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# Supporting Information



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# Solvothermal Formation of $MoO_3$ Fibers studied by Complementary *in situ*-EXAFS/EDXRD Techniques

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## 1. High pressure in situ-EXAFS experiments of both the solid and the liquid phase

The newly designed spectroscopic cell (Figure SI-1) enables the *in situ* monitoring of the changes occurring in the bulk liquid as well as at the liquid/solid interface of heterogeneous reactions at elevated pressure and temperature. Therefore, the dimensions of the high pressure cell were chosen as follows: the liquid/solid interface is monitored at the bottom of the cell with a path length of 4 mm, and the liquid part can be observed with a path length of 15 mm at a height of 10 mm above the bottom of the reactor cell. Details will be given in ref. [38]. The cell interior consists of a PEEK container (polyetheretherketone, density 1.3 g $cm^{-3}$) that is embedded in a stainless steel cell (Figure SI-1). PEEK displays a high resistance against alkalis, acids and organic solvents. It is superior to many other chemically resistant thermoplastics (e. g. Teflon) due to its high transparency for X-rays above 9 keV and its high operating temperature (250 °C). Four windows (5 × 1 mm) were inserted into the stainless steel container so that the X-ray beam passes through the cell at two positions (cf. Figure SI-1). The *in situ* cell is applicable to a pressure up to 250 bar and 200 °C and it is equipped with a magnetic stirrer and a thermocouple. The reaction of $MoO_3 \cdot 2H_2O$ in water was conducted in the presence of a separating glass wool layer between the solid and the liquid phase. The experiments were performed at beamline X1 (HASYLAB, DESY, Hamburg), providing a white X-ray beam between 6 and 60 keV. A Si(311) double-crystal monochromator was used and higher harmonics were effectively removed by detuning of the crystals to 70% of the maximum intensity. During the measurements, the beam size was cut to 5 x 1 mm and the *in situ* batch reactor cell was aligned using the x,z,θ-table. Three ionization chambers before and after the *in situ* cell, together with a corresponding reference foil for energy calibration were used for the incident and outcoming X-ray intensities. The ionization chamber gas pressure

(Ar) was adjusted in a way that the first 10% were absorbed in the first ionization chamber and the following 40% in the second and third ionization chamber.

Figure SI-2 shows reference EXAFS spectra of $MoO_3$ and $MoO_3 \cdot 2H_2O$ together with the product formed in the *in situ* cell.

**2. in situ-EDXRD experiments**

The HASYLAB beamline F3 receives white synchrotron radiation from a bending magnet with a critical energy of 16 keV. An energy range from 13.5 to 65 keV can be received with a maximum at ca. 20 keV. The diffracted beam is monitored by a nitrogen-cooled solid state germanium detector. The detector angle was chosen to detect all the important Bragg reflections. The d-spacing range is given by $E = 6.199/(d \sin\theta)$. With a detector angle of approximately 1.90°, the observable d-spacing range is 2.9 – 13.8 Å. The energy resolution $\Delta d/d$ is about $10^{-2}$ above 26 keV. The beam was collimated to 0.2 mm for optimum results. For further experimental details cf. Lit. [22, 31].

