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Gas phase glycerol oxidative dehydration over bifunctional V/H-zeolite catalysts with different zeolite topologies

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ABSTRACT

The oxidative dehydration of glycerol to acrylic acid can be performed in one single step using bifunctional catalysts containing both acid and redox sites. In this sense, zeolites containing transition metals are promising catalysts. Zeolites of different topologies: FAU, FER, MEL, MFI, MOR, MWW and OFF were synthesized and further impregnated with 5% vanadium. The catalysts were characterized and evaluated in the gas phase glycerol oxidative dehydration. All catalysts showed high conversions of glycerol (100-78%). The acrolein selectivity decreases with the total density of acid sites in these zeolites. The selectivity to acrylic acid is related to the ability of each topology of stabilizing the redox pair V^{5+}/V^{4+}. The best performances were observed for zeolite catalysts with MWW, BEA and MFI topologies.

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1. Introduction

The conversion of glycerol into valuable products has been investigated as a strategy to attain a sustainable biodiesel production chain [1–3]. Gas-phase glycerol dehydration to acrolein is one of the most promising route, because acrolein is an important intermediary in the production of acrylic acid, superabsorbent polymers, pharmaceuticals and plasticizers. Many acid catalysts were investigated in the literature, such as heteropolyacids, mixed oxides, phosphates and zeolites, with satisfactory glycerol conversion and acrolein selectivity [4,5]. However, rapid deactivation by coke formation is still the main limitation in their use for industrial purposes and a lot of effort has been payed to solve this problem. Among the investigated strategies, one could mention the use of moving bed reactors [6], alternating cycles of reaction and coke burning [7] or oxygen co-feeding [8]. This last option seems to be the most adequate for practical purposes, since oxidative conditions favors desorption of the oxygenate oligomer compounds that would act as coke precursors, maintaining the surface acid sites

available for further catalytic cycles of reaction and improving catalyst lifetime [9].

The acrolein, produced in a first bed containing an acid catalyst (usually a zeolite or a heteropolycompound), can be further oxidized in a consecutive bed containing a redox catalyst, such as V-W-Nb mixed oxides [10,11], resulting in high yields of acrylic acid. On the other hand, the use of catalysts containing both acid sites and redox species has been envisaged as a way to produce acrylic acid in a one-step oxy-dehydration process [1]. In most cases, it is observed an acrolein yield higher than to acrylic acid [1,12,13]. Recently, catalysts based on phosphoric acid modified W-V-Nb catalysts have shown acrylic acid yields around 60% in a short time run [14]. There is no mention to long time stability.

Redox molecular sieves, such as zeolites containing transition metal oxides, are promising alternative catalysts for this purpose, but there are few studies in the literature. Pestana et al. [1] have evaluated the zeolite-β (BEA) containing 5 wt.% or 10% of vanadium, prepared by impregnation or physical mixture, in the glycerol oxidative dehydration at 275 °C, observing a selectivity to acrylic acid of 25% and 12%, respectively, at a glycerol conversion of ca. 75%. Acrolein and acetol were the main products formed. Other oxygenates, such as acetaldehyde and acetic acid were observed as minor byproducts, but a significant amount of unidentified products with high boiling points were also formed during the reaction.

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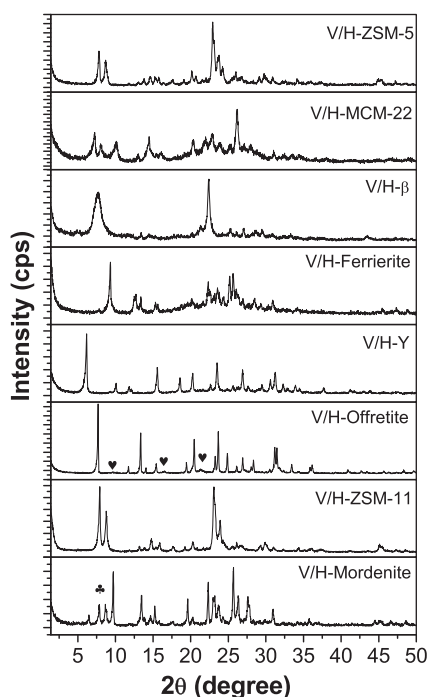(A.J.S. Mascarenhas).

Fig. 1. X-ray diffraction patterns of V/H-zeolites with different topologies. (Symbols indicate the following phases: ♥, erionite zeolite and ♣, layered silicate RUB-18).

Based on XPS measurements, the authors correlated the catalytic performances to the vanadium dispersion in the zeolite pores.

In a recent publication, Possato et al. [12] have studied the use of V_2O_5/H-ZSM-5 (MFI topology) prepared by using vanadyl sulphate ($VOSO_4$) or ammonium metavanadate (NH_4VO_3) as vanadium precursors. At 350 °C, glycerol conversions up to 97% and selectivity to acrylic acid of 17% were attained for the catalyst prepared by wet impregnation with $VOSO_4$ [12]. According to the authors, the presence of vanadium improved the catalyst lifetime, because catalyzes both the oxidation of acrolein to acrylic acid and the oxidation of coke precursors. The formation of acrylic acid depends on the dispersion of vanadium oxide, which facilitates the redox cycle V^{4+}/V^{5+}, as suggested by XPS and DTA analyses.

