

**ISOBUTANE AND ISOBUTENE OXIDATION OVER MOLYBDENUM OXIDE-BASED CATALYSTS,  
PREPARED STARTING FROM ANDERSON-TYPE POLYOXOMETALATES PRECURSORS**

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Molybdenum oxide-based systems represent an important class of heterogeneous catalysts for the selective oxidation of hydrocarbons [1]. In all Mo oxide-based catalytic systems the control of the redox properties of Mo is the key point for the development of active and selective species, aimed at the transformation of specific organic substrates. A control of the redox properties of Mo can be achieved either through the formation of molecular-type compounds, in which the properties of the basic structural unit can be controlled through the composition of the compound itself, or through the formation of multicomponent systems, like intermetallic compounds having defined stoichiometry or substitutional solid solutions. An alternative approach is the preparation of solid solutions starting from crystalline compounds of defined composition, like polyoxometalates, and then by decomposing them under controlled conditions. In such a way, elements are forced to stay in the same framework, and possible synergic interactions can develop. We have adopted this strategy for the preparation of several Mo-based mixed oxides, such as: Te/Mo/O, Cu/Mo/O, Co/Mo/O, V/Te/Mo/O, Ni/Te/Mo/O. In some cases, the precursors of these systems are the corresponding Anderson-type polyoxometalates, in which the heteroatom is represented by divalent or trivalent metal cations (Cu, Co, Ni), the polyoxoanion is the Mo<sub>6</sub>O<sub>24</sub><sup>12-</sup> unit, and the cation for the polyoxoanion is either ammonium or the divalent metal cation when the Anderson compound has been exchanged with the corresponding metal salt. Vanadium has been added by impregnation over the polyoxometalate. The precursors have then been thermally treated at 500°C, in order to decompose the structure and develop the corresponding mixed oxide. Catalysts prepared in such way have been characterized with several techniques. The thermal structural evolution has been followed by thermal analysis and by bulk-characterization techniques (XRD, Raman spectroscopy). Thermal-programmed-reduction has been used for the investigation of the redox properties.

Materials prepared have been checked as catalysts for the oxidation of isobutene and of isobutane. Systems were active in the oxidation of isobutene; the presence of V affects the activity, but the activity-enhancement was not strictly proportional to the V content. Besides methacrolein, by-products were carbon oxides, acrolein, and minor amounts of heavier compounds, including oxygenated aromatics. Methacrylic acid formed in all cases with selectivity lower than 5%. The distribution of products also was affected by the catalyst composition; maximum selectivity to methacrolein was close to 55%.

The oxidation of isobutane has been investigated over selected catalysts.

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1. P. Arpentinier, F. Cavani, F. Trifirò, “The Technology of Catalytic Oxidations”, Editions Technip, Paris, 2001, ISBN 2-7108-0777-7