



	Experiment title: Molecular level preparation and EXAFS characterisation of hydrodesulphurisation catalysts.	Experiment number: CH-442
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Report:

Molybdenum sulphide catalysts are used in the petroleum industry to remove sulphur and nitrogen atoms from molecules in oil fractions. In these catalysts, nickel and cobalt are often used as promoters [1]. A widely accepted model at the moment is the "NiMoS phase" model, in which it is assumed that Mo is present as MoS₂ and that the Ni promoter is present at the edges of the MoS₂ crystals. Ni can also be present in other forms, and therefore cause a decrease of the catalytic activity. Because of this inhomogeneity, the structure of the active site and the reaction mechanism are still unclear. To understand the reasons for the inhomogeneity in the sulphided samples, the structure of the promoter in the oxide samples has to be investigated. A way to make the oxide catalysts as homogeneous as possible must be found. For this reason catalyst precursors containing various chelating ligands were prepared. The presence of these ligands has a beneficial effect on the catalytic activity of the sulphided catalysts [2].

The presented measurements were concentrated on the effect that nitrilotriacetic acid (NTA) and ethylenediamine (EN) have on Ni in the catalyst precursors. Due to the low Ni concentration in the samples (1.3 wt %) 5 scans were averaged for every sample. The used k range was 3-14 Å⁻¹. The samples were pressed into self-supporting wafers and mounted in an EXAFS cell [3]. Measurements were carried out at liquid nitrogen temperature.

Results

Fig.1 shows the Ni K-edge Fourier-transformed $\chi(k)\cdot k^3$ functions of the catalyst precursor prepared without adding any ligand and of four catalyst precursors containing different amounts of EN. The first signal of the lowest spectrum has been ascribed to the oxygen atoms surrounding Ni (CN 4.5) at a distance of 1.99 Å, whereas the second one is due to the presence of Si atoms (CN 4.5, distance 3.35 Å) in the second shell around Ni. The observation of Si neighbours demonstrates that Ni is interacting with the support in the catalyst precursor. From the figure it is furthermore visible that the addition of the organic ligand causes the gradual decrease of the Ni-Si signal. In the spectrum of the catalyst precursor with the molar ratio EN:Ni=6.66, the Ni-Si signal has completely disappeared but a new signal at 2.3 Å (phase uncorrected) has grown, due to the presence of the carbon atoms belonging to EN. In fact, at such a high EN concentration, three molecules of the chelating agent surround Ni and EXAFS can detect their presence.

Fig. 2 shows a series of spectra of catalysts containing increasing amounts of NTA. A comparison with Fig.1 clearly reveals that a smaller amount of NTA is needed to eliminate the Ni-SiO₂ interactions. In fact, at a molar ratio NTA:Ni=0.66 no Ni-support interaction is observed, whereas with EN the Ni-Si signal disappears only at a molar ratio EN:Ni=3.33.

The demonstration of the presence of a Ni-SiO₂ interaction is an essential piece of information for the understanding of the sulphidation process that precedes the catalytic reaction. The collected data show that an isolation of Ni is achieved by adding chelating ligands during the preparation of catalyst precursors [4]. Moreover, the different effects of EN and NTA on Ni could be investigated in detail.

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3. F. W. H. Kampers, T. M. J. Maas, J. van Grondelle, P. Brinkgreve and D. C. Koningsberger, *Rev. Sci. Instrum.*, 60 (1989) 2635.
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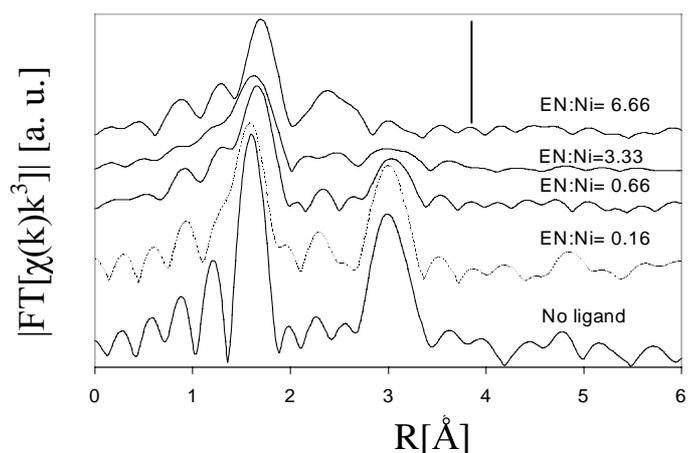


FIG. 1. Absolute parts of the Ni K-edge Fourier transformed EXAFS functions of NiMo/SiO₂ catalyst precursors containing different amounts of ethylenediamine.

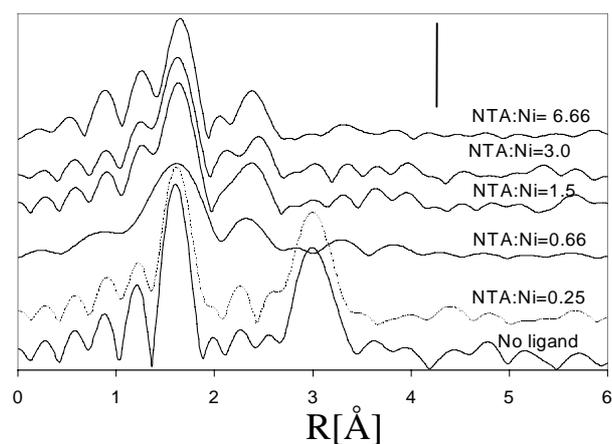


FIG. 2. Absolute parts of the Ni K-edge Fourier transformed EXAFS functions of NiMo/SiO₂ catalyst precursors containing different amounts of nitrilotriacetic acid.