



Study of the gas-phase glycerol oxidehydration on systems based on transition metals (Co, Fe, V) and aluminium phosphate



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ABSTRACT

The gas-phase glycerol (Gly) transformation in the presence of oxygen has been studied on cobalt oxide systems (10 and 20 wt% Co) supported on a synthetic mesoporous aluminium phosphate (AlPO₄) calcined at 350 °C, as well as on a binary Co-Al phosphate with a Co content of 10 wt%. Synthetic binary phosphate of Al-M (M = Fe, V) have also been tested. The acidity (number and nature of acid sites) of the solids was determined by pyridine adsorption, whereas the reducibility was determined by H₂ TPR. The propene oxidation was employed as a test reaction. The influence of the amount of oxidant agent and the reaction temperature on both the glycerol conversion and the yield to reaction products was studied. The formation of acrylic acid; acetic acid and carbon dioxide was favoured for values of O₂/Gly ≥ 2 molar ratio and of temperatures beyond 250 °C. The Co oxide species in the supported systems that were the easiest to reduce (lower H₂ desorption temperature) exhibited the highest activity to produce acrylic acid. The formation of acetic acid and carbon dioxide was also promoted, suggesting the participation of the acid sites in addition to redox sites. Among the metals investigated here, Co would form part of the required catalyst for the formation of acrylic acid from glycerol. Based on the identified products in this study, some possible reactions involved in the glycerol transformation into oxidized compounds, have been suggested.

1. Introduction

The production of biodiesel generates glycerol as the main sub-product, which implies a financial and environmental problem in the biodiesel industry. The transformation of glycerol through several reactions has been widely studied giving rise to different valuable compounds such as hydrogen, acrolein (ACR), dihydroxyacetone, propylene glycol, glyceric acid, polyglycerol, glycerol ethers, glycerol ester, di-oxolane and dioxane, etc [1,2]. Acrylic acid (AA) is one of these value-added chemical molecules, which has several uses such as adhesive, paint, plastics, superabsorbent polymer and rubber synthesis [3,4]. 85% of acrylic acid worldwide is produced from conventional acrolein usually on catalysts based on mixed oxides [5,6], traditionally starting from propene via two sequential oxidation steps [7]. Other alternatives to obtain acrylic acid are direct oxidation of propane [8,9] or sugar fermentation [10].

Obtaining acrylic acid from glycerol implies a two-step reaction, the first step being the dehydration of glycerol to acrolein, which has been widely studied on solid acid catalysts, as indicated in a recent review

[11]. Given that acrolein is highly reactive, its storage and transport continue to be a challenge. Therefore, its transformation into a stable product by in-situ subsequent oxidation would solve these problems. The second step, the oxidation of acrolein into acrylic acid has not been the subject of extensive research, in contrast with glycerol dehydration.

The oxidehydration of glycerol to acrylic acid has been tested in both liquid [12–14] and gas phase [3,15–24], although the study has been developed much more in the latter. It is possible to carry out the reaction in the gas phase by using a single bifunctional catalyst via the one-pot approach [15–20,22,24] or by using a process that involves two separate steps with a double-catalyst bed [3,21,23]. One-step synthesis of acrylic acid from glycerol is more economically viable than the two-step transformation. Moreover, a potential advantage of bifunctional catalysts contained in a single catalytic bed would be the better long-term performance, although obtaining a bifunctional catalyst would be a more laborious task.

In the two-bed reactor approach, a high yield to acrolein (Y_{ACR}) is necessary in the dehydration step in order to avoid the oxidation of glycerol and to obtain a high yield to acrylic acid (Y_{AA}).

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Witsuthammakul et al. [3], by using HZSM-5 as the first catalytic bed and V-Mo oxides as the second, reported a $Y_{AA} = 38\%$, while the mixture of both catalysts promoted the direct oxidation of glycerol to an undesirable oxygenated C_2 , therefore producing less amount of acrylic acid. The same conclusion was achieved by Liu et al. [21] who reported a $Y_{AA} = 75\%$ by using $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on Nb_2O_5 and vanadium-molybdenum oxides supported on the silicon carbide. This high Y_{AA} was obtained given that the optimum reaction temperature and the oxygen/glycerol ratio for these two catalysts were very similar.

