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Catalytic selective oxidation of isobutane to methacrylic acid on supported $(NH_4)_3HPMo_{11}VO_{40}$ catalysts

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ABSTRACT

Catalysts containing 10–50 wt.% of $(NH_4)_3HPMo_{11}VO_{40}$ (APMV) active phase supported on $Cs_3PMo_{12}O_{40}$ (CPM) were prepared, characterized, and evaluated in the selective oxidation of isobutane to methacrolein and methacrylic acid. The fresh and spent catalysts were characterized by N_2 physisorption, TGA, XRD, FT-IR, and Raman spectroscopies, as well as by XPS, H_2-TPR, and NH_3-TPD in order to study their thermal stability, structural, and textural properties. Catalysts containing high amounts of APMV (i.e., 40–50 wt.%) exhibit an increased stability against structural alteration. Besides sintering, the cross-transfer of V species from the surface to the bulk of the solids and of Cs species in the opposite direction was found to be responsible for the partial deactivation of the catalysts. The catalytic performances were directly correlated with the amount of strong and very strong acid sites, itself also depending on the APMV loading.

1. Introduction

Methacrylic acid (MAA) is generally esterified to produce methyl methacrylate (MMA), which is an important monomer for the production of poly-methyl-methacrylate (PMMA). The commercial process used for MMA production is traditionally based on the acetone-cyanohydrin (ACH) route [1]. Three steps are necessary for getting the final product, and the process suffers from many drawbacks, especially in light of the recent green trends in the modern chemical industry. For example, the highly toxic and expensive hydrogen cyanide raw material is used, and a large quantity of ammonium bisulfate, which is further contaminated by organic compounds, is co-produced [2,3]. Lots of efforts have been performed in order to improve or even get rid of this conventional process. Syntheses starting from C_2, C_3 and C_4 hydrocarbons were actually widely developed [4–7]. While some positive outcomes were obtained, the price of the reactants, the drastic reaction conditions, and the number of reaction steps through complex processes restricted the industrial application of these new developments. In this context, the selective oxidation of isobutane (IBAN), which would provide a one-step route to methacrylic acid, is still a reaction of high interest that therefore deserves research efforts. As a matter of fact, the low cost of the main raw material, the lower negative impacts on the environment, and the lower amounts of co- or by-products are significant advantages of this direct route. However, the challenge remains the development of an efficient and stable catalyst that would make this new route competitive compared with the ACH one.

Heteropolyacids and their salts, known as well as polyoxometalates, are extensively used as homogeneous and heterogeneous catalysts [8–12]. Their acidity and redox properties are two very important features, which can be easily tuned by adjusting the amount of protons and changing the metal atoms in the primary structure, respectively. The acidity plays an important role in activating the C—H bonds, and the redox properties are responsible for the oxygen insertion reactions necessary to generate the oxidized products. Therefore, heteropolycompounds catalysts generally display good performances in catalytic oxidation (or ammoxidation) [13–15], oxidative dehydrogenation [16–18], but also in isomerization [19,20], dehydration [21,22], alkylation [23,24], etc. A particularly high number of papers were devoted to the oxidative dehydrogenation of isobutyric acid to MAA over Keggin-based

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heteropolymolybdates catalysts, whose process came up to the pilot scale [25–28].

The introduction of V into the Keggin unit, like in $H_4PMo_{11}VO_{40}$, for instance, yields a significant effect of catalytic performances enhancement. Among other effects, which are quite well documented now, the substitution of one Mo atom by one V atom in the primary structure of fresh catalysts fastens both the reduction and reoxidation steps, which results in an improvement of the activity and of the selectivities to methacrolein (MAC) and MAA [29,30]. The partial or complete substitution of H atoms in the heteropolyacids with other transition or alkaline metal elements is a good way to improve the textural properties of the solids, while leading to a substantial improvement of the catalytic performances [31–33]. Currently, research works are more and more concentrated on the preparation of high surface area catalysts, for instance by supporting the heteropolyacid (or -salt) active phase on silica [30,34,35], different types of molecular sieves [36–38], carbon materials [39–41], metal oxides [10,42], or salts of heteropolyacids [22,30]. However, these catalysts are seldom used to directly oxidize IBAN to MAC and MAA [43,44].

In a previous work, we studied the kinetics of IBAN oxidation, using a mixed cesium–ammonium salt of *11*-molybdo-*1*-vanadophosphoric acid [45]. It was shown that the reaction obeys the Mars and van Krevelen (redox) mechanism, and that the rate-determining step was the reaction between IBAN 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 in maintaining a partially reduced active phase at the steady state [46]. Cesium-containing heteropolysalts, namely $Cs_3PMo_{12}O_{40}$ and $HCs_3PMo_{11}VO_{40}$, which were obtained using a well-controlled synthesis [46], were used as carriers to disperse $H_4PVMo_{11}O_{40}$. The IBAN conversion and the yield of the desired oxygenates increased along the $H_4PVMo_{11}O_{40}$ < $H_4PVMo_{11}O_{40}/Cs_3PMo_{12}O_{40}$ < $H_4PVMo_{11}O_{40}/HCs_3PVMo_{11}O_{40}$ series of bulk catalysts [47]. Very recently, we have shown that the protonated ammonium salt of *11*-molybdo-*1*-vanadophosphoric acid, $(NH_4)_3HPMo_{11}VO_{40}$ (APMV), behaves as a selective catalyst. The influence of the supports, including SiO_2, SBA-15, ZrO_2/SBA-15 and $Cs_3PMo_{12}O_{40}$ (CPM), on the catalytic properties and catalytic reaction performances were investigated [48]. Compared with silica-supported catalysts, which were poorly stable, three main effects were observed upon supporting APMV on the CPM support: (i) the resulting multilayer dispersion limited the thermal decomposition of the active phase, (ii) the acidity of surface species was much stronger, and (iii) the surface acid site density was found higher that in the case of other supported catalysts.

