

In situ XAS Characterization of Heteropoly Acids During Temperature Programmed Decomposition

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Cesium salts of molybdovanadophosphoric acid are industrial catalysts for oxidation of methacrolein and isobutyric acid to methacrylic acid [1]. In this work the temperature-programmed decomposition of various heteropoly acids (HPA) was investigated to elucidate whether the catalytically active phase consists of intact Keggin anions or of decomposition products of the Keggin structure [2].

From X-ray absorption spectroscopy (XAS) studies on the thermal treatment of HPA information on the short-range order structure, on the average valence of the constituent metals, and on chemical speciation can be obtained. The in situ capabilities of XAS combined with mass spectrometry permit to monitor the structural evolution of heteropoly acids during thermal decomposition (activation) and to correlate the structure of the material under reaction conditions with the onset of the catalytic activity. In addition, in situ X-ray diffraction (XRD) experiments were performed to reveal the evolution of the long-range order structure of the HPA during decomposition. Using the two complementary techniques XAS and XRD enables us to describe the decomposition process of HPA both on the long-range and on the short-range order scale and to correlate the structural evolution observed with catalytic activity.

Heteropoly acids with a nominal composition of $H_4[PMo_{12}O_{40}] \cdot xH_2O$ were studied under various conditions with in situ XAS and in situ XRD. The chemical composition of the samples used is varied by partial substitution of the protons by cesium ions and substitution of one of the molybdenum atoms by vanadium. Temperature programmed decomposition was carried out in atmospheres of 20 % oxygen in helium, 10 % propene in helium and 10% propene + 10 % oxygen in



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helium. The in situ XAS measurements were performed at the molybdenum K edge and at the vanadium K edge in the transmission mode.

By a detailed analysis of the Mo K edge EXAFS measured for the various HPA compounds, the local coordination of molybdenum inside the Keggin anion could be unambiguously modeled using theoretical EXAFS calculations (based on single crystal structure data [ICSD 93]). The good agreement between experimental and theoretical EXAFS function for the HPA studied, enables us to follow the structural

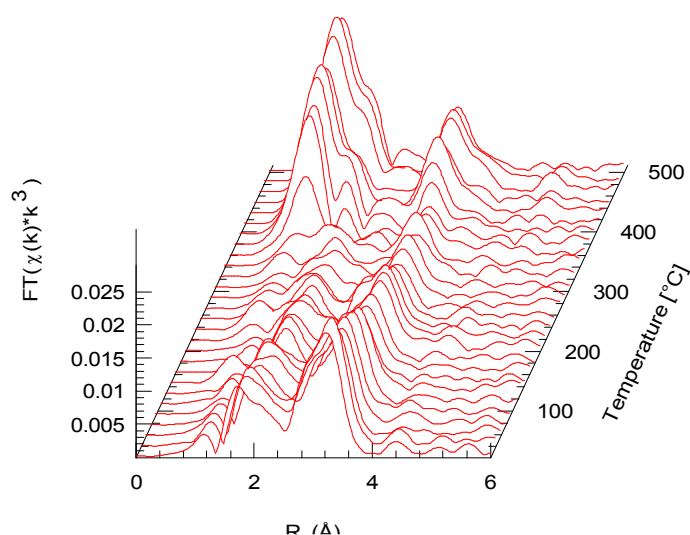


Figure 1 Evolution of the radial distribution function during TPR of $H_5[PVMo_{11}O_{40}] \cdot xH_2O$ in 20% oxygen @ 5 K/min. MoO_3 is formed as final product.

evolution of the Keggin anion with temperature (Figure 1). Hence, the collapse of the HPA structure can be observed in situ and correlated to the onset of partial oxidation activity observed in the evolution of the gas phase composition. Accordingly, on the one hand the first removal of water, which is ascribed to crystal water, did not affect the structure of the Keggin anion. On the other hand, the removal of the structural water at around 620 K

results in the decomposition of the Keggin anion structure and the onset of catalytic activity. From the vanadium K edge spectra, it was not possible to describe the V coordination sphere by assuming that V occupies Mo sites in the Keggin structure. This indicates that a considerable fraction of the vanadium atoms is not localized inside the Keggin anion. In addition, the evolution of the XANES region at the V K edge, show that the vanadium structure is also affected by the lost of the structural water. During the decomposition, however, it seems that molybdenum is reduced prior to vanadium in the HPA structure.

[1] Watzenberger, O., Emig, G., Lynch, D., *J. Catal.* **124** (1990) 247

[2] Mizuno, N., Tateishi, M., Iwamoto, M., *J. Catal.*, **163** (1996) 87-94



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