

## Isobutane selective oxidation to methacrylic acid: Still a challenge after 25 years!

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The development of a catalytic process for the selective oxidation of isobutane into methacrylic acid has been representing for more than 25 years a difficult but fascinating challenge. As a matter of fact such a process coupled to the esterification of the methacrylic acid obtained by methanol would give an access to a very competitive shortcut for producing methyl methacrylate - the monomer of poly(methyl methacrylate) better known under its commercial names Plexiglas® or Altuglas®. Actually, the current industrial process - the so-called acetone-cyanohydrin (ACH) route - suffers from serious environmental and economic drawbacks which need to be addressed. During the oxidation of isobutane into methacrylic acid, a double C=C bond has to be formed and one methyl group has to be converted into a carboxyl group. Therefore, a bifunctional catalyst presenting both acid and redox properties - which are responsible for the oxidative dehydrogenation and the insertion of oxygen, respectively - is necessary. In this context Keggin-type heteropolyacid such as  $H_4PMo_{11}VO_{40}$  and its salts like  $Cs^+$  and  $NH_4^+$  have proved to be interesting candidates because of their simultaneous strong acidity and redox properties which are moreover easily tunable. In this seminar I will describe our work aiming at developing an efficient catalyst for the reaction and at understanding the role of each element present in the catalytic formulation. In a first step the kinetics of the reaction was studied, using a mixed cesium-ammonium salt of 11-molybdo-1-vanadophosphoric acid. It shown that the reaction obeys the Mars and van Krevelen redox mechanism and that the rate-limiting step was the reaction between isobutane and the oxidized sites of the catalyst. Moreover, the influence of the relative amounts of  $NH_4^+$  and  $Cs^+$  cations was demonstrated, the ammonium ions being essential to get high selectivity to MAA by helping to maintain a partially reduced active phase at the steady state. On one hand, the cesium cations proved to be essential to form a cesium salt on which the active phase is dispersed while, on the other hand, the presence of vanadium is necessary to improve the redox process. From this basis  $Cs_3PMo_{12}O_{40}$  and  $HCs_3PMo_{11}VO_{40}$  heteropolysalts, that could be obtained by a controlled synthesis, were used as carriers to disperse firstly the simple  $H_4PVMo_{11}O_{40}$  active phase and then the more efficient protonated ammonium salt of 11-molybdo-1-vanadophosphoric acid,  $(NH_4)_3HPMo_{11}VO_{40}$  (APMV). The influence of the nature of the support (i.e.  $SiO_2$ , SBA-15,  $ZrO_2/SBA-15$  and  $Cs_3PMo_{12}O_{40}$  (CPM)) on the catalytic properties and the catalytic reaction performances has also been investigated. Compared with silica-supported catalysts which were poorly stable, two main effects were observed upon supporting APMV on CPM support: (i) the resulting multilayer dispersion limited the thermal decomposition of the active phases, and (ii) the acidity of surface species was much stronger. To confirm these findings and optimize the properties of APMV/CPM catalyst, a series of catalysts with 10-50 wt.% loading of APMV on CPM was prepared. Their physicochemical properties, their reactivity in reducing atmosphere, and, of course, catalytic performances in the isobutane oxidation were studied. As a result one of the best conversion of isobutane (15.3%) and yield of the desired products (MAC+MAA, 8.0%) reported up to now in the open literature were achieved.

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