



Experiment Report Form

	Experiment title: EXAFS Study of Highly Dispersed Mo-containing Phosphides on SiO ₂ and Al ₂ O ₃ carriers	Experiment number: 01-01-631
Beamline: BM01B	Date of experiment: from: 18/06/2003 to: 20/06/2003	Date of report: 8/03/2004
Shifts: 6	Local contact(s): Wouter van Beek	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Nicosia Daniele*, Gerhard Pierngruber*, Eveline Bus*, Pijus Kanti Roy*, Prof. Roel Prins Institute for Chemical- and Bioengineering ETH Zürich Wolfgang Pauli Strasse 10 8093 Switzerland		

Report:

Nickel and molybdenum supported catalysts have been extensively used as catalysts for the removal of sulfur from feedstocks. When sulfur-containing molecules are burned in industrial plants, sulfur oxides are released, thus giving rise to the formation of acid rains. Nowadays, laws concerning the emission of pollutants are becoming very strict. Therefore, it is very important to improve the activity of such catalysts. It has been reported that phosphate addition during catalyst preparation increases activity [1]. Our previous Raman studies revealed that molybdenum salts react with phosphate forming a phosphomolybdate species. However, the way in which phosphorus improves the catalytic activity and how it can interact with the support is still unclear. Structural studies are essential to give more insight in this problem.

The aim of the experiment N° 01-01-631, was to study the effect of the support on NiMo catalysts containing phosphate by studying the local structure around the molybdenum atoms. We prepared NiMoP/γ-

Al₂O₃ and NiMoP/SiO₂ catalysts by pore-volume impregnation of γ -Al₂O₃ and SiO₂ supports with an aqueous solution of phosphoric acid containing nickel and molybdenum salts. Mo-K edge EXAFS experiments were then carried out. Mo-K edge EXAFS measurements of Na₂MoO₄, MoS₂ and MoP reference compounds were performed as well in order to fit the contributions of Mo-O, Mo-S and Mo-P respectively. All the measurements were carried out in transmission mode. The temperature was 77 K in order to reduce thermal disorder. Each spectrum was averaged over 3 scans in order to increase the signal-to-noise ratio.

Results

Mo-K edge XANES spectra of the NiMoP/ γ -Al₂O₃ (solid line) and NiMoP/SiO₂ (dashed line) are reported in fig.1A. Both spectra show a pre-edge at about 20000 and 20015 eV. However, the pre-edge of the NiMoP/SiO₂ sample is definitely much broader than that of NiMoP/ γ -Al₂O₃. This proves that the two supports have different effect on the Mo local environments of the NiMoP supported catalysts. Figure 1B reports the Fourier transformation of the NiMoP/ γ -Al₂O₃ (solid line) and NiMoP/SiO₂ (dashed line) EXAFS functions. In the region between 0.5 and 2 Å the two spectra hardly differ. However, there is a pronounced difference between 2.5 and 4 Å. We performed quantitative EXAFS analysis of the two measurements. By means of the XDAP algorithm [2], we performed a fit in this region (fig. 2A and 2B); the results are shown in Table 1. In the case of the NiMoP/ γ -Al₂O₃ sample, we could fit the peak between 2.5 and 4 Å with a Mo-Mo contribution at 3.32 Å that is typical of the NiMoO₄ salt [3]. In the case of the NiMoP/SiO₂ sample we found a Mo-Mo contribution at 3.38 Å and a Mo-P contribution at 3.5 Å that are typical of a phosphomolybdate salt, namely P₂Mo₅O₂₃⁶⁻ [4].

