

Characteristic Defects in the Bulk Structure of a MoO₃ Partial Oxidation Catalyst

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Introduction

Molybdenum trioxide, MoO₃, is an active catalyst for the oxidation of propene. Moreover, MoO₃ constitutes a suitable three-dimensional model system for more complex molybdenum based mixed oxide catalysts. Hence, the structural features and the catalytic properties of MoO₃ have been investigated in detail over the last five decades in order to reveal structure-activity relationships and to aid rational design of improved catalyst materials.^[1] Although it is assumed that the lattice oxygen of MoO₃ participates in the oxidation of propene, little is known about defects in the regular layer structure of MoO₃ that may form under reaction conditions, or about the structural properties and the role of these defects in partial oxidation reactions proceeding on the surface of the MoO₃ catalyst. In this work in situ XAS combined with mass spectrometry was employed to elucidate phase compositions and short-range structural evolution of MoO₃ during temperature-programmed reaction of propene and oxygen.

Experimental

Molybdenum trioxide (MoO₃) was prepared by thermal decomposition of ammonium heptamolybdate (AHM), (NH₄)₆Mo₇O₂₄·4H₂O (Aldrich Co.). For in situ XAS experiments, MoO₃ was mixed with boron nitride (ratio 1:4) and 37 mg of the mixture was pressed with a force of 1 ton into a 5 mm diameter self-supporting pellet. The absorption jump, Δμ_x, at the Mo K edge was ~ 1.5. In situ XAS experiments were performed in transmission in a flow-reactor at atmospheric pressure in flowing reactants (~30 ml/min). The gas phase composition at the cell outlet was continuously monitored using a mass spectrometer in a multiple ion detection mode (QMS200 from Pfeiffer). In situ transmission XAS experiments were performed at the

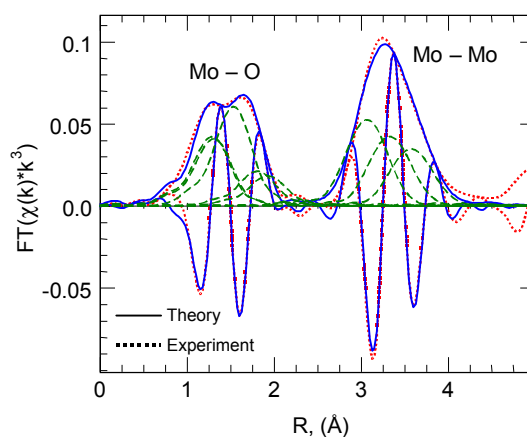
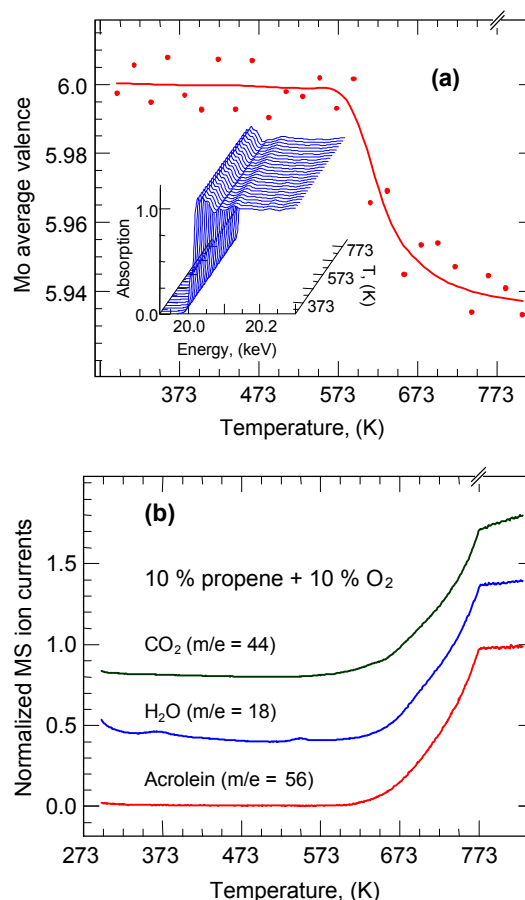


Figure 1 XAFS refinement of a theoretical Mo K edge $\chi(k)$ (solid) to an experimental Fourier transformed $\chi(k)$ of MoO₃ (dotted). The main Mo – O and Mo – Mo single-scattering paths are indicated (dashed).

