

Bulk Structural Investigation of the Reduction of MoO₃ with Propene and the Oxidation of MoO₂ with Oxygen

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Abstract

Reduction of MoO₃ in propene and oxidation of MoO₂ in oxygen are investigated by in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Temperature-programmed and isothermal experiments (573 K - 773 K) are performed to elucidate the structural evolution of phases present during the reactions and, in addition, to reveal the solid-state kinetics of the processes involved. During the reduction of MoO₃ in propene and the oxidation of MoO₂, only crystalline MoO₃ and MoO₂ were detected by in situ XRD. The formation of a “Mo18O52” type shear-structure as intermediate during reduction of MoO₃ in propene and during oxidation of MoO₂ in oxygen was observed by in situ XAS. The solid-state kinetics of the reduction of MoO₃ in propene exhibits a change in the rate-limiting step as a function of both temperature and extent of reduction. The solid-state kinetics of the oxidation of MoO₂ is governed by three-dimensional diffusion. A schematic reaction mechanism for the reduction of MoO₃ in propene and re-oxidation in oxygen is proposed that consists of (i) generation of oxygen vacancies at the (100) or (001) facets by reaction with propene, (ii) vacancy diffusion in the MoO₃ bulk, (iii) formation of “Mo18O52” type shear-structures in the lattice, and (iv) formation and growth of MoO₂ nuclei. With respect to a redox mechanism for the partial oxidation of propene on MoO₃, three stages are distinguished. (i) At temperatures below ~ 600 K the participation of oxygen from the MoO₃ bulk is negligible. (ii) At temperatures between ~ 600 K and ~ 700 K oxygen vacancy diffusion in the bulk is sufficient to make a redox mechanism feasible, affording a partially reduced MoO₃ under reaction conditions. (iii) At temperatures above ~ 700 K sufficiently fast oxygen diffusion in the lattice combined with rapid formation and annihilation of crystallographic-shear planes permits the participation of a considerable amount of the lattice oxygen of MoO₃ in the partial oxidation of propene.