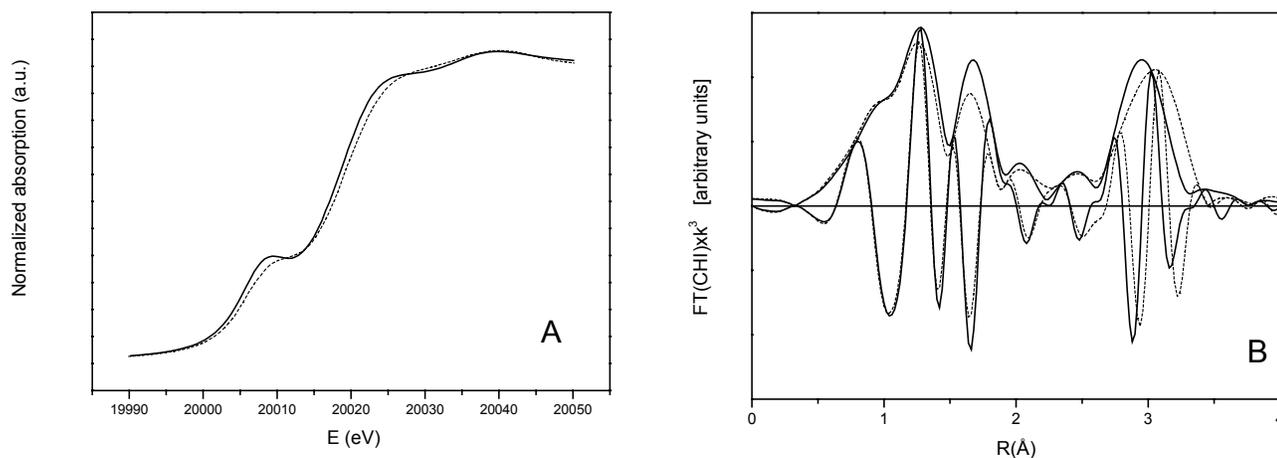


Figure 1.: A: Mo K-edge XANES of NiMoP/ γ -Al₂O₃ (solid) and NiMoP/SiO₂ (dashed); B: Fourier transformation of the NiMoP/ γ -Al₂O₃ (solid) and NiMoP/SiO₂ (dashed) EXAFS functions.

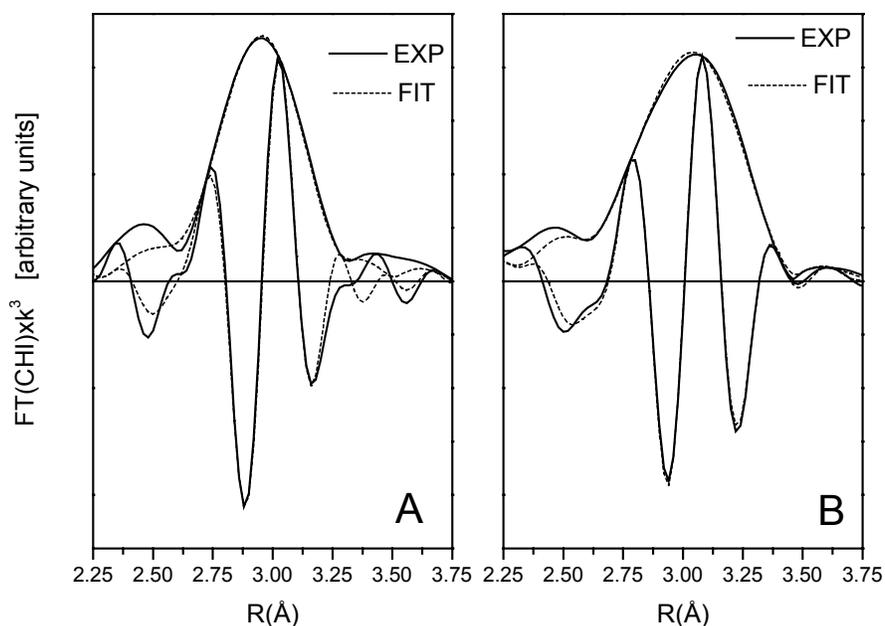


Figure 2.: Fit analysis of (A) NiMoP/ γ -Al₂O₃ and (B) NiMoP/SiO₂ EXAFS functions.

Table 1

Fit parameters resulting from the Mo K-edge Fourier filtered k^3 weighted EXAFS function of the NiMoP/ γ -Al₂O₃ and NiMoP/SiO₂ ($\Delta k = \Delta R = 0.8\text{-}3.3 \text{ \AA}$)

Catalyst	Shell	N	R (Å)	$10^3 \Delta \sigma^2 (\text{\AA}^2)$	ΔE_0 (eV)
NiMoP / γ -Al ₂ O ₃	Mo-Mo	1.5	3.32	-0.6	6.3
NiMoP /SiO ₂	Mo-Mo	1.8	3.40	-2.0	5.5
	Mo-P	1.0	3.50	0.05	2.1

Conclusion

These experiments gave further insight onto the effect of the support on the molybdenum local structure of NiMoP/ γ -Al₂O₃ and NiMoP/SiO₂ catalysts. The presented results based on EXAFS analysis, showed that on γ -Al₂O₃ the Ni and Mo precursors lead to the formation of a supported NiMoO₄ salt, whereas on SiO₂ support they lead to the formation of a supported phosphomolybdate species. Such behaviour might be due to the fact that phosphomolybdate species decompose over the γ -Al₂O₃ support by reacting with the γ -Al₂O₃ acid sites. The SiO₂ support is less acidic than γ -Al₂O₃ and the decomposition of the phosphomolybdate species does not occur.

References

- [1] M. Jian, J. L. R. Cerda, R. Prins, *Bull. Soc. Chim. Belg.* 104 (1995) 225
- [2] M. Vaarkamp, I. Dring, R. J. Oldman, E. A. Stern, D. C. Koningsberger, *Phys. Rev. B* 50 (1994) 7872.
- [3] M. Wiesmann, H. Ehrenberg, G. Wltschek, P. Zinn, H. Weitzel, H. Fuess, *J. Mag. Mag. Mat.* 150 (1995) L1.
- [4] B. Hedman, R. Strandberg, *Act. Cryst. B* 35 (1979) 278.