



One-pot glycerol oxidehydration to acrylic acid on multifunctional catalysts: Focus on the influence of the reaction parameters in respect to the catalytic performance



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ABSTRACT

We report on a study of the key reaction parameters in glycerol oxidehydration into acrylic acid over W–V–Nb mixed oxides with a hexagonal tungsten bronze structure. This investigation demonstrated that the optimal control of the two consecutive steps of acid-catalysed glycerol dehydration into acrolein and aldehyde oxidation into acrylic acid, and of the parallel reaction of acrolein transformation into by-products (ketals and oligomers), was achieved in the presence of a defined glycerol-to-oxygen inlet ratio. Indeed, oxygen played the fundamental role of accelerating the oxidation of the intermediately formed acrolein into acrylic acid, by allowing a greater concentration of the oxidizing V⁵⁺ sites. In fact, an unprecedented higher yield to acrylic acid and acrolein compared to W–V bronzes was registered (maximum acrylic acid yield 50.5%) together with an increase of more than one order of magnitude in productivity, because of both the greater concentration of glycerol used in the inlet feed and the lower contact time needed. Further experiments were carried out by reacting acrolein and methanol in oxidative conditions, the latter as a model molecule for the determination of surface acid and redox properties.

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1. Introduction

With the aim of reducing the carbon footprint of fuels, biodiesel represents one of the most important options, theoretically providing a neutral CO₂ balance and significant reduction in greenhouse gas emission [1–3]. The growing biodiesel production trend goes hand-in-hand with the availability of large volumes of glycerol, co-produced via the conventional transesterification reaction used to synthesize the bio-fuel [2,4]. Since the late 1990s, this abundance of glycerol has significantly impacted the glycerin market, resulting in a lowering of its price [5,6], and making glycerol become a desirable, low-cost raw material for conversion into different chemicals with higher economic value. On the other hand, it must be mentioned that starting in 2007, the glycerin market has faced very volatile conditions, recent price increases, and a supply shortage

of refined glycerol [7] which, today, makes difficult any accurate economic evaluation of chemical processes designed for its transformation. However, since the over-supply of crude glycerol from biodiesel production (bio-crude) is one of the main reason for price volatility, the transformation of glycerol toward more added-value products is a key element for developing a new bio-based chemical industry.

Among the several options focused on glycerol conversion, a great deal of attention has been paid to the dehydration of glycerol into acrolein [1,4,7–31], and, more recently, also to the oxidehydration of glycerol into acrylic acid [32–42]. From both the economic and the engineering standpoint, an interesting option for performing the latter reaction is the one-pot (single-step) transformation, by means of a multifunctional catalyst able to carry out both the dehydration of glycerol into acrolein and the aldehyde oxidation into acrylic acid.

Previously we reported that W–V oxides with hexagonal tungsten bronze (HTB) structure and V⁴⁺ incorporated into a WO₃ lattice are effective catalysts for the direct synthesis of acrylic acid from glycerol [38]; under the best conditions these systems showed 25% acrylic acid yield plus 11% yield to residual acrolein. Later we studied the influence of Nb addition to V-doped HTB structures, with the aim of improving the acidic features of the catalysts so as to

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enhance the glycerol dehydration step. Three-component catalysts (W–V–Nb–O) further increased the catalytic performance, leading in the end to 33% acrylic acid yield plus 17% yield to residual acrolein [41]. Moreover, since the optimum working condition for W–V–Nb–O catalysts is situated at a much lower contact time (from 0.38 s to 0.15 s) than for the W–V–O system, the catalyst productivity was also consistently increased.

In order to fully investigate the catalyst activity of the best-performing tri-component sample (reported as WVNb-1 sample) [41], we report here a complete study of the catalyst behavior as a function of reaction conditions, which enabled us to reach unprecedented values of acrylic acid yield and productivity. Moreover, we also report on the methanol oxidative gas-phase transformation into formaldehyde and dimethyl ether (DME) on both W–V–O and W–V–Nb–O catalysts; indeed, methanol is known to be a suitable probe for exploring the acid and redox properties of metal oxides [45,46]. The results obtained make it possible to draw important general conclusions on the relation between the reaction conditions and catalyst features needed to convert oxygenated molecules by means of direct processes, using a single multifunctional catalyst.

Finally, so as to support the conclusions depicted on HTB doped structures, the same reactions were carried out on Mo–V–(W) oxides with Mo₅O₁₄-type bronze structure. In order to obtain a complete picture of the catalysts behavior, the acrolein oxidation reaction was also studied on both HTBs and Mo₅O₁₄-type bronzes.

2. Experimental

2.1. Synthesis of multicomponent catalysts

The W–V and W–V–Nb catalysts, with HTB structure, were prepared hydrothermally from gels obtained from the aqueous solution of corresponding salts: ammonium metatungstate hydrate (≥ 85 wt% WO₃ basis, Sigma–Aldrich), vanadium (IV) oxide sulfate hydrate ($\geq 99.99\%$, Sigma–Aldrich) and niobium oxalate (monooxalate adduct, ABCR), with a W/V and W/V/Nb molar ratio in gel of 1/0.2 and 1/0.2/0.15, respectively. The hydrothermal synthesis was carried out at 175 °C for 48 h. Then the solid was washed and dried at 100 °C overnight. Lastly, the solid was heat-treated in N₂ at 600 °C for 2 h. More details on the preparation have already been reported elsewhere [38,41].

