

**Experiment title:**

*In situ* XAFS study of the sulphidation process of Ni-Mo/SiO<sub>2</sub> catalyst precursors.

**Experiment number:**

CH-366

**Beamline:**

ID24

**Date of experiment:**

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15

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**Report:**

Nickel-molybdenum sulphide catalysts are used in the petroleum industry to remove sulphur and nitrogen atoms from molecules in oil fractions. In recent studies we showed that substantial improvements in catalytic activity can be obtained by the addition of complexing agents to catalyst precursors.

In this study, energy dispersive Ni and Mo K-edge X ray absorption spectra were recorded during the sulphidation process of NiMo(Ligands) catalyst precursors. Three kinds of precursors were investigated; a precursor without ligands (NiMo), with nitrilotriacetic acid (NiMo(NTA)), and with ethylenediamine (NiMo(EN)). A powder sample was pressed into a self-supporting wafer and mounted in an *in situ* cell with Kapton windows. Then the sample was exposed to H<sub>2</sub>S + H<sub>2</sub> (H<sub>2</sub>S 10%) mixed gas and heated gradually to 400°C. The flow rate of the mixed gas, the heating rate, and time resolution were 30 ml min<sup>-1</sup>, 6 K min<sup>-1</sup>,

and 6 sec (1°C), respectively. The sulphidation process was divided into four parts (20- 100, 100-200, 200-300, and 300-400°C), because the background should be measured every 20 min. Useful data were obtained for the Mo-K edge. The data for the Ni-K edge, on the other hand, were very noisy because of a low Ni concentration and a large background.

Figure 1 shows Fourier-transformed Mo K edge EXAFS functions of the NiMo(EN) precursor sulphidated at 300-400°C. The FT k-range was 3- 10 Å<sup>-1</sup>. A Mo-Mo contribution (peak at 3.0 Å) appeared at 330°C accompanied by a increasing Mo-S peak (at 1.7 Å) intensity. This result suggests that the crystallization of small MoS<sub>2</sub> particles occurred above 330°C and that the particles were amorphous below this temperature. This essential information could not have been obtained from a conventional EXAFS measurement.

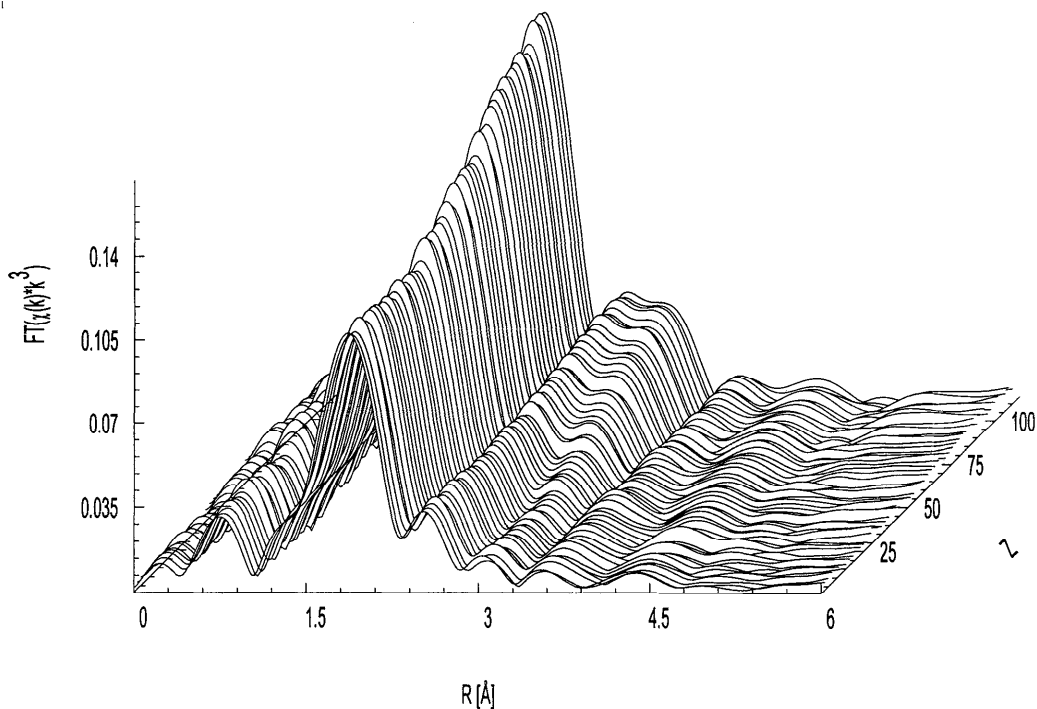


Figure 1. FT of  $k^3\chi(k)$  for NiMo(EN)/SiO<sub>2</sub> sulphidated at 300-400°C. Spectra were measured about every 1 °C, and their sequence number is plotted along the Z axis.