	Experiment title: Time-Resolved XAS Studies on MoO_{3-x} Catalysts for Selective Oxidation of Alkenes	**Experiment number**: CH-761
Beamline: ID24	**Date of experiment:** from: 29.09.99 to: 04.10.99	**Date of report:** 10.02.99
Shifts: 15	**Local contact(s):** Dr. Thomas Neisius	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Thorsten Ressler[*, a], Prof. Dr. Robert Schlögl[a], Dr. Thomas Neisius[*, b]

[a]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Inorganic Chemistry
Faradayweg 4-6, D-14195 Berlin, Germany
E-mail: Ressler@FHI-Berlin.MPG.de

[b]ESRF, Experiment Division, Grenoble, France

Report:

Reduction of MoO_3 with hydrogen (50 - 100 vol-%) in the temperature range from 723 K to 823 K was studied by in situ X-ray absorption spectroscopy. The experiments performed focused on elucidating phase composition, structural changes, and their evolution with time under isothermal as well as temperature programmed reduction conditions. The results obtained clearly demonstrate the potentials XAFS to reveal phase composition and kinetics of solid state reactions.

XAFS experiments were carried out at the Mo K-edge (20.0 keV) utilizing an energy-dispersive XAFS spectrometer (ID24) equipped with a curved Si(220) monochromator in transmission mode. Figure 1 shows Mo K edge XANES spectra measured during reduction and reoxidation with H_2 and O_2, respectively, at 823 K with a time resolution of 2.8 s/frame. The corresponding Mo K edge-shift is depicted in Figure 2. It is evident from Figure 2 that (i) the rate of MoO_3 reduction is considerable affected by changing the reaction temperature, in contrast to the rate of reoxidation, (ii) two different reaction kinetics govern reduction of MoO_3 and reoxidation of MoO_2, and (iii) reoxidation proceeds more rapid than reduction and appears to be only gas phase transport limited (similar slope of O_2 MS signal and edge-shift curve). A quantitative phase analysis (factor analysis plus reference fits) of the XANES spectra in Figure 1 revealed the presence of a third phase, namely Mo_4O_{11}, during reduction of MoO_3 at 823 K.
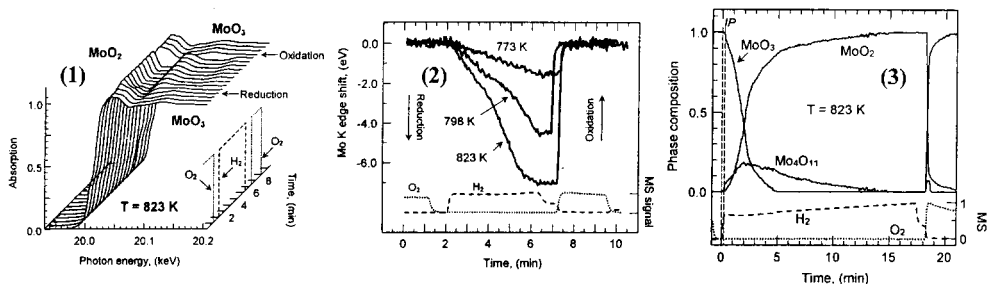
From the complementary application of in situ XAFS and XRD a reduction product diagram could be assembled (Figure 4). It can be seen that at reaction temperatures below 698 K the reduction of MoO_3 is a one-step process ($MoO_3 \rightarrow MoO_2$). At reduction temperatures above 723 K and H_2 concentrations higher than 10 vol-%, Mo metal is the final product of the reduction of MoO_3 ($MoO_3 \rightarrow MoO_2 \rightarrow Mo$). In addition, at temperatures above 698 K the formation of Mo_4O_{11} was observed. However, Mo_4O_{11} is not an intermediate of the reduction of MoO_3 but is being formed in a parallel reaction from MoO_3 and MoO_2 at temperatures above 698 K. No other well-defined suboxides were observed during the reduction of MoO_3 under the reaction conditions investigated. Quantitative analysis (Figure 3) revealed a sigmoidal shape (Avrami-Erofeev) of the evolution of MoO_3 and MoO_2 phases during reduction of MoO_3. Apparent activation energies calculated for the reduction of MoO_3 in hydrogen confirm the existence of two competing reactions, i.e. reduction of MoO_3 and formation of Mo_4O_{11}, with the later exhibiting the larger activation energy.

A more detailed analysis of the short "induction period" in the reduction of MoO_3 (IP in Figure 5) revealed the evolution of water already during this early stage without apparent changes in the XANES. From an EXAFS analysis, however, it was found, that the short-range structure of MoO_3 is considerable changed during the "induction period". This feature and the corresponding MoO_{3-x} structure will be subject of future in situ XAFS investigations.