

# New Cs-containing Structural Analogues of Mo-V-Nb-Te-O Type Oxides – Highly Prospective Catalysts for the Partial Oxidation of Methacrolein to Methacrylic Acid

*S. A. Schunk<sup>1\*</sup>, H. Hibt<sup>2</sup>, A. Sundermann<sup>1</sup>*

<sup>1</sup> *hte Aktiengesellschaft, Kurpfalzring 104, 69123 Heidelberg, Germany,*

*[www.hte-aktiengesellschaft.com](http://www.hte-aktiengesellschaft.com),*

<sup>2</sup> *BASF Aktiengesellschaft, Chemicals Research and Engineering, 67056 Ludwigshafen, Germany, [www.basf.com](http://www.basf.com)*

*\*[stephan.schunk@hte-company.de](mailto:stephan.schunk@hte-company.de)*

## Introduction

The extensive research performed by numerous groups on the structural identity of Mo-V-Nb-Te-O type oxides [1] has revealed a number of important findings that have led to a better understanding of the structure-property-relationships that render these materials active and selective compounds in the direct conversion of alkanes [2]. A core finding was the identification of two phases, namely i- and k-phase, which are the two crystalline products which can be obtained phase pure or may evolve as phase mixture under non-optimum synthesis conditions [3]. The i-phase with the conventional composition Mo-V-Nb-Te-O is isostructural with the oxidic bronze  $\text{Cs}_{0.5}[\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}]$ , [4] which can also be obtained in highly crystalline and phase-pure form. The  $\text{Cs}_{0.5}[\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}]$  bronze structure shows identical structural motifs with regard to the channel forming oxide species of group V and VI.

Based on the observation of the isotypic crystallization of Mo-V-Nb-Te-O and  $\text{Cs}_{0.5}[\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}]$  experiments were done to introduce Cs into the channel lattice of Mo-V-Nb-Te-O and therewith to get close to the compositional range of conventional Cs-P-Mo-V-Sb-O with the Keggin-structure of heteropoly compounds which until now are the only satisfying catalytic system for the selective oxidation of methacrolein to methacrylic acid. Indeed, it was possible to prepare new compounds with the pure crystalline phase of the i-phase with the compositional systems Cs-Mo-V-Sb-O and Cs-Mo-V-Bi-O. A further improvement of the catalytic properties is possible by doping the phase-pure, Cs-containing i-phases with phosphorous.

## Materials and Methods

As described above the target lead structure of the Cs-substituted i-phase is ideally suited for a high throughput experimentation campaign entailing automated synthesis and testing of the potentially catalytically active components. The i-phase oxides were synthesized hydrothermally and if necessary post-treated using incipient wetness techniques for additional doping with various elements. The testing campaigns were initiated by subjecting the i-phase oxides to standard gas mixtures containing propane, isobutane, acrolein and methacrolein in mixture with oxygen, water and nitrogen as balance gas at the ratios of (1-5%):(7-15%):(2-22%) for a GHSV between 1.000 to 4.000  $\text{h}^{-1}$ . All tests were carried out in 48-fold test reactors with GC-analysis allowing full carbon balance.

## Results and Discussion

Although iso-typic with the well known i-phase based on Mo-V-Nb-Te-O type oxides rendering best results known in the conversion of propane to acrylic acid, the results obtained for the direct oxofunctionalisation of the alkanes was frustrating for the Cs-containing structural analogues. No oxygenates other than COx could be obtained with the hydrocarbon feeds of propane and isobutane. The picture is totally different for the conversion of unsaturated aldehydes like methacrolein: here the samples proved to be active and selective for the partial oxidation of methacrolein to methacrylic acid.

The general finding within the test library was that Cs, Mo and V with the framework elements Sb, Se, Bi and Nb showed superior performance with regard to the selectivity towards methacrylic acid. Apart from marginal amounts of acetic acid, the main by-products observed in the reaction were COx. For the dependency of the oxygen concentration it was generally found that only below a threshold of the oxygen concentration around 8% the selectivity to methacrylic acid would decrease substantially. With regard to the water concentration dependency the materials already show an interesting behaviour, that could be of relevance for a later chemical process: lower water concentrations of around 2% render the materials more selective. This water concentration is far below the water concentration needed for the currently used industrial catalyst based on heteropolyacids. The selectivity of the oxidation of methacrolein to methacrylic acid can be increased substantially by doping of the materials with phosphorous. With regard to the phosphorous content clear performance changes can be seen: for a phosphorous content of 0,2 a dramatic increase in the selectivity to methacrylic acid is observed, this is especially true for conversion degrees of the aldehyde up to 40% where selectivities over 80% to the C4-acid are seen. Materials with this degree of phosphorous doping in general display X-ray diffraction patterns typical for the i-phase also after the catalytic performance test.

## Significance

Our studies have led to a new alternative oxidation catalyst which shows features that render the material attractive to industrial application. It is also the first time that a stoichiometric alkali bronze is found to be a useful catalyst in a partial oxidation reaction.

Cesium containing i-phase type materials show unexpected behavior in the partial oxidation of methacrolein to methacrylic acid. Improvements in the performance of the catalysts can be observed upon doping with phosphorous. The phosphorous doping does not lead to a destabilization of the solid state material accompanied by heteropolyacid formation. Therewith a new and stable catalytic system for the selective oxidation of methacrolein to methacrylic acid has been found.

## References

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