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Report:

One pure Ni, one bimetallic NiMo and one trimetallic NiWMo unsupported catalyst were prepared via a pH-controlled co-precipitation method [1]. A part of the obtained green oxide precursors were subsequently sulfided at 18 bar in a flow of 10% H₂S in H₂ at 400 °C for 12 h [2]. XANES and EXAFS at the Mo K-edge, W L_{III}-edge and the Ni K-edge of reference compounds, the oxidic precursor before activation and of the activated sulfided were collected in He flow and at liquid N₂ temperature (LNT). All spectra were recorded in transmission mode. The spectra of the sample and the corresponding metal foils were measured simultaneously to correct the monochromator energy calibration between two measurements. To enhance the signal to noise ratio, at least two spectra of each sample were averaged. The grained samples were prepared as self-supporting wafers and placed into a stainless steel in situ flow cell. The cell design allows not only the cooling of the sample to LNT, but also the heating in different gas atmospheres [3]. All sulfided catalysts needed to be resulfided in-situ to remove physisorbed water and oxygen and to resulfide the partial oxidized surface. The resulfidation was performed in a flow of 10 vol% H₂S in H₂ for 30 min at 400 °C with a heating rate of 5 °C/min. Afterwards the cell was flushed with He and cooled to LNT before XANES and EXAFS scans were performed. The XANES and EXAFS data were evaluated with IFEFFIT containing the Horae-package (ATHENA and ARTEMIS, version 1.2.11.) [4, 5]. The scattering contributions in the pre- and post-edge of the background were removed from the X-ray absorption using a third-order polynomial function, afterwards all spectra were normalized to the average post-edge and the oscillations of the EXAFS were weighted with k^3 and Fourier-transformed. Unfortunately, the quality of the spectra were not so good as expected, especially the background removal at the Ni K-edge turned out to be difficult and enabled a FT within the limit of just 3.3-9 Å⁻¹.

The normalized XANES of all samples and measured reference compounds are shown in Figure 1 and the Fourier transforms (FT) are summarized in Figure 2. The XANES of the three samples in oxidic as well as in sulfided state at all three edges are quite similar to each other and are comparable to the reference bulk material. Given that the adsorption edge energy and the white lines of the oxide materials are always higher in

comparison to their sulfide counterparts, Ni, Mo and W seem to be reduced in all sulfide materials.

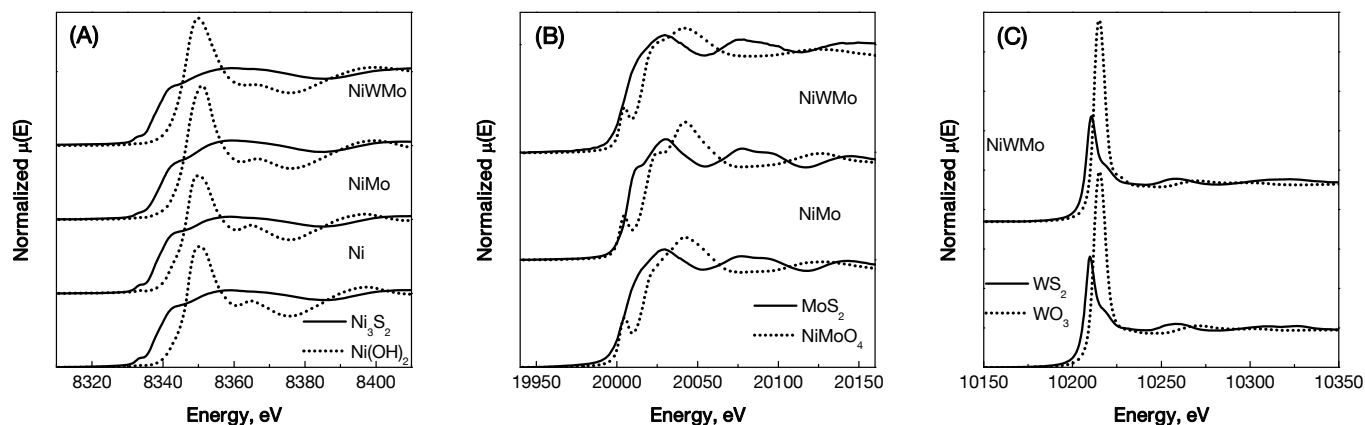


Figure 1: XANES at Ni K-edge (A), Mo K-edge (B) and W L_{III}-edge (C) of reference compounds and the samples Ni, NiMo and NiWMo in oxidic (dotted line) and activated sulfided state (solid line).

