ESRF	**Experiment title:** In situ characterization by EXAFS of Ni-sulfide, Mo-sulfide and W-sulfide phases formed during sulfidation of NiMo/Titania, NiW/ASA, NiW/Titania, NiW/Alumina and NiW/Carbon hydrotreating catalysts, respectively.	**Experiment number:** CH–797
Beamline: BM 01B	**Date of experiment:** from: 11/11/99 to: 16/11/99	**Date of report:** 20/04/00
Shifts: 15	**Local contact(s):** H. Emerich	*Received at ESRF:*

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Report:

Within our research project it has been demonstrated that NiW supported on alumina has good prospects for deep hydrodesulfurization (HDS) of diesel fuel [1]. The high performance in the HDS of substituted dibenzothiophenes, which have been identified as the key sulfur compounds in deep HDS applications, is believed to be due to a limited sulfidation of W to WS_2 on this support material. In the present work, the influence of the support on the sulfidation and genesis of different phases in NiW catalysts is investigated.

The allocated beam time was used to study NiW catalysts on activated carbon (C), alumina (Al_2O_3) and amorphous silica alumina (ASA) with Ni–K EXAFS and W–L_{III} EXAFS. Catalysts were pressed in self-supporting wafers and mounted in an *in situ* EXAFS cell. The NiW catalysts were studied after stepwize sulfidation in a 10 vol% H_2S/H_2 mixture at the following ($T_S = z$ K) temperatures: 300, 373, 473, 573 and 673 K. Spectra were recorded at liquid nitrogen temperature after each sulfidation step at the Ni–K edge and the W–L_{III} edge consecutively.

[1] Reinhoudt, H.R., Troost, R., Van Schalkwijk, S., Van Langeveld, A.D., Sie, S.T., Van Veen, J.A.R. and Moulijn, J.A., *Fuel. Proc. Technol.* 61 (1999) 133

Since the W–support interaction is expected to be minimal in carbon supported NiW, it serves as our model system. Figures 1 and 2 show the XANES spectra of carbon supported NiW measured at the Ni–K edge and the W–L_{III} edge, respectively. Analysis of the Ni data showed that Ni sulfidation aleardy starts after sulfidation at room temperature, although an oxygen contribution is present with a coordination number of 1.8. This Ni–O contribution disappears at 373 K, as can also be seen in Figure 1as a decline of the white line in the spectrum. The shift in edge position originates from experimental conditions. Upon increasing sulfidation temperatures, the coordination number of Ni–S increases to 6.2 at 673 K.

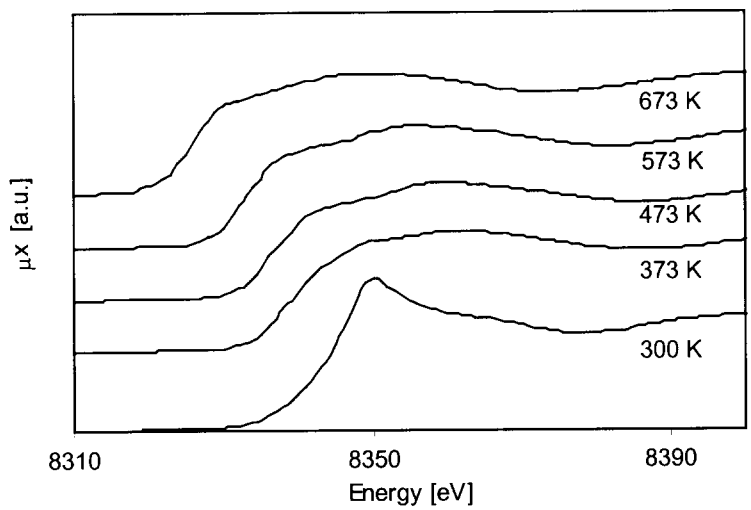

Figure 1: Ni–K edge XANES spectra of carbon supported NiW after sulfidation at indicated temperatures.

At low sulfidation temperatures W is in an oxidic state. Sulfidation of W starts above 473 K, which is also visible as a change in the shape of the XANES spectrum in Figure 2.

