



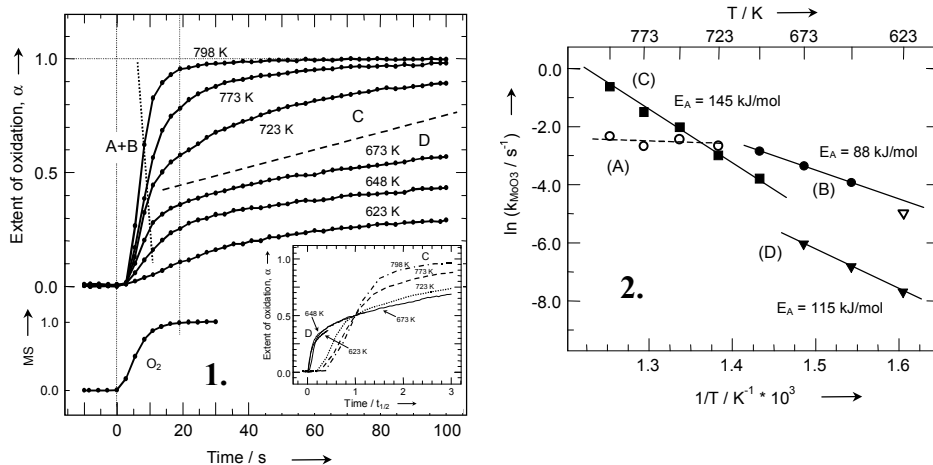
	Experiment title: Studies on the Dynamic Behaviour of Molybdenum Oxide Catalysts using TR-XAS	Experiment number: CH-869
Beamline: ID24	Date of experiment: from: 10.05.00 to: 17.5.00	Date of report: 15.08.00
Shifts: 21	Local contact(s): Dr. Thomas Neisius	<i>Received at ESRF:</i>
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Report:

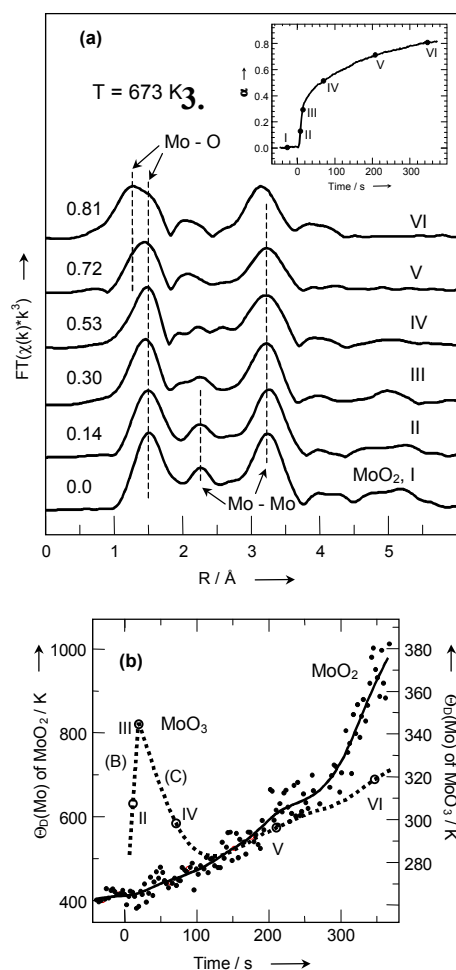
Oxidation of MoO₂ with oxygen (20 - 100 vol-%) in the temperature range from 623 K to 823 K was studied by in situ X-ray absorption spectroscopy. A detailed kinetic evaluation of the evolution of the extent of oxidation at different temperatures was performed to reveal mechanisms and rate-limiting steps. In the Mars-van-Krevelen mechanism for partial oxidation reactions on metal oxides, for instance, diffusion of oxygen in the bulk is the rate-determining step. Hence, to assess a mechanism that involves the catalyst bulk, a complete understanding of the mechanism and the kinetics of both reduction of the bulk oxide and its reoxidation with oxygen from the gas phase is required.

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(111) monochromator in transmission mode. In Figure 1 the evolution of the extent of oxidation (α) of MoO₂ to MoO₃ in the temperature range from 623 K to 798 K in 100 % oxygen is depicted. The four stages that govern the rate of oxidation of MoO₂ at different reaction temperatures or with the advancing extent of oxidation include (A) *mass transport*, that is the transport of oxygen from the gas phase to the MoO₂ crystallites. A constant rate is observed (T between 723 K and 798 K), with the rate constants nearly independent of the reaction temperature. Hence, in this stage of the oxidation of MoO₂ the reaction rate is mainly determined by the rate of gas phase transport through the in situ cell and sample. (B) Reactions occurring at the *boundary* between MoO₂ and MoO₃. Again, a constant reaction rate is

obtained, but in this stage the rate constants exhibit an Arrhenius type temperature dependence ($E_A = 88$ kJ/mol). Depending on the reaction temperature the oxidation of MoO_2 proceeds to an extent between 0.15 and 0.5 (T between 648 K and 698 K) before a change in the rate-determining step takes place. (C) Growing MoO_3 nuclei eventually "overlap" during the proceeding oxidation of MoO_2 which results in a decrease of the oxidation rate. For this stage reaction rate constants can be calculated with an Avrami-Erofeev type equation. From the temperature dependence of the rate constants an apparent activation energy of 145 kJ/mol is obtained. (D) Diffusion of oxygen through a layer of MoO_3 formed around a MoO_2 crystallite during oxidation. In this case rate constants are obtained from the Ginstling-Brounshtein equation with an apparent activation energy of 115 kJ/mol.



In addition to a quantitative phase analysis of the XANES region, the EXAFS can be used to reveal the short-range order structural evolution of the chemical species present during the reaction. Here, the phase information obtained from XANES analysis (species and quantification) is used to refine a sum of theoretical EXAFS functions for each phase present. In this way, structural information can be obtained to corroborate the solid state reaction mechanism as deduced from the reaction rate law. Selected radial distribution functions ($\text{FT}(\chi(k) * k^3)$) measured during the oxidation of MoO_2 at 673 K are depicted in Figure 3. A transition from a MoO_2 radial distribution function to a MoO_3 dominated radial distribution function can be seen. However, this transition does not appear to be continuous. Instead, stages (I) through (III) correspond to MoO_2 dominated radial distribution functions, where the presence of MoO_3 results only in a slight distortion, observed as a slight reduction in $\text{FT}(\chi(k))$ amplitude. Only between stages (V) and (VI) does an increase in the structural order of MoO_3 seem to take place, resulting in a MoO_3 dominated radial distribution function at stage (VI).



Assistance of the ID24 staff is gratefully acknowledged.