The Ni K-edges of the oxidic precursor and of Ni(OH)₂ were observed at an energy of 8347 eV, whereas for the sulfide catalysts and for Ni₃S₂ an absorption edge energy of around 8338 eV was observed (Figure 1 (A)). Furthermore, a small pre-edge at around 8334 eV was found in the XANES of the sulfided samples due to the electronic 1s→4d transition, typical for the tetrahedral coordination of Ni^{1.3+} in Ni₃S₂ [6]. The Mo K-edge XANES of the two Mo containing catalyst precursors exhibits a characteristic pre-edge peak at around 20005 eV, similar to NiMoO₄ (Figure 1 (B)). This 1s→4d transition indicates a tetrahedral or distorted octahedral coordination of Mo⁶⁺ [7]. After sulfidation, the pre-edge disappears and the adsorption edge energy shifted from 20018 eV to 20007 eV due to the reduction of Mo⁶⁺ to Mo⁴⁺. The adsorption edge energies of the intense white lines at the W L_{III} edge, probing 5d orbital occupation, were found at 10212 eV for NiWMo in oxidic state and for WO₃ and for the sulfided NiWMo and WS₂ at 10207 eV (Figure 1 (C)).

All Fourier transformed EXAFS (see Figure 2,) showed defined backscattering signals (coordination shells) and the more distant shells, especially at the Mo K- and W L_{III}-edge, which are overlapping with low intensities indicating low coordination numbers and a disordered structure [7]. Moreover, given that Mo and W largely differ in their backscattering, the less intense metal-metal scattering contribution around 3 Å (not phase corrected) could be caused by Mo and W in direct neighborhood in the same crystal structure [8].

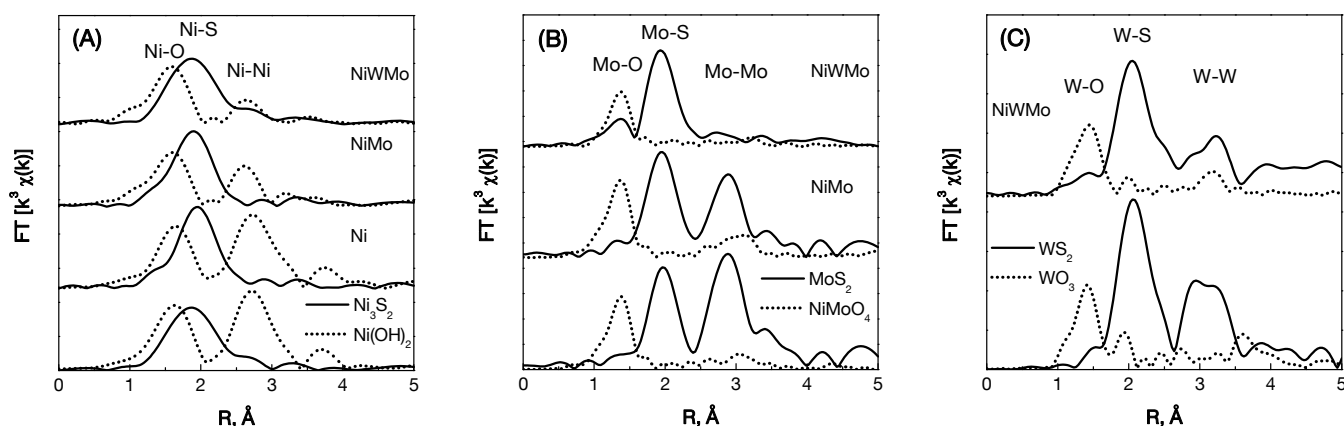


Figure 2: FT of EXAFS at Ni K-edge (A), Mo K-edge (B) and W L_{III}-edge (C) of reference compounds and the samples Ni, NiMo and NiWMo in oxidic (dotted line) and activated sulfided state (solid line).

The FT of all oxidic materials at the Ni K-edge exhibit two broad signals at around 1.6 Å and around 2.7 Å (Figure 2 (A), not phase corrected) due to Ni-O and Ni-Ni scattering, respectively [9]. In comparison to the high crystalline Ni(OH)₂ reference compound, the Ni-Ni coordination is much smaller in the NiMo and NiWMo catalyst precursors and slightly shifted to smaller distances. At the Mo K-edge, the FT of the EXAFS of the catalyst precursors exhibit only one strong backscatter contribution at around 1.4 Å assigned to Mo-O contributions (Figure 2 (B)). In the NiMo catalyst precursor, an additional Mo-Mo backscatter signal at around 3.2 Å appears [7]. At the W L_{III}-edge, the EXAFS of the NiWMo precursor presents

similarities to the WO_3 reference regarding the first W-O contribution [10]. The EXAFS of the sulfides are comparable to the sulfide reference compounds since the distances of the first metal-S shells are equivalent to Ni_3S_2 , MoS_2 and WS_2 . By adding Mo and W to the unsupported Ni catalysts the Ni-S contribution is broadened. Moreover, the Mo-Mo and W-W backscatter signals decreased in comparison to the respective reference compounds MoS_2 and WS_2 . Referring to literature, these observations allow the assumption of the presence of Ni in neighborhood of Mo and W [10, 11]. The detailed analysis of the local environment of the Ni, Mo and W atoms will be done in the future by fitting in k-space with the experimental data of reference compounds and calculated reference spectra.

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