Figure 3 shows that at 473 K the spectral intensity is very low: the W–O contribution has decreased upon increasing the sulfidation temperature from 300 to 473 K, while the W–S contribution increases tremendously only after sulfiding at 673 K. The W–S and W–W distances of 2.40 and 3.15 Å respectively and the W–S coordination number of 6 (T_S=673 K), correspond well with the values for bulk WS_2. The W–W coordination number at 673 K is 2.5, which is much lower than the bulk value of 6. This could either point to well dispersed WS_2 or could be an indication for WS_2 that is not as crystalline as bulk WS_2.

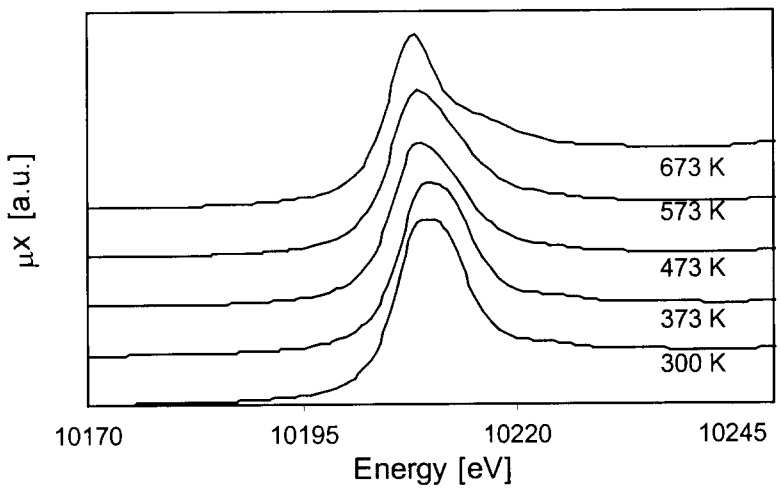

Figure 2: W–L_{III} edge XANES spectra of carbon supported NiW after sulfidation at indicated temperatures.

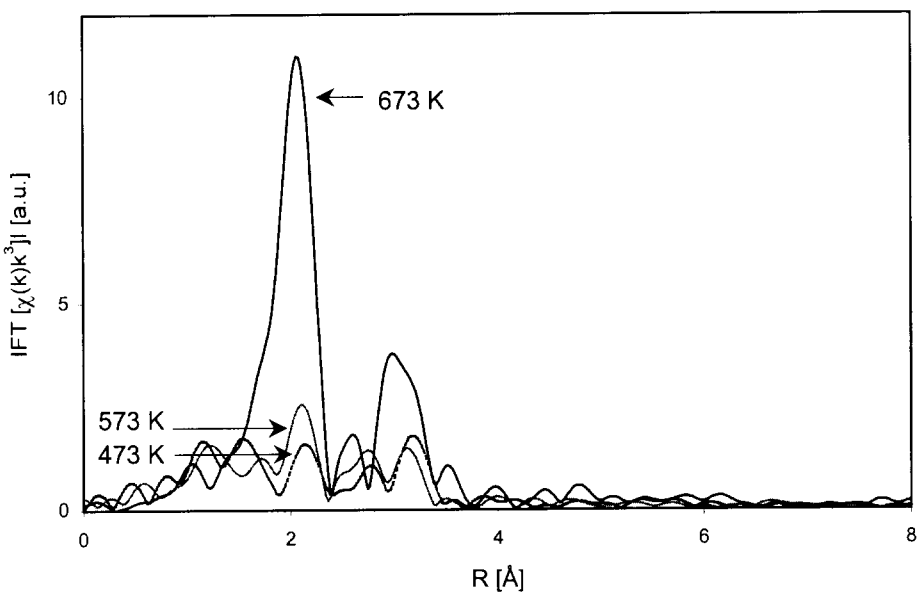

Figure 3: W-L_{III} edge EXAFS k^3 weighted FT functions of carbon supported NiW after sulfidation at 473 , 573 and 673 K.