



MAX-PLANCK-GESELLSCHAFT

11th CRC, Sapporo, Japan



Evolution of Molybdenum HPA under temperature-programmed-reaction conditions – An in situ EXAFS study

J. Wienold, O. Timpe, R.E. Jentoft, G. Mestl, T. Ressler

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

Cesium salts of molybdophosphoric acid (heteropolyacids, HPA), $Cs_xH_z[AMo_{12-y}B_yO_{40}] \cdot nH_2O$ (A=P or Si; B=V/W), are used industrially as catalysts for the partial oxidation of methacrolein and isobutyric acid. The role of the structure forming kegggin-anions ($AMo_{12-y}B_yO_{40}$) in the catalytic process is not yet fully understood. The influence of the hetero-atoms (P/Si) and the role of the addenda substituents (V/W) is still under investigation. Ex situ XAFS at the phosphorus K-edge of activated HPAs was carried out to reveal the electronic structure and the coordination of the P atoms in as-synthesized and activated HPA samples. Recent studies indicated, that the kegggin-anion may not be catalytically active itself but that its fragments exhibit catalytic activity. To elucidate the evolution of the kegggin-anions during activation and the nature of transient fragmentation compounds, in situ time resolved EXAFS studies on HPAs of different composition under different reaction atmospheres, were performed. Simultaneously, the gas phase composition is monitored by mass spectrometry. The evolution of the EXAFS combined with that of the oxidation state and the gas phase composition during the activation/decomposition clearly shows the fragmentation of the kegggin and the formation of new structural phases. The structural evolution of the HPA observed is correlated with the catalytic activity of the system in partial oxidation of propene.