Microsc. Microanal. 21 (Suppl 3), 2015
doi:10.1017/S1431927615004808 Paper No. 0401

A *Quasi In Situ* HRTEM Study of the Air Stability of (Ni/Co)MoS_2 Hydrodesulfurization Catalysts.

G.M. Bremmer[1], L. van Haandel[2], E.J.M. Hensen[2], J.W.M. Frenken[1], P.J. Kooyman[3]

[1.] Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands.
[2.] Schuit Institute of Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands.
[3.] ChemE, Delft University of Technology, Delft, The Netherlands.

(Ni/Co)MoS_2 catalysts are widely used for the hydrodesulfurization (HDS) of fossil fuels, in the form of nanometer-sized slabs on a high-surface-area support (e.g. γ-Al_2O_3). As environmental legislation pushes oil refineries towards producing transportation fuels with progressively lower sulfur levels, research on HDS catalysts is an ongoing effort both in industry and in academia [1]. Traditionally, the preparation and characterization of catalyst samples is performed *ex situ*, subjecting the material to ambient air. Earlier work by Kooyman and Van Veen revealed the destructive effect of air on these HDS catalysts. Their HRTEM study showed a decrease in size of the MoS_2-slabs after careful exposure to ambient air [2].

Promoting the MoS_2-slabs with Ni/Co atoms, which are incorporated in the slab structure, has the effect of enhancing catalytic activity and selectivity [3,4]. The stability towards ambient air of Ni/Co-promoted MoS_2-catalysts has not yet been studied. As the Ni/Co promoter atoms have such a significant effect on the catalytic behavior, these atoms might also influence the stability of the slabs as a whole.

To investigate this issue, we analyzed the slab lengths of a series of γ-Al_2O_3-supported (Ni/Co)MoS_2 catalysts using HRTEM without any exposure to air, using a protective atmosphere sample transfer holder [5]. After 24 h of contact with ambient air and after 1 month in air, the samples were measured again (Fig. 1). Using the same approach of controlled air exposure, XPS measurements were conducted on an identical set of samples, to obtain information on changes in the elemental composition.

The XPS measurements reveal that during the air exposure, the MoS_2-slabs get oxidized. As shown in Fig. 2, the atomic structure of MoS_2-slabs consists of one layer of Mo atoms sandwiched between two layers of S atoms. Using TEM measurements, the length of these slabs can be determined when the slabs are in plane with the electron beam, as shown in Fig. 2b. In HDS catalysis, the Mo atoms located on the very edge of the slabs are the catalytically active sites, which can get oxidized in air to form MoO_3. Locally, the planar structure is then lost, causing the slabs to appear shorter on TEM micrographs. Quantitative analysis of the resulting images shows that Ni/Co-promoted MoS_2-catalysts do decay due to oxidation (Fig. 3), indicating the necessity of shielding these samples from ambient air.

References:

[1] S Brunet *et al.*, Applied Catalysis A: General **278** (2005), p. 143.
[2] PJ Kooyman and JAR van Veen, Catalysis Today **130** (2008), p. 135.
[3] EJM Hensen *et al.*, Catalysis Letters **84** (2002), p. 59.
[4] AK Tuxen *et al.*, Journal of Catalysis **295** (2012), p. 146.
[5] HW Zandbergen *et al.*, Electron Microscopy 1998, in: Proc. ICEM 14, Cancun, Mexico, 31 Aug.–4 Sept. 1998, Symposium W, Volume II, (1998), p. 491.

[6] This work was supported by the Netherlands Organisation for Scientific Research (NWO/OCW) as part of the Frontiers of NanoScience (NanoFront) program.

