase mixture that can be analyzed by linear combination method. Therefore, we used linear combination analysis for EXAFS, not XANES spectra. The k-range for linear combination is 2-13 Å^{-1}. Figure 3 shows the results of linear combination fitting of $NiS_x\text{-}R$ spectrum to the spectra

of NiS_x and α-Ni_3S_2. It was found sample NiS_x-R was composed of 19.0% α-Ni_7S_6 and 81.0% α-Ni_3S_2, which is in agreement with the phase calculation by nickel content measured from chemical analysis.
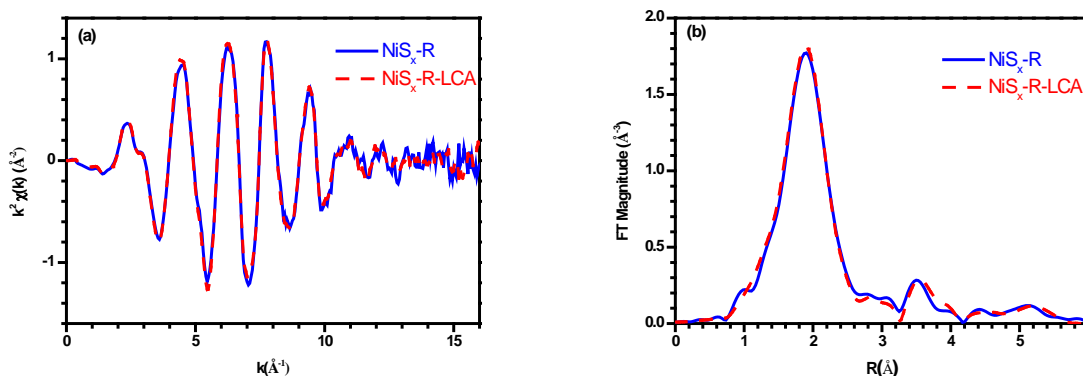

Figure 3. Linear combination analysis in k^2chi data for NiS_x-R spectrum (k-weight = 2 and k-range = 2-13 $\mathring{A}^{-1}$).

3.3. Considerations of the in situ methods for investigating the mechanism of sulfiding process for industrial nickel catalysts

The purpose of this work was to investigate the sensitivity of XANES and EXAFS to structure changes of nickel sulfide. As emphasized in the introduction, this knowledge is important for guiding *in situ* experimental design for investigating the mechanism of sulfiding process for real nickel catalysts.

One analysis demonstrated important complementarity of synchrotron-based characterization by XAS and the lab-based XRD studies. Specifically, laboratory X-ray diffraction turned out to be adequate for detecting the phase change of nickel sulfide but it failed to analyze the phase composition in the real catalyst system due to the diffraction peaks from the catalyst support. XANES analysis showed no sensitivity to the local structure and phase composition changes of nickel sulfide. EXAFS analysis by fitting methods is not suitable for obtaining the coordination number changes during the phase transformation of α-Ni_7S_6 to α-Ni_3S_2 because of the large structural disorder and because EXAFS fitting method is not generally applicable for phase speciation in multi-component mixtures [20]. Linear combination analysis of EXAFS data in k-space was a good alternative to the above methods and was used in this work to calculate the mixing fractions of different phases in this model catalyst, hence, show a strong promise as a technique of choice in real catalytic investigations.

4. Summary and conclusions

We presented a method, based on in situ XAS studies and ex-situ characterization by XRD and chemical analysis techniques, to measure the phase composition and phase stability of nickel sulfide-based catalysts during an online sulfiding process and evaluate possible sulfur loss or addition. Our results are potentially useful for a large class of nickel sulfide catalysts used in hydrodesulfurization reactions.

Acknowledgements

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