

Solid State Kinetics from Time-resolved in situ XAFS Investigations: Reduction and Oxidation of Molybdenum Oxides

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Reduction and reoxidation of MoO_3 with hydrogen and oxygen, respectively, were studied by in situ X-ray diffraction and X-ray absorption spectroscopy (XAS). The experiments performed focused on elucidating phase composition and evolution under isothermal reduction conditions. Under all conditions studied the reduction of MoO_3 to MoO_2 was found to be a one-step process. At temperatures higher than 723 K the formation of Mo_4O_{11} was observed. However, Mo_4O_{11} is not an intermediate in the reduction of MoO_3 but rather it is formed in a parallel reaction between MoO_3 and MoO_2 . During MoO_3 reduction the evolution of the MoO_3 and MoO_2 phases exhibited a characteristic sigmoidal shape which indicates that under the conditions studied nucleation-growth kinetics govern the reduction. Different apparent activation energies were obtained for the reduction of MoO_3 below and above 698 K. Reoxidation of MoO_{3-x} in oxygen was found to proceed much faster than its reduction in hydrogen. Evolution of the MoO_3 phase is dependent on both temperature and degree of oxidation. At temperatures below 823 K first a linear and then a parabolic rate law was observed, indicating that the progress of MoO_{3-x} oxidation is first boundary controlled and then diffusion controlled. This work clearly demonstrates the potentials of time-resolved in situ XAS as a novel tool to investigate the kinetics of solid state reactions.



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