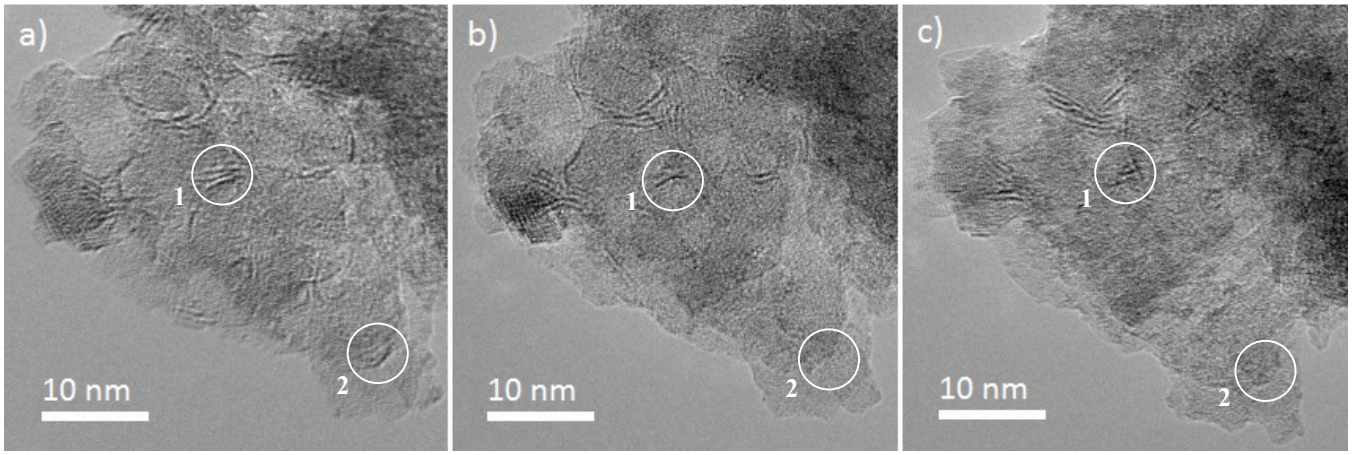

Figure 1. HRTEM images of $CoMoS_2$ catalyst slabs on γ-Al_2O_3 a) without any contact to air, b) the same sample region after 24 h of contact to air, c) the same sample region after 1 month in air. The sample region labeled '1' shows a stack of slabs that decreases in size after 24 h, while the sample region labeled '2' shows a slab that has completely disappeared after 24 h.

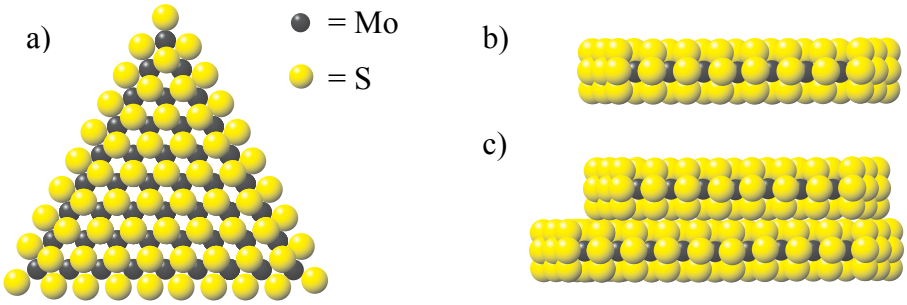

Figure 2. a) Atomic structure of a MoS_2-slab, showing the single Mo layer, sandwiched between two layers of S atoms. b) Side view of the slab, as it is visible in TEM measurements. c) A stack of slabs.

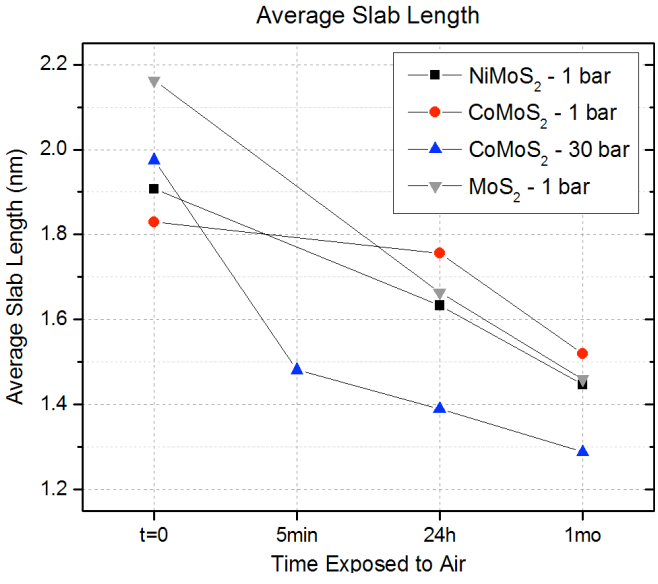

Figure 3. Average slab length as a function of exposure time to ambient air, showing a decrease in average length for all samples. Sulfidation pressures during sample preparation are indicated in the legend.