



European Journal of Inorganic Chemistry, 2 (2003) 301-312.

Evolution of defects in the bulk structure of MoO₃ during catalytic oxidation of propene

T. Ressler*, J. Wienold, R.E. Jentoft, F. Girgsdies

Department of Inorganic Chemistry, Fritz-Haber-Institut der MPG,
Faradayweg 4-6, D-14195 Berlin, Germany

E-mail: Ressler@fhi-berlin.mpg.de, Phone: (+49) 30 8413 3192, Fax: (+49) 30 8413 4405

Abstract

The evolution of characteristic defects in the bulk structure of MoO₃ under propene oxidation conditions was investigated by in situ X-ray absorption spectroscopy and X-ray diffraction. Under the reaction conditions employed (273 K to 773 K, and propene to oxygen ratio from 1:1 to 1:5), orthorhombic MoO₃ remains the only crystalline phase detected by XRD. The onset temperature of the reaction of propene and oxygen in the presence of MoO₃ coincides with the onset of the reduction of MoO₃ in He, H₂ and propene (~ 620 K). At temperatures below ~720 K and independent of the atmosphere used, partial reduction of MoO₃ is observed resulting in the formation of “Mo₁₈O₅₂” type defects in the layer structure of α -MoO₃. At temperatures above ~720 K and in oxygen or in an oxidizing atmosphere, the “Mo₁₈O₅₂” type defects are re-oxidized to MoO₃. Evidently, the catalytically active molybdenum oxide phase develops under partial oxidation conditions at temperatures below 720 K and does not possess the undisturbed ideal layer structure of orthorhombic α -MoO₃. The results presented clearly show the necessity and the large potential of bulk structural investigations of heterogeneous catalysts under reaction conditions. The bulk structure and particularly the type and amount of defects in the material (“real” structure) considerably affect the catalytic properties. Hence, in order to rationally design a most active heterogeneous catalyst, both structure and reactions of the surface, and structure, defects, and reactions of the bulk need to be known in detail and carefully considered.