The Mo–V–(W) catalyst, with a Mo₅O₁₄ type structure, was prepared from an aqueous solution of ammonium heptamolybdate (GR for analysis, MERCK), vanadium (IV) oxide sulfate hydrate and ammonium metatungstate (with a Mo/V/W molar ratio of 0.68/0.23/0.09), by evaporation in a rotavapor (at 50 °C). The solid was dried at 100 °C overnight and then calcined in air at 350 °C. Lastly, the solid was heat-treated in N₂ at 500 °C for 2 h.

2.2. Catalysts characterization

Surface areas were obtained from N₂ adsorption isotherms using the BET method; a Micromeritics ASAP 2000 instrument was used. Samples were degassed in situ under vacuum at 250 °C.

Powder X-ray diffraction patterns (XRD) were collected using a PANalytical X'Pert PRO diffractometer with CuK α radiation and an X'Celerator detector in Bragg–Brentano geometry.

Scanning electron microscopy (SEM) micrographs were collected in a JEOL 6300 microscope operating at 20 kV, 2×10^{-9} A beam current and 15 mm as working distance. The quantitative EDS analysis was performed using an Oxford LINK ISIS System with the SEMQUANT program, which introduces the ZAF correction. The counting time was 100 s for major and minor elements.

Infrared spectra were recorded at room temperature in the 300–4000 cm⁻¹ region with a Nicolet 205xB spectrophotometer

equipped with a data station at a spectral resolution of 1 cm⁻¹ and accumulations of 128 scans. Raman spectra were obtained with an “in via” Renishaw spectrometer, equipped with an Olympus microscope. The exciting wavelength was 514 nm from a Renishaw HPNIR laser with a power of approximately 15 mW on the sample. The dehydration of catalysts (under 20 mL min⁻¹ argon flow at 150 °C) was carried out by using a home-designed microreactor for in situ Raman spectroscopy measurement.

Temperature-programmed reduction (TPR) experiments were carried out on 10–20 mg of catalyst with a N₂:H₂ flow (10% H₂, total flow 50 mL min⁻¹). The temperature range explored was from room temperature to 650 °C. The heating rate was maintained at 10 °C min⁻¹.

Experiments of temperature-programmed desorption of ammonia (TPD) were carried out on a TPD/2900 apparatus from Micromeritics. A 0.30 g sample was pre-treated in a He stream at 450 °C for 1 h. Ammonia was chemisorbed by pulses at 100 °C until equilibrium was reached. Then, the sample was fluxed with a He stream for 15 min, prior to increasing the temperature up to 500 °C in a helium stream of 100 mL min⁻¹ and using a heating rate of 10 °C min⁻¹. The NH₃ desorption was monitored with a thermal conductivity detector (TCD) and a mass-spectrometer following the characteristic mass of ammonia at 15 a.m.u.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a SPECS spectrometer equipped with a Phoibos 150 MCD-9 detector using a monochromatic AlK α (1486.6 eV) X-ray source. Spectra were recorded using analyzer pass energy of 50 V, an X-ray power of 200 W, and an operating pressure of 10⁻⁹ mbar. Spectra treatment was performed using the CASA software. Binding energies (BE) were referenced to C1s at 284.5 eV.

2.3. Reactivity experiments

Reactivity experiments for glycerol, acrolein and methanol transformation were carried out using a continuous flow reactor made of glass, operating at atmospheric pressure. For each condition, all the reaction parameters are always listed in each figure. A catalyst amount ranging from 0.10 to 0.30 g was loaded in powder form. Residence time (calculated as the ratio between catalyst volume (mL) and total gas flow (mL s⁻¹), the latter being measured at room temperature) was varied; for better clarity, the time factor (calculated as the ratio between catalyst mass (g) and total gas flow (mL min⁻¹), the latter being measured at room temperature) was also reported. Inlet feed molar ratios between reactants were also changed according to the desired compositions. If not differently specified, the catalytic results were obtained after 90 min reaction time.

For both glycerol oxidehydration and acrolein oxidation, the effluent stream was bubbled through two in-series abatement devices, which were filled with water (but in some cases anhydrous acetone was used, for the identification of compounds which are less soluble in water) and held at a temperature of 0–2 °C; a third refrigerated condenser was left without any solvent. After this abatement, the gaseous stream, still containing oxygen and carbon oxides, was fed to an automatic sampling system for gas-chromatography (GC–TCD) analysis. The water solution containing the unconverted glycerol and reaction products was analyzed by GC, using a Hewlett-Packard 5890 instrument equipped with a FID detector. A semi-capillary wide-bore OV 351 (polyethyleneglycol treated with terephthalic acid) column was used for the separation of condensed compounds [41]. Two wide-bore columns were used for the separation of non-condensable products: a Molecular sieve 5A for oxygen and CO, and a Silica Plot for CO₂ (oven temperature 80 °C). Compounds were identified by means of both GC–MS and the injection of pure reference standards for the comparison of

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