Experiment Title:

EXAFS study of supported Nickel phosphide catalysts

Beamline: BM1B

Experiment number: 01.01.271

Shifts: 6

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Report:

Introduction

Standard hydrodenitrogenation/hydrodesulfurization (HDN/HDS) catalysts consist of Co- or Ni-promoted MoS_2-type phases supported on γ-Al_2O_3 [1]. Future, more stringent environmental regulations lead to an ever-growing interest in the development of alternative compounds to the widely used sulfides, such as transition-metal carbides, nitrides and phosphides [2]. A variety of bulk transition metal phosphides, among which Ni_2P and NiMoP, were synthesized and displayed some activity in the HDN of o-propylaniline [3]. In order to attain a high dispersion, those Ni-containing phosphides, as well as $Ni_{12}P_5$ and Ni_3P, were prepared on a silica support. We aimed to utilize EXAFS to characterize these materials, gain some information about their molecular structure, and understand the correlation between the structure and the HDN activity of those compounds.

Experimental

The catalysts were pressed in self-supported wafers, and mounted in a sealed EXAFS cell. Ni-containing transition metal phosphides in bulk form and supported on a silica carrier were investigated. Bulk Ni_2P and NiMoP were used as reference materials to help

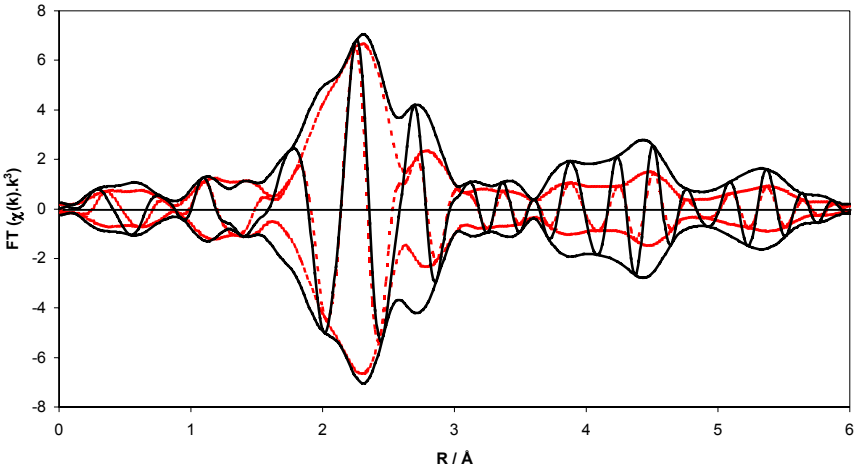
characterize Ni_2P, $Ni_{12}P_5$, Ni_3P and NiMoP supported on SiO_2. Mo K-edge and Ni K-edge EXAFS spectra were recorded in transmission mode at liquid nitrogen temperature. The program XDAP – version 2.3.3 was used to analyze and fit the data as described in the literature [4].

Results

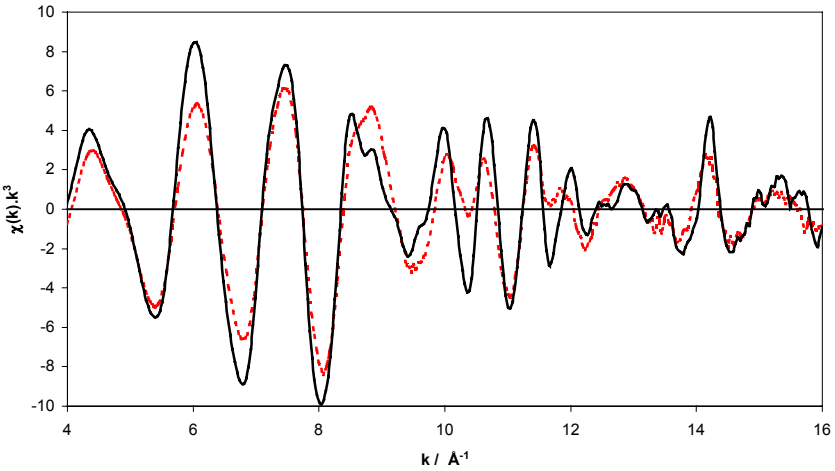
Figure 1 shows the Fourier transformed (Fig. 1a) and the $\chi(k)\cdot k^3$ (Fig. 1b) Mo K-edge EXAFS functions of the bulk and SiO_2-supported NiMoP catalysts in the range of 4 Å< k <16 Å. The spectra display similar features revealing that the same structure, i.e NiMoP, is formed when the phosphide is prepared as a bulk material or supported on SiO_2. However, it can be seen on Fig. 1a that the amplitude of the signal corresponding to the first Mo shell found at 2.58 Å (no phase correction) is smaller for the supported sample than for the bulk one. This indicates a lower coordination number for this Mo shell, and a higher dispersion for the SiO_2-supported NiMoP material. Between 1.9 and 2.4 Å (no phase correction), one P shell and one Ni shell are overlapping and the data analysis of this sample is still under progress in order to better distinguish between the Ni and P contributions.