In the present work, to optimize the properties of the APMV/CPM catalytic system, a series of catalysts with 10–50 wt.% loading of APMV on CPM was prepared and tested under various operating conditions including reaction temperature from 280 to 350 °C and contact time in the range 3.6–7.2 s. The fresh and spent catalysts were characterized by N_2 physisorption, TGA, XRD, FT-IR and Raman spectroscopies, as well as by XPS, H_2-TPR and NH_3-TPD in order to study their thermal stability, to identify their bulk structure, to determine the active species, and to evaluate the extent of the modifications of the structural and textural properties after reaction. Finally, correlations between structural and/or textural properties, catalysts stability, and catalytic performances are proposed.

2. Experimental

2.1. Catalyst preparation

The CPM support was prepared by a precipitation method. An aqueous solution of Cs_2CO_3 (0.1 M, Fluka) was added *via* a pump into an aqueous solution of $H_3PMo_{12}O_{40}$ (0.1 M) at a controlled flow-rate of 2 mL/min. The temperature of the mixture was maintained at 45 °C under vigorous stirring. After 2 h, the solid was recovered by removing the solvent under reduced pressure. The sample was further dried at 70 °C for 24 h, followed by a calcination under static air for 3 h at 350 °C, this temperature being reached at a heating rate of 2 °C/min.

The $H_4PMo_{11}VO_{40}$ acid was typically synthesized as follows [15]: 15.8 g of MoO_3 and 0.9 g of V_2O_5 were dissolved in 350 mL of deionized water and heated to boiling. Then, 1.2 g of H_3PO_4 (85 wt.%) were added. The resulting reaction mixture was kept under reflux for another 6 h. A clear solution was obtained after cooling to ambient temperature. The product was concentrated by evaporation of the solvent, before finally recrystallizing the resulting solid.

The series of catalysts based on cesium-phosphomolybdic acid (APMV/CPM) with various amounts of APMV (10–50 wt.%) were prepared by a deposition–precipitation method. The CPM was suspended in 35 mL of deionized water at 45 °C under vigorous stirring for 1 h. Then, the aqueous solutions of NH_4NO_3 and $H_4PMo_{11}VO_{40}$ were simultaneously pumped to the suspension; the conditions were the same as those used during the preparation of CPM. The resulting precursor was calcined under static air for 3 h at 350 °C, this temperature being reached at a heating rate of 3 °C/min. Samples are labeled as *x*APMV/CPM, where x = 10–50 wt.%. Bulk APMV was also prepared as a reference catalyst.

2.2. Catalysts characterization

The surface area and total pore volume of the catalysts were measured by N_2 physisorption/desorption technique, using a Micromeritics ASAP 2010 analyzer at the temperature of liquid nitrogen. The specific surface area (S_{BET}) was calculated using the BET method. The total pore volume (V_p) was determined using the measurement taken at relative pressure P/P_0 = 0.995. The samples were outgassed at 150 °C for 3 h prior to analysis.

Thermogravimetric analysis (TGA) was performed using a TA instruments 2960 SDT to study the thermal decomposition of the fresh catalyst. The samples were heated from room temperature to 700 °C with an increasing rate of 3 °C/min, under air flow.

Infrared spectra (FT-IR) were recorded on a Thermo Nicolet 480 equipped with a MCT detector. The samples were pressed to form KBr pellets (1 wt.%) for analysis, and the spectra were recorded from 400 to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1} and using 256 scans.

Raman spectra were measured on a Jobin–Yvon LabRam Infinity apparatus equipped with a CCD detector operating at liquid nitrogen temperature. A D2 filter was used to protect the catalyst structure from possible modification by the laser (λ = 520 nm) due to overheating. The Raman shift was recorded in the range of 200–1400 cm^{-1}. The homogeneity of the samples was checked by performing the analysis on at least 3 different locations for each sample.

The bulk structure of the catalysts was examined by the X-ray diffraction (XRD) technique on a Bruker D8 Advance diffractometer, using the Cu Kα radiation (λ = 1.5418 Å) as a X-ray source. A range of $10° < 2\theta < 80°$ was scanned with steps of 0.02°/s and a 2 s acquisition time. The crystallite size was estimated by Scherrer's equation $L = 0.89\lambda/\beta(\theta)\cos\theta$, where L is the crystallite size, λ is the wavelength of the radiation, θ is the Bragg diffraction angle, and $\beta(\theta)$ is the full width at half maximum (FWHM) [49,50]. Temperature-programed XRD measurements were performed under a 3 vol.% H_2 in He atmosphere on a D8 Advance (Bruker AXS). During these experiments, the temperature was increased from ambient to 700 °C with a ramp of 10 °C/min.