



Temperature programmed decomposition of heteropolyacids - An in situ XAS characterization

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Heteropolyacids (HPA) with Keggin structure of the general composition $(H/Cs)_{3+x}[PV_x(Mo/W)_{12-x}O_{40}]^*yH_2O$ ($x=1-2$), are used as catalysts for the partial oxidation of methacrolein and isobutyric acid to methacrylic acid on an industrial scale [1]. However, the use of these catalysts is limited by their low stability under catalytic conditions. Connected to these phenomenon is the question, whether the intact 'Keggin-Anion' is the active phase at all. In the literature, a general agreement seem to exist that the active catalyst exhibits an intact Keggin structure. In this investigation we studied the influence of different reactant atmospheres on thermal decomposition products and on the decomposition mechanism. Attention is focused on the stability of the 'Keggin anion', from which the structures are built. For comparison the so called free acids (without Cs), which exhibits much lower stability, are examined under the same conditions as the Cs-salts. The short range order evolution of the HPA were investigated with in situ X-ray absorption spectroscopy (XAS). Simultaneously recorded data of mass spectroscopy allow to correlate changes in the short range order with catalytic activity or evolution of decomposition fragments in the gas phase. It is shown that a detailed analysis of the short range order is possible. Simulations of the radial distribution function (RDF), on the basis of single crystal data, were fitted to the experimentally RDF. Our investigations indicates that the intact Keggin HPA alone may not be the active catalyst. It is suggested that its fragments of decomposition or a combination of both, the intact Keggin and the fragments, build the active phase. This results are supported by in situ XRD investigations. Former investigations have shown that in situ XAS-studies in combination with the results of in situ XRD studies are a powerful tool to elucidate the evolution of structures in long range and short range order [2].

[1] Mizuno N., Misono M., *Journal of Molecular Catalysis*, **86** (1994) 319-342

[2] T. Ressler, R.E. Jentoft, J. Wienold, M.M. Günter, O. Timpe, *J. Phys. Chem. B*, **104** (2000) 6360