The Fourier transformed and the $\chi(k)\cdot k^3$ Ni K-edge EXAFS functions of the bulk and SiO_2-supported NiMoP catalysts in the range of 3.92 Å< k <14 Å are shown in Figure 2. The spectrum obtained for NiMoP/SiO_2 (Fig. 2a: dotted line) resembles that of the bulk sample (Fig. 2a: plain line) for the first P, Mo and Ni shells (between 1.6 and 2.5 Å (no phase correction)). For the further shells, and as observed for the Mo K-edge measurements (Fig. 1a), the amplitude of the signal is lower for the supported NiMoP than for the bulk sample, indicating the presence of smaller particles.

Figure 1: Fourier transformed (a) and k^3-weighted Mo K-edge EXAFS functions (b) of bulk NiMoP (plain line) and NiMoP/SiO_2 (dotted line)

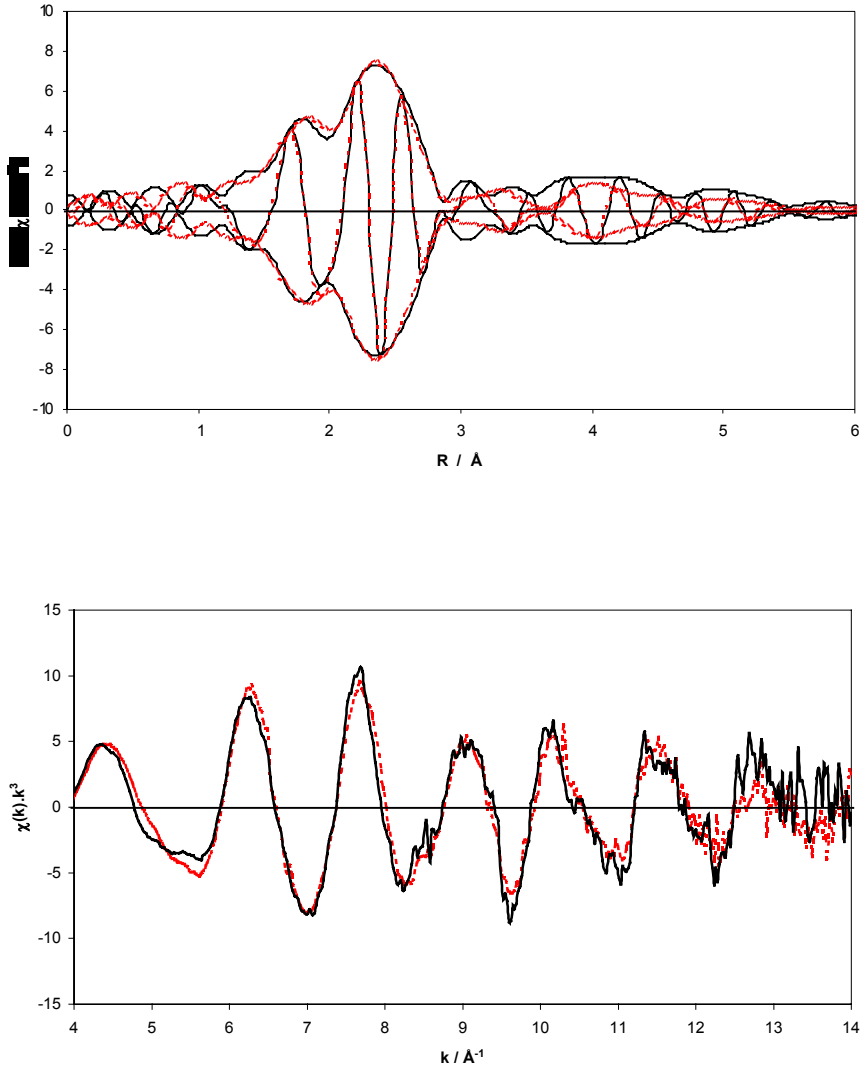


(a)



(b)

Figure 2: Fourier transformed (a) and k^3-weighted Ni K-edge EXAFS functions (b) of bulk NiMoP (plain line) and NiMoP/SiO_2 (dotted line)



References

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