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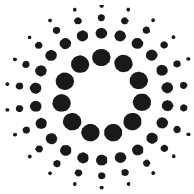

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF. This double-page report will be reduced by ESRF to a one page, A4 format, and will be published in the Annex to the ESRF Annual Report.

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Note that requests for further beam time must always be accompanied by a report on previous measurements.

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ESRF	**Experiment title:** Collection of high quality Ni K-edge data on NiMo hydrotreating catalysts	**Experiment number**: 1-01-257
Beamline: BM1B	**Date of experiment**: from: 08 June 2001 to: 12 June 2001	**Date of report**: 27/09/2001
Shifts: 12	**Local contact(s)**: Dr. Wouter VAN BEEK	*Received at ESRF:*

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Dr. Viviane Schwartz

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Report:

Introduction

Hydrotreating reactions are used to substantially reduce the content of sulfur, nitrogen, oxygen, and aromatics of petroleum feedstocks and these reactions constitute one of the most important steps in refining [1]. Among the most common catalysts in hydrotreating are the tungsten(or molybdenum)-based materials promoted by Ni or Co. A major question still remains regarding how Ni(CO) is situated and what kind of interaction exists between W(Mo) and the promoter [1,2]. However, EXAFS data at the Ni K-edge have yielded limited information so far, since good quality data is restricted by the low promoter concentration and the simultaneous presence of W. The aim of this work was to collect good quality Ni K-edge EXAFS data by increasing the accumulation time of the data points during the measurements.

Experimental

The catalysts were pressed in self-supported wafers, sulfided in the chemistry laboratory and mounted in a sealed EXAFS cell. In this work, we investigate the progress of sulfidation of alumina-supported tungsten-based catalysts prepared from an oxidic precursor, WO_3, and from a sulfidic precursor, ammonium tetrathiotungstate (ATT).

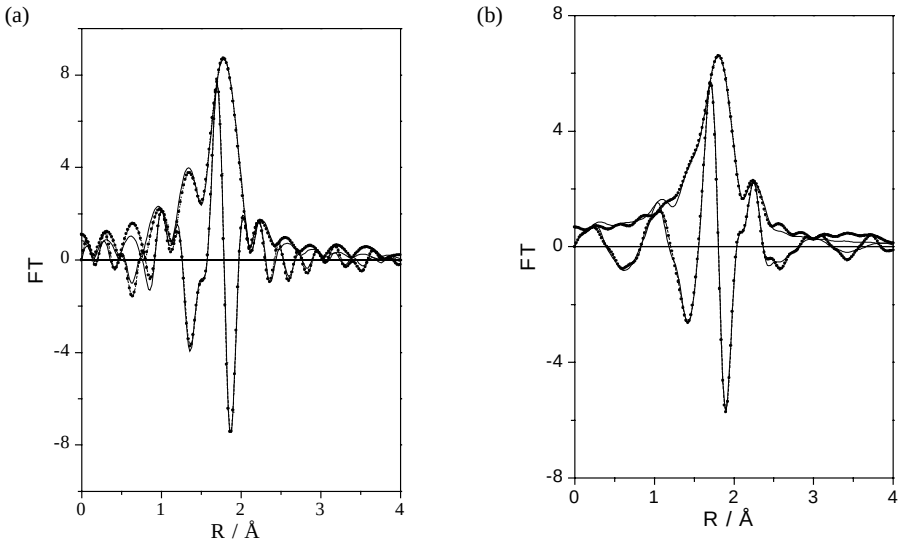

Figure 1: Fourier Transformed of K3 weighted Ni K-edge function of (a) Ni-WO_3/Al_2O_3 and (b) Ni-ATT/Al_2O_3. Measured data ——— and curve fitting results ..... .

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 [3].

Results

EXAFS data were recorded after the sulfidation of the catalysts and the Fourier transformed of the experimental and fitted data of Ni-WO_3 and Ni-ATT catalysts are shown in Figure 1. The sulfided Ni-WO_3 catalyst (Fig. 1a) was fitted with one oxygen shell and one sulfur shell that, due to their proximity, overlap in the region from 1.1 to 2.1 Å (not phase-corrected). In the case of the Ni-ATT catalyst (Fig. 1b), a good fit was only achieved with two sulfur shells. The shells are then shifted to a higher R region, ranging from 1.6 to 2.4 Å (not phase-corrected). The Ni-O contribution lies at the same distance as the one found for cubic NiO, in which nickel atoms are octahedrally surrounded by six oxygen atoms. In the case of the ATT catalyst, nickel is completely sulfided and has a lower coordination number. Two sulfur shells are identified for this catalyst at distances of 2.2 Å and another lying in the region between 2.36 and 2.43 Å. Sulfidation of the Ni-ATT catalysts at 150°C mainly forms the Ni-S coordination at 2.2 Å, which transforms to the longer Ni-S coordination at 2.35 Å during sulfidation at 400°C. This fact is believed to be due to the combination of nickel sulfide with WS_2 to form the NiWS phase.

References

[1] H. Topsøe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysts, Science and Technology, Springer, New York, 1991.
[2] R. Chianelli, M. Daage, and M.J. Ledoux, *Adv. Catal.* 40, 177(1994).
[3] M. Varkaamp, J.C. Linders, D.C. Koningsberger, Phys. Rev. B 209 (1-4), 159 (1995).