In this work, a series of catalysts were prepared by wet impregnation with 5 wt.% of vanadium using NH_4VO_3 and evaluated in the gas phase oxidative dehydration of glycerol, in order to evaluate the effect of zeolite topology on the nature, dispersion and reducibility of vanadium species in the selectivity to acrylic acid.

2. Experimental

2.1. Preparation of the catalysts

Zeolite ZSM-5 (MFI), Beta (BEA), ferrierite (FER), zeolite Y (FAU), offretite (OFF) and mordenite (MOR) were synthesized according to the IZA methods [15]. The zeolite ZSM-11 (MEL) was synthesized by the method proposed by Gonzales et al. [16]. Zeolite MCM-22 (MWW) was synthesized with molar ratio $SiO_2/Al_2O_3 = 30$ by the method proposed by Carriço et al. [7]. The calcined materials were ion exchanged with a solution with $0.1\,mol\,L^{-1}$ NH_4NO_3 and further calcined to obtain the acid form of the respective zeolites. The thus prepared H-zeolites were wet impregnated by adding the adequate volume a solution of $0.2\,mol\,L^{-1}$ ammonium metavanadate (NH_4VO_3) in order to obtain 5% of vanadium. The solvent was removed in a rotary evaporator at 65 °C, 30 rpm, under reduced pressure. The samples V/H-zeolite were calcined at 500 °C, for 3 h, under air flowing ($50\,mL\,min^{-1}$).

2.2. Characterization of the catalysts

The X-ray diffraction patterns (XRD) were collected on a Shimadzu XRD-6000, operating with CuKα radiation at a voltage of 40 kV, current of 30 mA, and graphite monochromator, in the region of 1.4°–80° 2θ at scan rate of 2° min^{-1}.

Elemental analyses were performed by energy dispersion X-ray spectrometry in an equipment Shimadzu EDX 720, operating with rhodium radiation source at 15 kV (Na-Sc) or 50 kV (U-Ti) and a 10 mm collimating slit.

Textural analyses were carried out by nitrogen physisorption on a Micromeritics ASAP 2020, at −196 °C. The samples were pretreated at 350 °C for 3 h under vacuum (2 μm Hg) before collecting the isotherms. BET, t-plot and BJH models were used to obtain textural properties.

Temperature programmed desorption of ammonia profiles (NH_3-TPD) were collected in a Micromeritics 2720 Chemsorb. Initially the samples were pretreated in a helium flow at 300 °C for 1 h. NH_3 adsorption (9.9% mol/mol NH_3/He) was carried out at ambient temperature with a flow rate of $25\,mL\,min^{-1}$ for 1 h. After removal of physisorbed ammonia at 150 °C for 1 h, the samples were heated from room temperature up to 800 °C, at 10° min^{-1}, under helium flow ($25\,mL\,min^{-1}$). The desorbed ammonia was monitored using a thermal conductivity detector (TCD). All NH_3-TPD profiles were deconvoluted and the amounts of weak, moderate and strong acid sites were calculated.

The temperature programmed reduction profiles using H_2 (H_2-TPR) were conducted in a Micromeritics 2720 Chemsorb. The samples (50 mg) were pretreated in an air flow at 300 °C for 1 h. After cooling down to room temperature, a flow of $30\,mL\,min^{-1}$ of 10 mol% H_2/N_2 is admitted to the reactor, and the sample is heated from room temperature to 1000 °C at a heating rate $β = 10\,°C\,min^{-1}$. H_2 consumption was monitored using a thermal conductivity detector.

Diffuse reflectance spectra (DRS) in the UV–vis region were collected in a Thermo-scientific Evolution 600 spectrometer operating with a Harrick Praying Mantis^{TM} accessory in the range of 200–800 cm^{-1}.

Thermogravimetry (TG/DTG) of spent catalysts were conducted in a Shimadzu TGA-50 in a temperature range of 10–1000 °C at a heating rate of 10 °C min^{-1} under air flow (50 mL min^{-1}). The coke content was calculated from mass loss in the range of 300–1000 °C.

EPR spectra of V/H-Zeolites samples were collected in tubular quartz cuvettes (width of 0.3 mm) at 90 K (liquid nitrogen) with an EMX plus Bruker spectrometer using 100 kHz field modulation and 20 G standard modulation-width. Before the analysis, the solids samples were dried overnight at 100 °C.

2.3. Catalytic tests

The catalytic activity was evaluated in a borosilicate glass vertical fixed-bed reactor, containing 0.1 g of catalyst dispersed in glass beads, operating at atmospheric pressure and 320 °C for 10 h. A solution of 36 wt.% glycerol in water was fed using a peristaltic pump operating at 2 mL/h and an air flow of $30\,mL\,min^{-1}$ (W/F = 39.7 mmol g s^{-1}). The reaction products were condensed and absorbed in 10 mL of 0.1 wt% hydroquinone solution, used as polymerization inhibitor, and then analyzed by gas chromatography on a GC-FID Perkin Elmer Clarus 500 operating with a flame ionization detector using a CPWax column (15 m × 0.53 mm × 1.2 μm). Aliquots of 1 μL of the solution were injected. Both the injection port and detector were kept at 250 °C, while the following temperature program was used in the oven: i) the initial temperature was 50 °C for 1 min; ii) then the column was heated up to 80 °C, using a heating rate of 10 °C min^{-1}, and kept at this temperature for 3 min; and iii) finally heated up to 220 °C