One-step glycerol oxidehydration to acrylic acid on multifunctional zeolite catalysts

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ARTICLE INFO

ABSTRACT

The catalytic behavior of bifunctional V_2O_5/MFI catalysts with acid and oxidizing properties was investigated for the gas-phase oxidehydration of glycerol. One of the main reaction products was acrylic acid, produced by dehydration of glycerol to acrolein at an acidic site and subsequent oxidation at a redox site. Comparison of wet impregnation with vanadyl sulfate ($VOSO_4$) and ammonium metavanadate (NH_4VO_3) showed that $VOSO_4$ impregnation provided the best performance for the conversion of glycerol and selectivity towards acrylic acid. The chemical and structural properties of the catalysts were studied by X-ray diffraction, nitrogen adsorption–desorption isotherms, Raman spectroscopy, temperature programmed ammonia desorption, and X-ray absorption spectroscopy in the XANES region for the K-edge absorption of vanadium. XPS measurements of the fresh and spent catalysts enabled elucidation of the dynamic redox cycles of vanadium oxide during oxidation of acrolein. The presence of vanadium in the zeolite improved the catalyst lifetime, because of the multifunctional ability of the vanadium oxide species to convert acrolein to acrylic acid and act as co-catalyst for the oxidation of coked glycerol products. Qualitative and quantitative analyses of the coke deposited in the spent catalysts were performed using ^{13}C NMR and thermogravimetry, respectively.

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1. Introduction

In recent years, increased production of biodiesel from transesterification of renewable feedstocks such as vegetable oils has led to the co-generation of vast quantities of glycerol. The challenge is to transform glycerol into more valuable products in order to improve the economics of biodiesel production and, at the same time, provide industry with various important chemicals [1]. To this end, glycerol oxidehydration is potentially one of the reactions that can be used, and acrylic acid is one of the main target products.

Acrylic acid and its ester derivatives are the principal raw materials used in the manufacture of polymeric products that have many different applications. These polymers offer unique combinations of features such as colorless transparency, easy adhesion, elasticity, and stability towards light. Currently, more than 3 million tons per year of acrylic acid are produced by the petrochemical industry, using the two-step gas-phase oxidation of propylene [2]. It is therefore highly desirable to be able to synthesize acrylic acid by means of an integrated renewable route that minimizes the use of petrochemical resources as raw materials.

Glycerol oxidehydration can be conceived as proceeding in two steps (Scheme 1). In the first step, glycerol is dehydrated to 3-hydroxypropanal, a very reactive intermediate that readily dehydrates to acrolein [1]. The second step is the selective oxidation of acrolein in the presence of molecular oxygen to yield acrylic acid [3–7].

For the first step of Scheme 1, various acid catalysts have been studied for the dehydration of glycerol, including $MeO-Al_2O_3-PO_4$ (Me stands for transition metal) [8], WO_3/TiO_2 [9], and zeolites with different Si/Al molar ratios, such as MFI, BEA, FAU, and MOR structures [10]. Although acid zeolites have been identified as active catalysts for the production of acrolein, fast catalyst deactivation by deposition of non-reactive polyaromatic compounds that obstruct the micropores is a major problem that needs to be overcome. Quantities of carbonaceous species up to 30 wt.% can be deposited during glycerol dehydration catalyzed by an acid zeolite with MFI structure [11].

For the second step of Scheme 1, a redox catalyst is needed. Vanadium oxides have a very important redox characteristic in catalysis due to the capacity to adopt multiple oxidation states. This is the basis of the manufacture of several chemicals, such as the
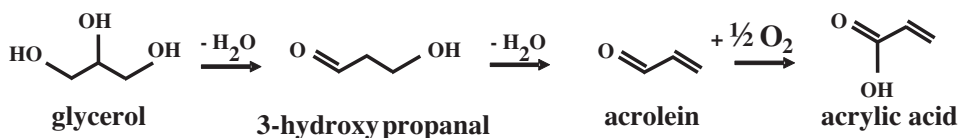
Scheme 1. Pathway of the glycerol oxidehydration reaction.

synthesis of sulfuric acid by catalytic oxidation of SO_2. The advantage of using vanadium-based oxides for acrolein oxidation in the presence of molecular oxygen is that an oxidative atmosphere, in combination with the redox properties of the vanadium oxides, is selective towards acrylic acid and effective for inhibiting the deposition of carbonaceous and non-volatile compounds [12–22].

However, in order to be efficiently used in the one-step glycerol oxidehydration, vanadium oxides need to have their properties altered by the incorporation of other additives. For example, the preparation of vanadium/tungsten mixed oxides enhances the acid properties of the catalyst and therefore diminishes the rate-limiting glycerol dehydration. As a second example, vanadium/molybdenum mixed oxides can enhance the catalytic activity because the combination of both elements facilitates the dynamic changes of V^{5+}/V^{4+} oxidation states during catalytic reaction by the Mars–Van-Krevelen mechanism. These examples illustrate some of the reasons for research concerning the synthesis of complex oxides based on vanadium, which could act as efficient multifunctional catalysts for glycerol oxidehydration. Vanadium pyrophosphate oxides were investigated in a series of studies conducted by Ueda [23–26] and López Nieto [27,28], and V/W mixed oxides with hexagonal tungsten bronze structure, as well as V/W/Nb mixed oxides, have been used in one-step glycerol oxidehydration [29].