## Supporting Figures

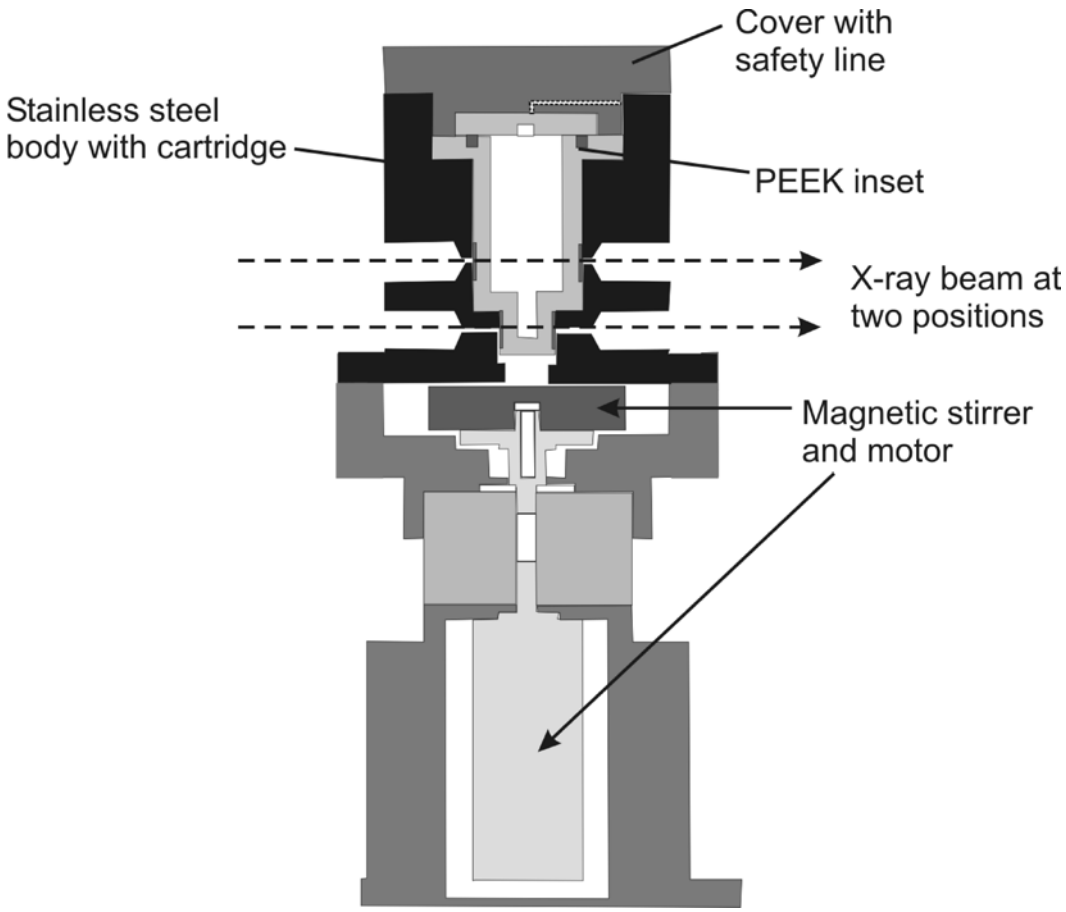


**Figure SI-1** Principal setup for the apparatus developed for *in situ* X-ray absorption spectroscopy studies. Solid-liquid reactions can be monitored *via* two separate windows.

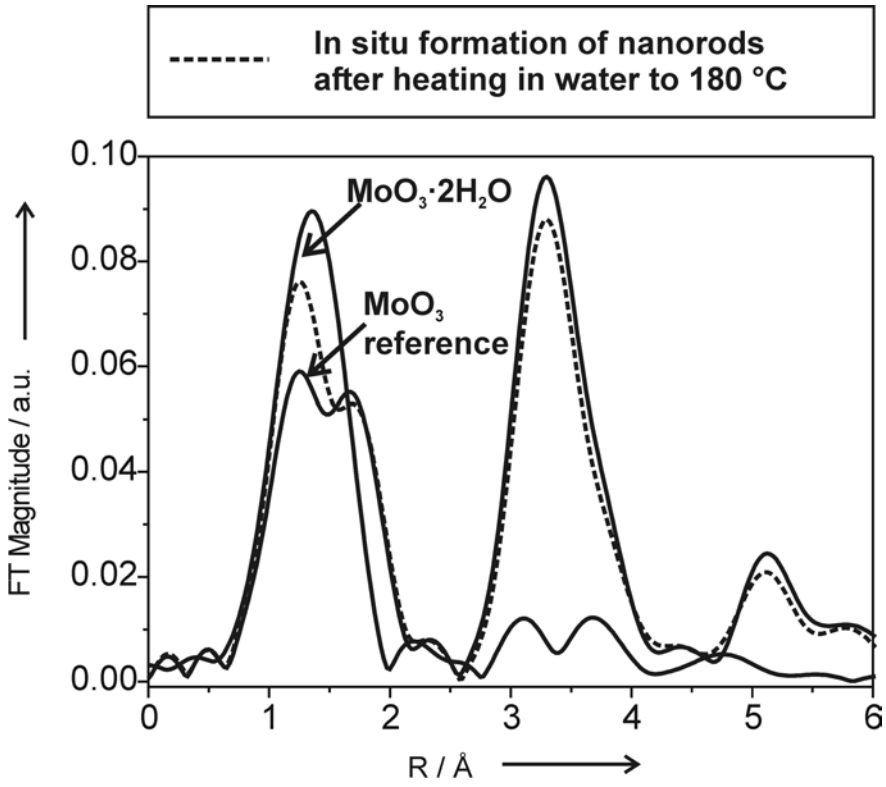


**Figure SI-2**: Comparison of Fourier transformed EXAFS spectra of $MoO_3 \cdot 2H_2O$ with the product formed in the *in situ* spectroscopic cell and with $MoO_3$ as a reference (Fourier transformation in the range 4 – 13.5 $Å^{-1}$).