Sulphidation of NiMo/SiO$_2$ hydrotreating catalysts followed by means of QEXAFS

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Supported nickel-molybdenum sulphide catalysts are used in the refining industry to remove sulphur and nitrogen atoms in oil feedstocks. Previous work showed that the addition of nitrilotriacetic acid during the preparation of the catalyst precursors allows a dramatic improvement of the activity of the sulphided catalysts [1-4]. In our project, NiMo/SiO$_2$ catalysts modified by the addition of chelating ligands are investigated and the relationship between structure and catalytic performance is searched. The catalytic activity is tested through hydrodesulphurisation (HDS) of thiophene, whereas the structures of oxidic precursors and sulphided catalysts are investigated by means of EXAFS, UV-Vis and Raman spectroscopies [5].

During our project at HASYLAB (Beamline RÖMO II), series of QEXAFS spectra were collected during the sulphidation of NiMo/SiO$_2$ catalysts prepared without any ligand and with ethylenediamine tetraacetic acid (EDTA), ethylenediamine (EN), 18-crown-6 (CE) and different concentrations of NTA. For all samples the Ni and Mo K-edges were measured. The samples were heated in special EXAFS cells, under a 10% H$_2$S/H$_2$ stream, to 400°C (heating rate 6°C/min) and kept at this temperature for 30 min. A spectrum was recorded every 3 min.

**Mo K-edge**

In Figure 1 the Fourier-transformed $\langle k \rangle k^3$ Mo K-edge QEXAFS spectra of the catalysts prepared without ligand are shown as a function of the sulphidation temperature (k range 3-17 Å$^{-1}$). The decrease of the Mo-O contributions (between 1 and 1.8 Å) can be observed until a sulphidation temperature of 245°C, whereas the growth of a new signal at 2 Å, attributed to sulphur, starts around 125°C. The signal at 3 Å (Mo-Mo contribution due to polymolybdates), disappears at about 140°C, and is newly formed at temperatures above 295°C, this time originating from the Mo-Mo contribution of MoS$_2$ crystallites. An interesting features appears in the spectra recorded between 260 and 280°C, in which a new signal is observed at about 2.6 Å, which then decreases and disappears at higher temperatures. The assignment of this signal is quite difficult; it could arise from a shorter Mo-Mo shell of an intermediate product.

![Figure 1. Mo K-edge Fourier-transformed QEXAFS functions of the sulphidation process of the catalyst prepared without ligands (NiMo=0.3:1, loadings Mo 7.1%, Ni 1.3%).](image-url)
The spectra of the catalyst prepared with NTA (molar ratio NiMoNTA=0.3:1:0.45, Figure 2), show some differences in comparison to the previous ones. The Mo-O contributions decrease much quicker, although they do not disappear completely, and the S signal starts to grow at much lower temperatures. In this case, it is possible to see that NTA forms complexes with Mo, because the Mo-Mo contribution at 3 Å is much smaller at low temperature. The signal at 3 Å observed at temperatures between 320 and 370°C indicates that the MoS₂ crystallites are slightly amorphous and become only more ordered at higher temperatures. The intermediate product with the signal at 2.6 Å seems to be present in a wider temperature range (245-285°C). In general, the sulphidation of Mo starts earlier when NTA is present but finishes at higher temperature.

**Ni K-edge**

The measurement at the Ni K-edge were poorer of information because of the low Ni-loading (1.3 wt.%). Nevertheless, a k-range from 3 to 10 Å⁻¹ could be used, what enabled to estimate the structure of the first shell and to follow the sulphidation of Ni. NTA and EDTA delay the sulphidation of Ni, whereas EN does not have any effect on the sulphidation process of the metal ion.

**Conclusions**

From the obtained results it is evident that QEXAFS is very useful in understanding the various stages of the sulphidation of Mo and Ni. The recorded spectra allowed us to obtain an overview on the whole sulphidation process and to point out the temperature ranges in which the main changes take place. These results enable to understand the factors which are essential for the formation of the active phase in HDS catalysts. We plan, then, to adapt the synthesis of the precursor catalysts in order to maximize the fraction of the active sites on the catalysts. In order to achieve this, additional information about the structure of the intermediate phases are needed, which is obtained by means of classical EXAFS at the promising temperatures discovered by the QEXAFS measurements. Moreover, the quality of the QEXAFS spectra collected at the Ni K-edge will be improved by increasing the accumulation time during the measurements.

**References**