For the one-step method, Deleplanque et al. [15] at $280^\circ C$ obtained a $Y_{AA} = 28\%$ on $MoVTeNbO$, but also a yield to acetic acid of 23% and to CO_x of 45% . Wang et al. [16] reported a $Y_{AA} = 14\%$ at $300^\circ C$ with iron oxide embedded in an iron orthovanadate, acrolein (28%) and acetic acid (24%) being the main products. They emphasize that the distance between the two phases of the solid was very important in its catalytic performance. Possato et al. [22] reported a $Y_{AA} = 16\%$ on $V_2O_5/MF1$, the importance of vanadium oxide species standing out in the conversion of acrolein to acrylic acid and in the oxidation of coke formed from glycerol. Nieto et al. [17,18,20] achieved a $Y_{AA} = 50.5\%$ at $265^\circ C$ on W-V-Nb mixed oxides with a hexagonal tungsten bronze structure, with productivity values of industrial relevance. They have also reported [24] that the formation of acrylic acid requires a close proximity of both acid and redox sites as well as acid sites with a sufficient strength to catalyse the dehydration reaction, allowing the desorption of acrylic acid.

We have previously studied the glycerol dehydration in the absence of oxygen over catalysts based on an amorphous mesoporous aluminium phosphate ($AlPO_4$) in liquid [25] and gas [26,27] phases, obtaining better results in the gas phase. The modification of aluminium phosphate with small amounts of a transition metal, especially V ($\sim 3\text{ wt}\%$) [26], as well as Fe and Co ($1\text{ wt}\%$) [27], gave rise to more active and selective catalysts to produce acrolein. Hence, the activity of the phosphates depends not only on their acidity (mainly acid sites of weak-medium strength), but also on the redox sites. Furthermore, the phosphates showed a high stability, not undergoing deactivation after 22 h of reaction [27]. Taking these previous results into account, in the present paper we studied the capacity of Al-M phosphates with a higher amount ($10\text{ wt}\%$ – $37\text{ wt}\%$) of Co, Fe and V to catalyse the transformation of glycerol to acrylic acid, via acrolein formation, in the presence of oxygen. In addition to those Al-M binary phosphates, we have also synthesized new systems of Co supported on $AlPO_4$. The structural characterization of the solids was carried out by X-ray diffraction (XRD) and ^{27}Al and ^{31}P Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy. Likewise, their textural properties were determined, as well as the surface acidity and the nature of the acid sites through pyridine (Py) chemisorption, by Temperature Programmed Desorption (TPD) and Diffuse Reflectance Infrared Fourier Transform (DRIFT), respectively. CO_2 chemisorption was employed to evaluate the basic properties of the solids, whereas H_2 Temperature Programmed Reduction (TPR) was used to evaluate the capacity of reducibility. Moreover, the propene oxidation was also employed in evaluating the redox sites.

2. Experimental

2.1. Catalyst preparation

The Co systems (10 and $20\text{ wt}\%$) were obtained by impregnation of a synthetic amorphous aluminium phosphate, $AlPO_4$, calcined at $350^\circ C$ (molar ratio $P/Al = 1$; $S_{BET} = 248\text{ m}^2/\text{g}$; $dp = 182\text{ \AA}$) with a solution of $Co(NO_3)_2 \cdot 6H_2O$ in methanol. After drying, the solids were calcined in air for 3 h at $450^\circ C$. These solids will be denoted as $xCo/AlPO_4-T$, where x represents the percentage in weight of Co and T , the calcination temperature.

The Al-Co phosphate ($P/(Al + Co) = 1$; $Al/Co = 3.5$; $10\text{ wt}\%$ of Co) was prepared by a sol-gel method as previously reported [27], from

aqueous solutions of $AlCl_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ and H_3PO_4 ($85\text{ wt}\%$). The precipitation agent, aqueous ammonia ($25\text{ wt}\%$), was slowly added stirring at $0^\circ C$. The pH value at the precipitation ‘end point’ was 6.7. After filtration, the solid was washed with 2-propanol and dried at $120^\circ C$ for 24 h.

