

Selective oxidation of i-butane and i-butene to methacrolein and methacrylic acid over Keggin-type polyoxometalate and MoVTenbO_x catalysts: A comparative catalytic and in situ-spectroscopic study

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The one-step selective oxidation of i-butane to methacrolein (MAC) and methacrylic acid (MAA) could be an attractive alternative to the traditional acetone-cyanohydrin process, due to its simplicity, inexpensive raw materials and negligible environmental impact [1]. While Keggin-type polyoxometalates (POM) are known as effective catalysts but suffer from long conditioning and fast deactivation, MoVTenbO_x catalysts were rarely studied, although they could be promising materials since they catalyze, too, the oxidation of propane to acrylic acid [2]. In this work, in situ spectroscopic investigations and catalytic tests were performed with both types of catalysts in the oxidation of i-butane and i-butene to MAC and MAA to derive information on the reaction mechanism and structure-reactivity relationships.

In situ-FTIR as well as simultaneous operando-EPR/UV-vis/Raman measurements were performed to study the interaction of feed components (i-butane/i-butene, O₂, H₂O) with decomposition products of the MoV_{0.36}Te_{0.17}Nb_{0.12}O_x-precursor [2] (K1-450, K1-600), H₄PVMo₁₁O₄₀·8H₂O (POM-1) and (NH₄)₄PVMo₁₁O₄₀·5H₂O (POM-2) obtained by calcination in N₂ at different temperatures. Catalytic tests were performed in a fixed-bed plug-flow reactor at 300°C - 400°C with a feed composition i-C₄ : O₂ : H₂O = 1 : 1.7 : 11, revealing that all catalysts are more active with i-butene than with i-butane. Their performance depends mainly on the redox activity and surface acidity and is also influenced by the catalyst structure.

During in situ-FTIR experiments at 300°C, a rapid formation of different carbonyl compounds was observed, among them methacrylate and cyclic anhydrides. Simultaneously, the evolution of CO_x was detected. The formation of adsorbates (but also of CO_x) was markedly more pronounced over K1-450 and POM-2, indicating their higher activity in comparison to POM-1 and K1-600. Based on this promising result, further optimization of the catalysts towards higher selectivity is under way. Upon contact with MAC/H₂O at 300°C, the same adsorbed species are formed, clearly indicating that MAC is formed as an intermediate during oxidation of i-butane/i-butene.

Simultaneous EPR/UV-vis/Raman studies during calcination of the H₄PVMo₁₁O₄₀·8H₂O precursor to the POM-1 catalyst indicate that, at 250 °C, V⁵⁺ is expelled leaving behind a lacunary Keggin anion which is not further disintegrated and forms the basis of POM-1. The expelled V is reduced and forms VO²⁺ clusters. This process continues in POM-1 during oxidation of i-butane and is dramatically enhanced by adding water to the feed. Under these conditions the H₄PVMo₁₁O₄₀·8H₂O is partly restored, however, without V being re-integrated into the Keggin anion. No degradation into ill-defined MoO₃ as during propene oxidation [3] was observed. This suggests that the intimate neighbourhood of Mo and isolated V as present in the intact Keggin anion is not crucial for high catalytic performance.

[1] F. Cavani, R. Mezzogori, A. Pigamo, F. Trifirò, E. Etienne, *Catal. Today* 71 (2001) 97.

[2] W. Ueda, K. Oshihara, *Appl. Catal. A: General* 200 (2000) 135.

[3] G. Mestl, T. Ilkenhans, D. Spielbauer, M. Dieterle, O. Timpe, J. Kröhnert, F. Jentoft, H. Knözinger, R. Schlögl, *Appl. Catal. A: General* 210 (2001) 13.