



Experiment Report Form

| | | |
|---|---|---|
|  | Experiment title: EXAFS Study of SiO ₂ -Supported Metal Phosphide Catalysts Active in Hydrotreating Reactions | Experiment number: 01-01-607 |
| | Beamline: BM01B | Date of experiment: from: 2/10/2002 to: 5/10/2002 |
| Shifts: 8 | Local contact(s): Hermann EMERICH | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): Virginie Zuzaniuk*, Nicosia Daniele*, Eveline Bus*, Jeroen A. van Bokhoven*, Prof. Roel Prins Institute for Chemical- and Bioengineering ETH Zürich Wolfgang Pauli Strasse 10 8093 Switzerland | | |

Report:

Hydrodenitrogenation (HDN) is an industrial process that requires the use of Co-promoted MoS₂ type catalysts (CoMoS). More stringent regulations concerning the emission of pollutants from the industrial plants lead to develop alternative compounds to the widely used CoMoS sulfides. Bulk CoMoP phosphides showed good activity in the HDN [1]. Transition metal phosphides are usually prepared by flowing pure hydrogen over the corresponding metal phosphate at very high temperature (900°C). By supporting these materials on SiO₂ powder, a better dispersion is obtained; therefore an increase of catalytic activity is achieved. However, such severe reaction conditions might cause a reaction between the silica support and the metal phosphate, thus affecting the formation of the CoMoP phosphides sites. By means of Co and Mo K-edge EXAFS experiments carried out on CoMoP supported on silica, we wanted to verify that silica support does not affect the formation of the CoMoP catalytic sites.

Experimental

The samples were pressed into self-supported wafers, and mounted in a sealed EXAFS cell. Co-containing transition metal phosphides in bulk form and supported on silica were investigated. Bulk CoP and MoP were used to characterize the CoMoP supported on silica at the Co and Mo K-edge respectively. The

measurements were performed in transmission mode at liquid nitrogen temperature. Each spectrum was averaged over 3 scans in order to increase the signal-to-noise ratio.

Results

Mo K-edge EXAFS function of the CoMoP and CoMoP/SiO₂ and their Fourier transforms are shown in Fig. 1a and 1b respectively. Both Fourier transforms show a main peak between 1.5 and 3 Å. We could fit this peak with a Mo-P contribution at 2.4 Å that is the typical Mo-P distance in the CoMoP framework. This result showed us that no molybdo-silicate specie has been formed during the preparation of the catalyst. On the other hand, the poor data quality of the Co K-edge EXAFS of the CoMoP/SiO₂ sample (Fig.2), did not allow us to obtain any significant result.

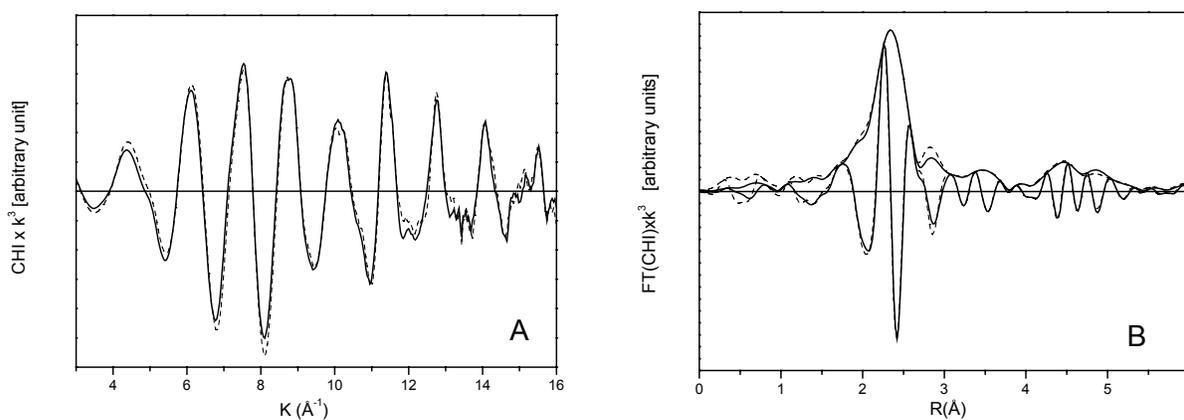


Figure 1: A) Mo K-edge EXAFS function and B) Fourier transforms and of CoMoP bulk (dashed) and CoMoP/SiO₂ (solid).

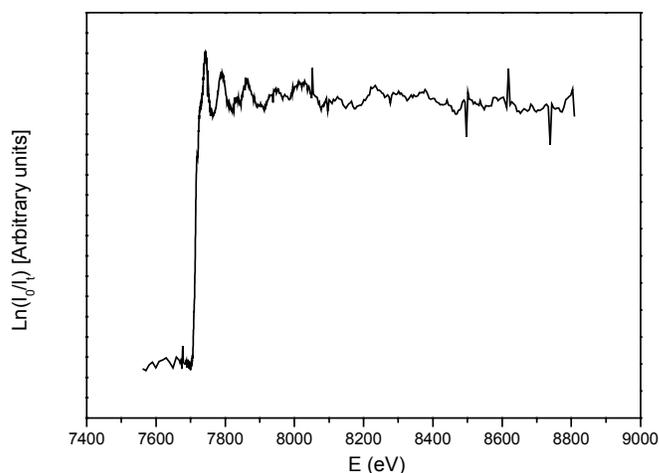


Figure 2: Normalized Co K-edge EXAFS of the CoMoP/SiO₂ sample.

Conclusion

Mo K-edge EXAFS of the CoMoP/SiO₂ sample showed that molybdenum might be in a CoMoP phosphide framework. However, due to the poor data quality of the Co K-edge measurements, we could not confirm that the CoMoP phase was not affected by the presence of the silica support. Therefore, further analyses are needed in order to elucidate the structure of the CoMoP catalyst supported on silica.

Reference

[1] C. Stinner, R. Prins, Th. Weber, J. Catal. 202 (2001) 438