



Experiment title: EXAFS of Ni-MoS ₂ and Co-MoS ₂ hydrodesulphurizaion catalysts	Experiment number : CH-216	
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Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. R. Prins
Dr. T. Weber
Dr. F. Wypych
Dr. T. Shido
R. Cattaneo

Laboratory for Technical Chemistry, ETH-Zurich

Report:

Previously, we showed that activities of Ni-MoS₂ catalysts are substantially improved by the addition of complexing agents to catalyst precursors. EXAFS studies of the sulphidation process of a nitrilotriacetic acid (NTA) modified Ni-Mo/SiO₂ precursor showed that molybdenum was sulphided before nickel in the presence of NTA, while the reverse was true in the absence of NTA (I). Recently, we found that addition of ethylenediamine (EN) instead of NTA to the precursor also improved the catalytic activities. Hence, we investigated the sulphidation process of the EN-modified precursor using XAFS to determine whether the sulphidation temperature is affected by ligands in this case, too.

Figure 1 shows Fourier transformed Mo-K EXAFS functions ($k^3\chi(k)$) sulphided at various temperatures. In the spectra of the fresh sample and that sulphided at 343 K, no clear peaks are observed. At 423 K, a Mo-S contribution was observed at 2.47 Å, and the distance decreased with increasing sulphidation temperatures. The Mo-S distance at 673 K was the same as that of bulk MoS₂ (2.41 Å). The coordination number (CN) of Mo-S was 3.6 at 423

K and increased with increasing temperature, to 6.3 at 673 K, which agrees with the value of bulk MoS₂. In addition, a Mo-Mo contribution was observed at 673 K at 3.16 Å with CN of 4.3. The EXAFS data of the Mo-K edge show that the sulphidation started at 423 K and was complete at 673 K. The proportion of sulphided molybdenum was ca. 60% at 423 K and increased slowly as the temperature increased.

Figure 2 shows Ni-K edge XANES spectra of the sample sulphided at various temperatures. Solid and dotted lines represent observed and calculated spectra, respectively. The spectra of the fresh sample and that sulphided at 673 K were taken as references of oxidic and sulphidic states; the other spectra were simulated by a linear function of the reference spectra. The calculated spectra reproduced the observed spectra well at every temperature, showing that the samples were a mixture of oxidic and sulphidic nickel. The XANES analysis shows that about 80% of nickel is already sulphided at 343 K and that sulphidation was complete at 493 K.

The sulphidation process of the EN-modified precursor is more similar to that of an unmodified precursor than to that of the NTA-modified one, which means that the activity does not relate to the sulphidation feature in the case of EN. Further investigation is required to understand the role of ligands under sulphidation conditions and the structure of the active site.

1. L. Medici and R. Prins. *J. Catal.* 163, 38 (1996).

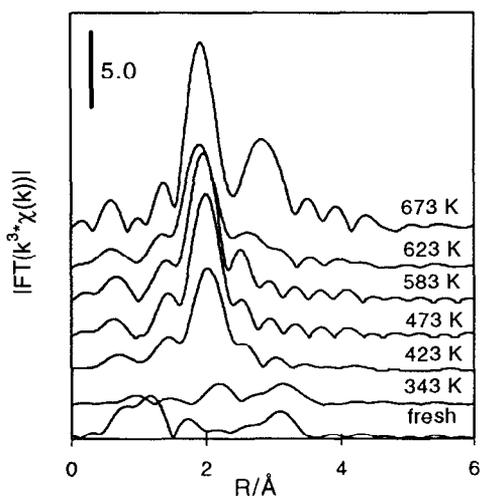


Figure 1. FT of Mo-K EXAFS of Ni-Mo/SiO₂ precursor sulphided at various temperatures.

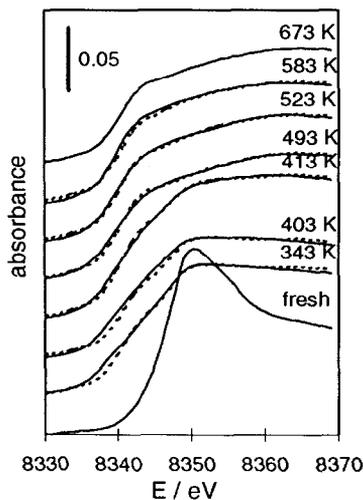


Figure 2. Ni-K XANES of Ni-Mo/SiO₂ precursor sulphided at various temperatures.