For the synthesis of Al-Fe and Al-V phosphates, an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ and vanadyl oxalate, respectively, were employed as previously reported [28,29]. The amount of Fe in the Al-Fe phosphate was $20.5\text{ wt}\%$ (molar ratio $Al/Fe = 1$) [28], whereas the amount of V in the Al-V phosphates was $27\text{ wt}\%$ ($Al/V = 0.6$) and $37\text{ wt}\%$ ($Al/V = 0.2$) [29].

The binary phosphates will be denoted as $AlMPO(x)T$, where x indicates the Al/M theoretical molar ratio and T , the calcination temperature.

As a reference, simple phosphates of Al ($AlPO_4$); Co ($Co_3(PO_4)_2$) and Fe ($FePO_4$) were also synthesized by the aforementioned method with a molar ratio $P/M = 1$ [26,27].

All the solids were calcined at $450^\circ C$ in air for 3 h, and screened at $< 0.149\text{ mm}$ to avoid internal diffusion limitations in the reaction.

2.2. Characterization of catalysts

The textural properties were determined from the adsorption–desorption isotherms of nitrogen at its liquid temperature ($-196^\circ C$), using a Micromeritics ASAP 2000 apparatus. Prior to measurements, all samples were degassed to 0.1 Pa . BET surface areas were determined applying equation at relative pressures in the range $p/p_0 = 0.05$ – 0.30 , assuming a cross-sectional area of 0.162 nm^2 for the nitrogen molecule. The pore size distribution was calculated using the method of Barrett, Joyner and Halenda (BJH) assuming a cylindrical pore model.

X-ray diffraction (XRD) patterns were obtained using Ni-filtered K_α radiation ($\lambda = 1.5418\text{ \AA}$). Finely ground samples were scanned at a speed of $2^\circ/\text{min}$ ($2\theta = 2$ – 80°) using a Siemens D-500 diffractometer (40 kV , 30 mA).

^{31}P and ^{27}Al nuclear magnetic resonance spectra were collected on a BRUKER AVANCE 400WB spectrometer using a 4 mm BRUKER double resonance MAS probe. All experiments were performed at room temperature. ^{27}Al and ^{31}P MAS NMR were recorded at resonance frequencies, ν_0 , of 104.26 MHz and 161.98 MHz , respectively. $Al(H_2O)_6^{3+}$ and H_3PO_4 solutions were used as external standard references for Al and P chemical shifts, respectively. The data were processed by Fourier transformation, phase correction and baseline correction using the Dm2005test NMR data processing software.

Total acidity was measured by Temperature Programmed Desorption of pyridine (Py-TPD), using an apparatus from PID Eng& Tech with a TCD (thermal conductivity detector). Before the adsorption experiments started, the catalyst (30 mg) was pre-treated in situ from room temperature to $400^\circ C$ (rate of $20^\circ C/\text{min}$). After the catalyst pre-treatment, saturation of the sample with pyridine was carried out at $50^\circ C$ for 30 min, thereafter, physisorbed pyridine was desorbed at $50^\circ C$ for 60 min. Then the measurements were performed in the range of 50 – $450^\circ C$, with a heating rate of $10^\circ C/\text{min}$ to remove the chemisorbed pyridine.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra of adsorbed Pyridine were recorded on a FTIR instrument (Bomem MB-3000) equipped with an ‘environmental chamber’ (Spectra Tech) placed in a diffuse reflectance attachment (Spectra Tech, Collector). A resolution of 8 cm^{-1} was used with 256 scans to obtain a spectrum from 4000 to 600 cm^{-1} . The reference spectrum of the sample was recorded at $350^\circ C$. Pyridine (99.8% from Aldrich) adsorption was carried out at $120^\circ C$ for a certain period of time (typically 1 h), allowing the saturation of the catalyst surface. The samples were subsequently degassed in 4 stages of 1 h each at $50^\circ C$, $150^\circ C$, $200^\circ C$ and $300^\circ C$, respectively.

H_2 TPR experiments were performed on a Micromeritics Autochem

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