The combination of these two reaction steps in a single bifunctional (redox and acid) catalytic bed could offer several advantages for glycerol conversion to acrylic acid. For instance, an optimal thermal balance could be provided by coupling of the exothermic oxidation reaction with the endothermic dehydration reaction [7]. Furthermore, the combination of both acid and oxidizing sites should make it possible to achieve continuous oxidation of undesired dehydration byproducts.

In a publication of 2013, the production of acrylic acid from glycerol oxidehydration using vanadium impregnated on an acid zeolite with BEA structure was mentioned for the first time [30]. Despite the importance of the findings, only very few aspects of the catalyst performance were explored. Aiming to contribute to the identification and understanding of efficient catalysts for glycerol conversion, the present work evaluates an acidic zeolite with MFI structure, impregnated using vanadium oxide.

The characteristics of this zeolitic catalyst are explored using a combination of physico-chemical techniques: XRD, nitrogen adsorption–desorption isotherms, Raman spectroscopy, NH_3-TPD, XANES in the region of vanadium K-edge absorption, XPS, ^{13}C NMR, and thermogravimetry. It is shown that the presence of vanadium oxides near the zeolite acid sites inhibits the formation of carbonaceous species by the oxidation of reactive carbon monomers before they oligomerize and block the active sites. The multifunctional feature of this catalyst enabled long-term control of the balance between the production of acrylic acid and the avoidance of carbon deposition, features that should contribute to integrated glycerol chemistry.

2. Experimental

2.1. Preparation of catalysts

The MFI zeolite (Si/Al molar ratio = 40) in the ammonium form, kindly provided by Zeolyst, was initially used as received.

The vanadium precursors, $VOSO_4$ (V^{4+}) and NH_4VO_3 (V^{5+}), and vanadium oxides (V_2O_3, V_2O_4, and V_2O_5) were purchased from Sigma–Aldrich. The vanadium oxide-impregnated MFI zeolites were obtained by wet impregnation of the zeolite using aqueous solutions of either $VOSO_4$ or NH_4VO_3 (0.05 mol/L). The mixtures were stirred for 1 h at room temperature, followed by water removal in a rotary evaporator and calcination of the catalyst precursor at 500 °C for 2 h under an air flow, resulting in V_2O_5 supported on a protonic MFI zeolite. The volume of the solution of the vanadium precursor was calculated in order to give a constant V/Al molar ratio of 5.5. The zeolites impregnated with $VOSO_4$ and NH_4VO_3 were denoted V_AMFI and V_BMFI, respectively.

Pure vanadium oxide samples, denoted V_2O_5-A and V_2O_5-B, were prepared by thermal decomposition (at 500 °C) of the $VOSO_4$ and NH_4VO_3 precursors, respectively.

2.2. Characterization of the catalysts

The crystalline phases present in the calcined catalysts were analyzed by X-ray diffraction using a Siemens D5000 diffractometer, with Cu Kα radiation selected by a curved graphite monochromator. Data were collected in the 2θ range from 5 to 40°, using a step size of 0.01° and a counting time of 4 s.

Nitrogen adsorption–desorption isotherms were recorded at liquid nitrogen temperature, within a relative pressure interval of 0.001–0.998, using a Micromeritics instrument (Model ASAP 2010). Prior to the measurements, the samples were evacuated at 200 °C for 12 h under 1×10^{-5} Pa of vacuum.

Raman scattering spectra were recorded using a Horiba Jobin–Yvon LabRAM 800HR micro-Raman spectrometer equipped with a He/Ne laser excitation source (632 nm). Good spectral resolution was achieved using 50 mW of transmitted laser power, integration time of 20 s, and accumulation of 7 spectra.

In situ XANES spectra at the V K-edge were measured in the region above 5420 eV. The analyses were conducted at the XAFS1 beamline of the Brazilian Synchrotron Light laboratory (LNLS), in Campinas, Brazil. The XAFS1 beamline is equipped with a Si (1 1 1) monochromator operating in Bragg mode for selection of the desired range of X-ray wavelengths. The monochromator was calibrated by setting the first inflection point at the K-edge spectrum of a metallic vanadium foil standard at 5465 eV. The samples were prepared in the form of self-supporting pellets composed of 20 mg of non-calcined catalyst and 80 mg of boron nitride (BN), and placed into a tubular quartz furnace, sealed with refrigerated kapton windows, for the transmission measurements. The calculated mass proportion of catalyst and BN ensured an edge jump of 1. The experiments consisted of *in situ* decomposition of the vanadium precursors during temperature-programmed oxidation under oxygen/nitrogen (20:80) flow during heating from room temperature to 500 °C at a rate of 10 °C/min.

Analysis of the XANES data was performed with Athena graphical interface software. In the case of dynamic studies, three spectra were merged in order to improve the signal-to-noise ratio. The spectra were then normalized using the flattening algorithm in the default energy range used by Athena. Speciation of the vanadium species present during the *in situ* treatments was achieved by linear combination (LC) of the XANES spectra (from −20 to 120 eV