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 H₄PMo₁₁VO₄₀ and its salts like Cs⁺ and NH₄⁺ 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 NH₄⁺ 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 Cs₃PMo₁₂O₄₀ and HCs₃PMo₁₁VO₄₀ heteropolysalts, that could be obtained by a controlled synthesis, were used as carriers to disperse firstly the simple H₄PVMo₁₁O₄₀ active phase and then the more efficient protonated ammonium salt of 11-molybdo-1-vanadophosphoric acid, (NH₄)₃HPMo₁₁VO₄₀ (APMV). The influence of the nature of the support (i.e. SiO₂, SBA-15, ZrO₂/SBA-15 and Cs₃PMo₁₂O₄₀ (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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Sébastien Paul is Professor at the Ecole Centrale de Lille, a Generalist Engineer School in the North of France, where he is the head of the Sciences of the Matter department since 2009. After his PhD in Chemical Engineering at the University of Technology of Compiègne, France (1996), he was hired by the Ecole Centrale de Lille as an Assistant Professor (1998). From 2004 to 2009 he was at the head of the “Chemical Engineering” Department which then became the “Sciences of the Matter” Department. In 2009 he was nominated Associate Professor and in 2011 Full Professor. He is involved in the development of a large variety of catalytic processes starting from compounds issued from the biomass or hydrocarbons. Finally, he is supervising or co-supervising 11 PhD, 10 post-docs, is co-author of 30 scientific articles, 3 patents, and 65 communications (oral and poster) in national and international congresses.