

**Experiment title:**

Correlation of bulk structure and activity of molybdenum oxide catalysts from time-resolved XAFS studies

Experiment number:

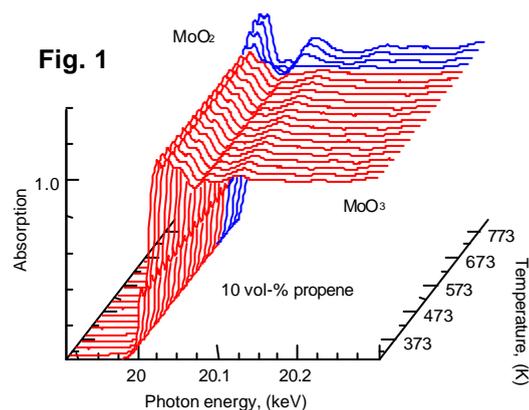
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Molybdenum oxide based catalysts are extensively employed for the partial oxidation of alkenes. One of the “model reactions” investigated in detail is the partial oxidation of propene to acrolein on molybdenum trioxide, MoO₃. The corresponding reaction mechanism is referred to as redox mechanism and consists of alternating oxidation and reduction of the metal oxide catalyst surface and/or bulk. During reduction of MoO₃ formation of partially reduced molybdenum “suboxides” has been reported as a result of the redox mechanism and the difference in rates of catalyst reduction and re-oxidation. The oxidation step needs to follow the reduction of the metal oxide by the alkene in order to replenish the oxygen in the bulk of the metal oxide catalyst.

Investigations of the correlation between structure and reactivity of heterogeneous catalysts need to be performed in situ with simultaneous monitoring of the catalyst structure and the gas phase composition. Of the bulk techniques, which can be employed to study a catalytically active material in situ, we used XAS and XRD. In addition to steady-state investigations, both techniques permit experiments with a suitable time-resolution to monitor the structural evolution of bulk phases and from that to elucidate the solid-state kinetics of the reactions involved (Figure 1).



Reduction of MoO_3 in propene and oxidation of MoO_2 in oxygen were investigated by in situ XRD and XAFS. Temperature-programmed and isothermal experiments were performed to elucidate the structural evolution of phases present during the reactions and, in addition, to reveal the solid-state kinetics of the processes involved. Molybdenum trioxide (MoO_3) was prepared by thermal decomposition of ammonium heptamolybdate in flowing synthetic air (RT – 773 K). Time-resolved in situ XAS experiments were carried out at the Mo K edge utilizing an energy-dispersive spectrometer (ESRF, ID24) equipped with a curved Si(111) polychromator in a transmission mode (measuring time ~ 3 s/scan).

During the reduction of MoO_3 in propene and the oxidation of MoO_2 , only crystalline MoO_3 and MoO_2 were detected by in situ XRD. However, analysis of the in situ XAFS data yielded the formation of “ $\text{Mo}_{18}\text{O}_{52}$ ” type shear-structures as intermediate of both the reduction of MoO_3 (Figure 2a + b) in propene and the oxidation of MoO_2 in oxygen. At temperatures below ~ 700 K oxidation of MoO_2 afforded a disordered MoO_3 with “ $\text{Mo}_{18}\text{O}_{52}$ ” type shear-structures in the lattice. Only at temperatures above ~ 700 K complete oxidation to MoO_3 was observed.

The solid-state kinetics of the reduction of MoO_3 in propene exhibits a change in the rate-limiting step both as a function of temperature and as a function of the extent of reduction. At a given temperature a transition from a nuclei growth kinetics to a three dimensional diffusion controlled regime is observed. With decreasing temperature (< 600 K) a transition to a regime that is entirely controlled by oxygen diffusion in the MoO_3 lattice was found. The solid-state kinetics of the oxidation of MoO_2 is governed by three-dimensional diffusion. A schematic reaction mechanism for the reduction of MoO_3 in propene and the re-oxidation in oxygen is proposed (Figure 3) that consists of (i) generation of oxygen vacancies at the (100) or (001) facets by reaction with propene, (ii) vacancy diffusion in the MoO_3 bulk, (iii) formation of “ $\text{Mo}_{18}\text{O}_{52}$ ” type shear-structures in the lattice, and (iv) formation and growth of MoO_2 nuclei. The mechanism is in agreement with previous reports of the propene oxidation on MoO_3 as being a structure-sensitive reaction.

