

Synthesis, Structure, and Properties of Selective Partial Oxidation Catalysts: Caesium Salts of Molybdovanadophosphoric Acid

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Introduction:

Heteropoly acids and their salts are used as catalysts in many selective oxidation reactions¹. The partly neutralised caesium salts of the molybdovanadophosphoric acid $H_4PVMo_{11}O_{40}$ are of special interest due to their high activity in the oxidation of unsaturated aldehydes as methacrolein to their corresponding acids. Despite this high catalytic potential, many questions have not been answered yet about the molecular processes which occur during their synthesis, their crystal structure and their physico-chemical properties. We report on new insights into the synthesis of the caesium salts and elucidate their crystal structures. Properties which depend on the caesium content will be rationalised with the knowledge of the structures.

Preparation Procedure and Methods of Investigation:

The salts were prepared by adding stoichiometric amounts of Cs_2CO_3 dissolved in water to an aqueous solution of $H_4PVMo_{11}O_{40}$, which yielded a dispersion of microcrystals. The solid product of a nominal composition $Cs_xA \cdot nH_2O$, $A = H_{4-x}PVMo_{11}O_{40}$, was obtained by distilling off the water and drying the solid in air at 383 K for 15 h. The isolation procedure was examined using DSC and XRD. The compositions of the water soluble and insoluble components, prior and subsequent to

¹ Y. Izumi, K. Urabe, M. Onaka, *Heteropoly Acid as Multifunctional Catalyst*, in: *Zeolite, Clay and Heteropoly Acid in Organic Reactions*, VCH Verlagsgesellschaft

distilling off the water and drying at 383 K, were determined by AAS, EDX and RFA. The secondary structures of the salts were investigated by cryo electron microscopy and powder XRD supported by computer simulations of the diffraction patterns.

Results:

Elemental analyses of the water soluble and insoluble components of the caesium salts, prior and subsequent to distilling off the water and drying at 383 K, lead to the conclusion that a homogenisation occurs in the case of Cs_xA , x : 1-3, during the isolation procedure. During this process, free acid is consumed yielding the product salt with a more homogeneous distribution of caesium ions. DSC experiments and powder XRD further indicate a homogenisation during the isolation. DSC confirms that Cs_2A can only be prepared when there are intimate contacts between the acid and the caesium salt. It is not possible to prepare Cs_2A starting from a physical mixture of acid and salt.

These results, however, cannot easily be transferred to the elemental composition of the salts in their solid state. Still, we are able to conclude that the caesium salts are also not completely homogeneous in their solid state.

The combined results of cryo electron microscopy and XRD supported by simulations of the diffraction patterns show that the secondary structures of $Cs_xA \cdot n H_2O$, (x : 2-4), can be derived from the crystal structure of $Cs_3A \cdot 7 H_2O$ (Pn3m, $a = 11.807 \text{ \AA}$) by introduction of statistically distributed defects either in the cation or in the anion sublattice by means of fractional site occupation factors. Therefore, all compounds belong to one phase with large stoichiometric variations. Only $Cs_1A \cdot 11 H_2O$ consists of a mixture of free acid and caesium salt.

With the knowledge of these structures, physico-chemical properties of the salts, which depend on the caesium content, can be rationalised. The highest thermal stability observed for Cs_3A in XRD and BET measurements (the specific surface area of Cs_3A is independent of the applied temperature treatment) is suggested to result from the absence of any structural imperfections. Due to the high space filling in the crystal structure of Cs_3A , which causes typical long-range effects, the internal stress and the lattice constants show maxima for this compound. In contrast to this, DRIFT spectra of the compounds in the Cs_xA series do not show any characteristic behaviour related to Cs_3A .