Mo K edge (19.999 keV) at beamline X1 at HASYLAB, using a Si(311) double crystal monochromator (measuring time ~ 4.5 min/scan). The storage ring operated at 4.4 GeV with injection currents of 150 mA.

X-ray absorption fine structure (XAFS) analysis was performed using the software package WinXAS v2.2 ^[ii] Background subtraction and normalization were carried out by fitting linear polynomials to the pre-edge and the post-edge region of an absorption spectrum, respectively. The Mo K edge absorption threshold was determined from the first root in the first derivative of the near-edge region (XANES). The X-ray absorption fine structure (EXAFS) $\chi(k)$ was extracted by using cubic splines to obtain a smooth atomic background, $\mu_0(k)$. EXAFS data analysis was performed using theoretical backscattering phases and amplitudes calculated with the ab-initio multiple-scattering code FEFF7. EXAFS refinements were performed in R space to magnitude and imaginary part of a Fourier transformed k^3 -weighted experimental $\chi(k)$ using the standard EXAFS formula (k range from 3.1 to 15.4 \AA^{-1} , R range 0.9 to 4.1 \AA) (Figure 1). ^[iii]

Figure 2 (a) Evolution of Mo K edge position (relative to the edge position of MoO_3 and displaced for clarity) during temperature-programmed reaction of propene and oxygen in the presence of MoO_3 (10 % O_2 and 10 % propene in He) (300 – 773 K, 5 K/min, held at 773) (inset shows evolution of XANES spectra during TPR). (b) Evolution of the corresponding gas phase composition (CO_2 ($m/e = 44$), H_2O ($m/e = 18$), acrolein ($m/e = 56$)) during temperature-programmed reaction of propene and oxygen.



Results and Discussion

Under the reaction conditions employed (273 K to 773 K and propene to oxygen ratio from 1:1 to 1:5), MoO_3 remains the only crystalline phase detected by XRD.

The onset temperature for the temperature-programmed reaction of propene and oxygen in the presence of MoO_3 coincides with the onset of the reduction of MoO_3 in He, H_2 , or propene (~ 620 K) (Figure 2). Thus, weakening of Mo – O bonds in MoO_3 , a sufficient mobility of

oxygen ions, and formation of defects are essential for the reduction of MoO_3 and for the material to function as a heterogeneous catalyst.

Various in situ experiments indicate that the structural evolution of MoO_3 during TPR, reduction, and treatment in He is surprisingly similar. At temperatures below ~ 720 K and independent of the atmosphere used, partial reduction of MoO_3 is observed resulting in the formation of “ $\text{Mo}_{18}\text{O}_{52}$ ” type defects in the bulk structure. At temperatures above ~ 720 K and in oxygen or in an oxidizing atmosphere (sufficiently low propene to oxygen ratio), the “ $\text{Mo}_{18}\text{O}_{52}$ ” type defects are re-oxidized to MoO_3 . Evidently, the catalytically active molybdenum oxide phase under partial oxidation conditions at temperatures below 720 K does not correspond to the original MoO_3 possessing the undisturbed ideal layer structure of orthorhombic α - MoO_3 . Instead, at these temperatures, the catalytically active phase, which is partially reduced and possesses a large amount of “ $\text{Mo}_{18}\text{O}_{52}$ ” type defects (crystallographic-shear structures) in the layer structure of MoO_3 , develops under reaction conditions.

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