

Heteropoly Acids: Preparation, Structural Characterisation and Catalytic Properties

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Introduction

Cesium salts of molybdovanadophosphoric (Cs_xA) acid are industrial catalysts for oxidation of methacrolein and isobutyric acid to methacrylic acid. However, they do not exhibit long-time stability. Accordingly, it is important to determine the relationship between their structure and catalytic activity/stability. Still, Cs_xA are the most stable compounds of the HPA family.¹ Hence it was suggested that the intact Keggin ion might be the active catalyst.² However, the most stable Cs_3A only shows minor activity,³ while the substitution of less than 3 protons per Keggin-unit gives the best results.⁴ Ethene and propene partial oxidation were chosen as test catalytic reactions for in situ UV/Vis, Raman, DRIFTS, XAS, and XRD experiments to elucidate the structure of the active catalyst.

Results

Cs_xA belong to one phase with large stoichiometric variations.¹ Their structures are derived from Cs_3A by introduction of structural defects into the cation or anion sublattice. TG-DTA and in situ XRD showed that the thermal stability of Cs_xA increases with decreasing number of defects. In helium, Cs_3A decomposes at 947 K into Mo/V/P-containing oxides. In ethane, the decomposition temperature is reduced to 927 K. The loss of water is the main feature at low temperatures. The structural water, i.e. the acidic protons, is subsequently expelled. This step starts a complex transformation to mixed oxides. The reduction of Mo(VI), V(V) is linked to this structural transformation. Reduction is not the cause but the consequence of the structural rearrangement!

Cs_0A , Cs_1A , and Cs_2A are active in the oxidation of ethene and propene. The formation of acetaldehyde starts at 373 K in case of Cs_0A and Cs_1A , and at 395 K in case of Cs_2A . Cs_3A was almost inactive. Total oxidation was detected for Cs_4A . Thus, the increasing number of structural cation defects in this series is related to the increasing catalytic activity. The deactivation rate also depends on the cesium content. This observation is explained by the increasing thermal stability with decreasing structural defects. Hence, it can be concluded that the intact structural motif of the Keggin anion $\text{PMo}_{12}\text{O}_{40}^{3-}$ is not responsible for catalytic activity. Only salts that allow the decomposition/rearrangement of Keggin anions, due to the presence of structural defects, give catalytically active materials upon thermal activation. Catalytic activity develops between the loss of structural water and the formation of the final crystalline decomposition products. Obviously, transient phases,

predetermined by the parent HPA, have to be considered as the active catalyst. Up to now, there is little knowledge about these phases.

Combined UV/Vis and Raman studies of the structural rearrangement of HPAs during thermal and catalytic load led to the model recently published.^{5,6} The actual catalyst comprises a crystalline core of stable, but inactive Cs₃A salt on which the active species are supported. Raman spectroscopy suggests that fragmentation intermediates are the active species, which comprise lacunary-type Keggin structures, molybdenyl and vanadyl species. The decomposition kinetics determined the species formed and only treatments at elevated temperatures and for long times led to the crystallization of MoO₃.

In-situ XAS investigations flanked by XRD confirmed these ideas about Cs_xA in oxidation catalysis. The expulsion of structural water occurs at ca. 593 K prior to any further structural change of the initial Keggin-arrangement. In temperature programmed XAS experiments of propene partial oxidation acrolein and acrylic acid were formed simultaneously with the collapse of the Keggin structure. In-situ XAS studies confirmed the Raman result that the final product of this decomposition (MoO₃ in oxidizing atmosphere) was not formed immediately after the loss of structural water. Again, the formation kinetics of well-ordered oxides depended on the composition of the parent HPA. Replacement of P by Si resulted in an accelerated structural rearrangement. Alkali counterions prevented the formation of the final oxides and stabilized intermediate states. The direct correlation of the local structure around the Mo atoms with the activity for propene oxidation ruled out that the intact HPA was the active oxidation catalyst.

Indeed, the V addenda atoms may exert a different role than the suggested Keggin-anion stabilizing and oxidation potential shifting role.⁷ XAS measurements of the V and Mo K-edge positions suggest that V is reduced subsequent to Mo. The XAFS results indicate that a considerable fraction of the V is not incorporated into the Keggin ion. This XAS results are in line with recent ESR studies on this system.⁸ XANES at the P-edge and ³¹P-NMR spectra of molybdophosphoric acids, on the other hand, differ significantly when Mo is formally replaced by V.

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