



Experiment title: Time-Resolved XAS Studies on MoO _{3-x} Catalysts for Selective Propen Oxidation	Experiment number: CH-528	
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Report:

Molybdenum oxide catalysts are extensively used in the selective oxidation of propene to acrolein and acrylic acid. In this studied we employed time-resolved in-situ XAFS to elucidate the behavior of MoO_{3-x} catalysts under reductive and oxidative reaction conditions. 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. With the set-up employed an energy range of 1.0 keV (~ 16 Å⁻¹) can be used for EXAFS analysis. In Fig. 1 an experimental FT($\chi(k)$) [2.0 – 14.0 Å⁻¹] of MoO₂ is displayed together with a theoretical XAFS refinement (FEFF, MoO₂ [P21/c], fit range 1.0 – 6.0 Å, 31 SS paths and 24 MS paths). Excellent agreement between experiment and theory clearly indicates that energy-dispersive XAFS data indeed can be utilized for accurate structure determination.

Oxidation and reduction of different molybdenum oxides were studied including (i) thermal decomposition of (NH₄)₆Mo₇O₂₄ (AHM, a typical precursor for MoO_{3-x} catalysts) in He and propene followed by a subsequent oxidation at 500 °C, (ii) oxidation of as-purchased MoO_{3-x} and MoO₂ at 500 °C in air, and (iii) hydrogen, oxygen, and propene pulse experiments utilizing the in-situ prepared MoO_{3-x} catalysts. Fig. 2 shows Mo K edge XANES spectra measured during a series of H₂ and O₂ pulses at 500 °C with a time resolution of 15 s/frame. Each increase and decrease in the Mo K edge whiteline height corresponds to a H₂ and O₂ pulse, respectively.

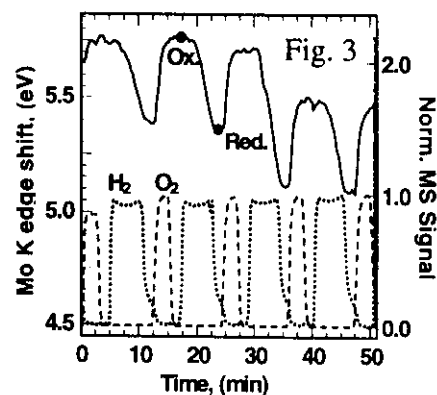
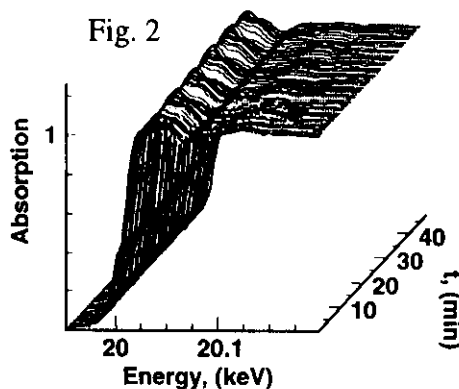
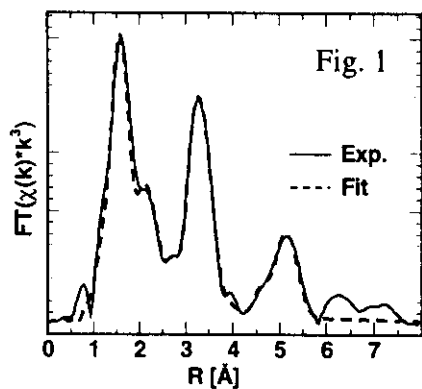


Fig. 3 depicts Mo K edge-shift data corresponding to absorption spectra in Fig. 2, together with the normalized mass spectrometer signal for H₂ and O₂. It can be seen from Fig. 3 that oxidation and reduction of the Mo catalyst proceed very rapidly and, thus, do not appear to be diffusion limited. Interestingly, oxidation and reduction exhibit different reaction rates as is evident from the slope in the edge shift curve associated to oxidation and reduction steps. From a comparison with MoO₂ and MoO₃ it was found that the valence of the reduced phase is ~ 5.4. Fig. 4 displays FT(χ(k)) of MoO₂, MoO₃, the oxidized and the reduced phase from Fig. 3. It can be noticed that both the reduced and the oxidized phase resemble MoO₃ rather than MoO₂. An increase in the first oxygen shell indicates a decrease in octahedron distortion upon reduction. In addition, an alteration in the first Mn peak height points to a change in the ratio of edge-shared to corner-shared coordination. Principal component analysis (factor analysis) of Mo K edge XANES spectra of one reduction – oxidation cycle identified two constituent components. Fig. 5 shows a plot of the eigenvalues associated to the two major components for spectra of one redox cycle. Obviously, all XANES spectra can be described by a linear combination of two phases, which yet have to be determined.

Furthermore, intriguing oscillatory behavior in the selective propene oxidation on MoO_{3-x} catalysts at 500 °C was observed. Fig. 6 shows oscillations in the Mo K edge position as obtained from fitting an ATAN step function to the Mo K edge XANES spectra (3 s/frame). However, the observed oscillations in Fig. 6 do not appear to be related to an oscillating oxidation – reduction of the Mo catalyst but rather to a change in the Mo 1s – 4d transition probability. This seems to indicate an oscillating alteration in the degree of distortion of MoO₆ octahedra in the structure. A detailed data analysis of the corresponding EXAFS spectra is underway.

Assistance of the ID24 staff during this experiment is gratefully acknowledged.

