

# Fundamentals of Catalysis - Spectroscopy, microscopy, and catalysis (Mechanistic Insights into the Thermal Degradation of Phosphomolybdic Acid)

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## Introduction

Heteropolyacids such as phosphomolybdic acid and phosphovanadomolybdic acid have been shown to be promising catalysts for the oxidation of isobutene to methacrylic acid. Though this process has highly desirable characteristics, it is limited by the structural degradation of the heteropolyacids during reaction, which reduces them into an inactive form<sup>1</sup>.

This work focuses on gaining insight into the structures of phosphomolybdic acid formed during the activation and deactivation of the catalyst and elucidating the mechanism of these structure changes with the ultimate aim of unearthing methods to preserve the stability of the active heteropolyacid structure. A combination of X-ray Absorption Spectroscopy (XAS), UV-visible Diffuse Reflectance Spectroscopy (UV-vis DRS) and High Resolution Transmission Electron Microscopy (HR-TEM) are used to study the heteropolyacid during degradation.

## Materials and Methods

Heteropolyacids were recrystallized from a 0.01 M aqueous solution for all studies. X-ray absorption studies were carried out at the Advance Photon Source, Argonne National Labs, IL. Spectra were collected at the Mo K-edge (19.999 5 keV) and W-L III edge (10.2068 keV). Samples were heated to 500 °C to monitor degradation.

TEM micrographs were collected on a Titan 80 Transmission Electron Microscope with applied voltage of 300 keV. Monolayer HPA layers were prepared by crystallizing phosphomolybdic acid from a 0.01 M solution onto a carbon grid. A heating holder was used to obtain micrographs during degradation.

## Results and Discussion

The major highlights of this work are summarized as follows.

- Isobutane oxidation reactions were carried out in a fixed bed reactor to study the activation process. As shown in Figure 1, it takes about 80 hrs for the phosphomolybdic acid (PMA) to activate and to reach maximum yields of methacrylic acid. UV-vis DRS and XRD studies show that the activation process involves a structural rearrangement similar to the thermal degradation process.
- XRD studies show that the structure of PMA changes by thermal degradation upon heating to 500 °C.
- Studies of the PMA upon thermal degradation with heating to 500 °C in the UV-vis spectrophotometer show that an additional absorption edge emerges in the spectra during degradation. This suggests the formation of a new species and the edge energy of this new domain indicates that the new species is bulk MoO<sub>3</sub>. Thus, the PMA degrades into a residual HPA structure and MoO<sub>3</sub>.

- EXAFS spectra collected during the heating of the PMA to 500 °C indicate the formation of a disordered structure (with a radial distribution function similar to ammonium heptamolybdate). This structure decomposes further when held at 500 °C, ultimately yielding a structure whose XAS spectra resembles MoO<sub>3</sub>, as also shown with UV-vis DRS – agreeing with previous reports<sup>2</sup>.

- Atomic resolution images were obtained for prepared PMA monolayer samples (Figure 2). Images were also simulated using an HR-TEM image simulation package called MacTempas to interpret the images. Micrographs were collected after heating the PMA to 500 °C. Images suggest the formation and propagation of a twinning defect (which involves the rotation of one part of the crystal with respect to the rest of the crystal) across the structure, which was possibly nucleated at vacancies in the primary structure. Formation of this twinning defect is suspected to be the mechanism of structural rearrangement in the PMA structure.

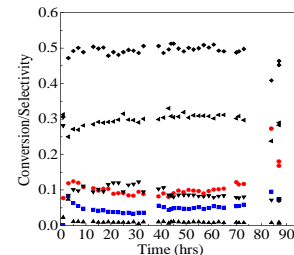


Figure 1: Performance of HPA catalyst as a function of time **Isobutane Conversion (■)**, **Methacrylic Acid Selectivity (●)**, **Methacrolein Selectivity (▲)**, **Acetic Acid Selectivity (▼)**, **Carbon Monoxide Selectivity (◆)**, **Carbon Dioxide Selectivity (◄)**

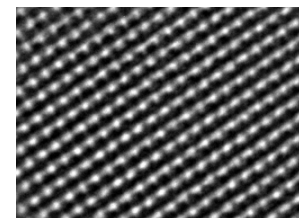


Figure 2: HRTEM image of a monolayer of PMA on C. Simulations show that the beam is falling on the 110 face of the PMA crystal and each bright spot corresponds to a Mo atom.

## Significance

This work demonstrates for the first time the use of HR-TEM and simulation of the HR-TEM images to obtain a highly localized, atomic scale picture of a working catalyst. This is a significant advantage in terms of being able to observe rearrangements at the atomic scale, whereas most techniques average the signal over much larger scales. This study demonstrates the strength of this technique and the possibility of using it for other systems.

## References

1. M. Misono, N. Nojiri, Applied Catalysis 64 (1990) 1
2. T. Ressler, O. Timpe, F. Girgsdies, J. Wienold, T. Neisius, Journal of Catalysis 231 (2005) 279