

Rapid Solid State Reduction / Oxidation measured by Time-Resolved X-ray Absorption Spectroscopy

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Introduction

Isothermal or temperature programmed reduction (TPR) studies can reveal information on suitable activation procedures and reduction kinetics; however, identification of phases present during reduction or the dependence of reduction on structural disorder or defects must be inferred indirectly from TPR patterns. In this work we present structural data obtained from in situ measurements of molybdenum trioxide under reducing and oxidizing reaction conditions which have been directly measured using both time-resolved X-ray absorption spectroscopy (TR-XAS) and gas phase analysis.

Experimental and Results

MoO₃ was prepared in situ by thermal decomposition (RT – 773 K) of ammonium heptamolybdate (AHM) in flowing He followed by oxidation in air at 773 K. Oxygen (100 % O₂) and hydrogen (100 % H₂) pulse experiments were performed at 773 K and changes in the electronic and geometric structure of molybdenum trioxide were measured by in situ XAS at the Mo K-edge utilizing an energy-dispersive spectrometer (ESRF, Grenoble; ID24) ¹. The reduction or oxidation of Mo causes a shift in the Mo K absorption edge to lower or higher photon energies, respectively. Figure 1 depicts Mo K edge-shift data measured during two H₂ - O₂ pulse cycles at 773 K and over a period of 30 min with a time resolution of 15 s/spectrum together with the normalized mass spectrometer signal for H₂ and O₂. It can be seen that under these conditions oxidation and reduction of Mo oxide proceeded rapidly (Figure 1). Interestingly, reduction and re-oxidation exhibit different reaction rates as is evident from the different slopes in the edge shift curve during subsequent O₂ and H₂ pulses. Re-oxidation appears to be very rapid and the edge-shift curve shows a slope similar to that of the mass spectral signal of oxygen. Thus, the reaction rate of the MoO_{3-x} re-oxidation seems to be determined by the O₂ pulse shape achievable in



the in situ cell employed and does not appear to be limited by diffusion of O_2 into the MoO_{3-x} bulk. Hence, the reaction appears to proceed at a rate similar to or faster than the rate of the gas phase transport. In contrast, the reduction with H_2 proceeds more slowly during the time period in which the system is exposed to hydrogen. Principal component analysis of Mo K edge XANES spectra of one reduction – oxidation cycle identified two constituent components (namely MoO_2 and MoO_3). The observed mixture of MoO_2 and MoO_3 seems to exclude the occurrence of structurally well-defined sub-oxides during reduction and re-oxidation of MoO_{3-x} at 773 K and is in agreement with the previously postulated mechanism^{2,3}.

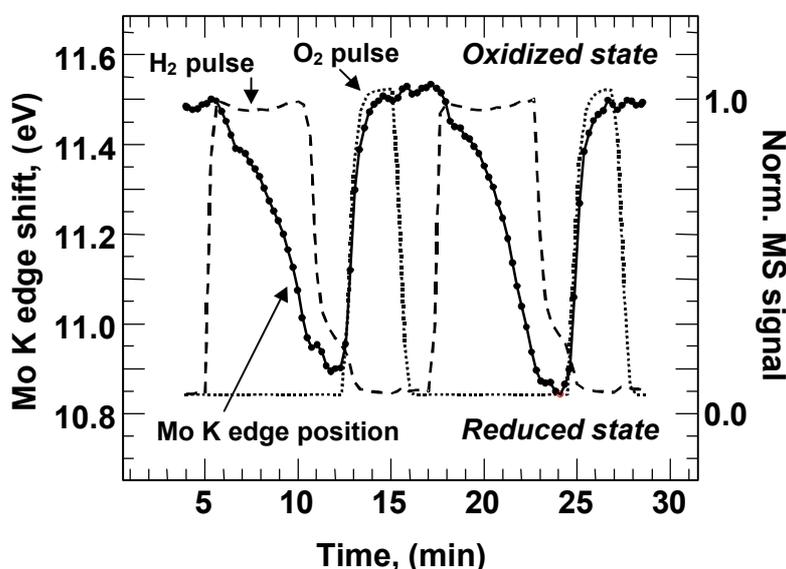


Figure 1. Mo K edge position (relative to Mo metal at 19.999 keV) of MoO_{3-x} during two reduction - oxidation cycles obtained from XANES spectra measured in situ ($T = 773$ K, 1 bar H_2). Oxidized and reduced state of Mo are indicated. Normalized O_2 and H_2 MS signals are shown. A rapid response of the entire bulk sample to changes in the gas composition can be seen.

Conclusion

The results presented here demonstrate the suitability of time-resolved energy-dispersive XAS experiments for in situ investigations of the bulk structure of heterogeneous catalysts. The presented structural analysis of molybdenum oxide in oxidizing and reducing atmosphere shows that highly reactive forms of this oxide transform their bulk structure rapidly with changing chemical potential in the gas phase.



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References

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