



One-step oxidehydration of glycerol to acrylic acid using ETS-10-like vanadosilicates



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ABSTRACT

Vanadosilicates isostructural to ETS-10 and AM-6 microporous materials were synthesized hydrothermally using derivatives of cis- and trans-3,5-dimethyl-piperidine as organic structure directing agents (SDAs) and were subsequently tested as heterogeneous catalysts for the oxidehydration of glycerol to acrylic acid. The best performances were obtained with vanadosilicates prepared with 1,1,3,5-tetramethyl piperidinium cations, which were capable of converting 93.6% of glycerol to acrylic acid in one step, with 85.4% selectivity. Other important chemicals such as acrolein (3.8%), propanal (2.3%), acetaldehyde (3.2%), acetic acid (2.5%), and propionic acid (1.4%) were produced in smaller amounts. The results clearly indicated that these vanadosilicates are potential multifunctional catalysts capable of performing the oxidehydration of glycerol to acrylic acid in a single step. Spectroscopic data obtained from ⁵¹VMAS-NMR, UV-Vis, XPS, and Raman scattering analyses suggested that the selectivity of these vanadosilicates for the oxidative dehydration of glycerol to acrylic acid could be attributed to the capacity of the vanadium species for dynamic adoption of multiple oxidation states during the catalytic reaction.

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1. Introduction

High purity glycerol is an important industrial feedstock that has applications in the food, cosmetics, and pharmaceutical industries, amongst others. However, it is expensive to refine crude glycerol, especially in medium-sized or small plants. Research in both academic and industrial laboratories has therefore focused on the development of innovative processes for the conversion of pure and crude glycerol into valuable products. Glycerol is considered one of the top twelve building block chemicals that can be derived from carbohydrates and converted to valuable commodity chemicals such as glyceric acid, propylene glycol, 1,3- and 1,2-propanediol, branched polyesters, and polyols [1]. These chemicals can be formed using different routes including selective oxidation, hydrogenolysis, dehydration, transesterification,

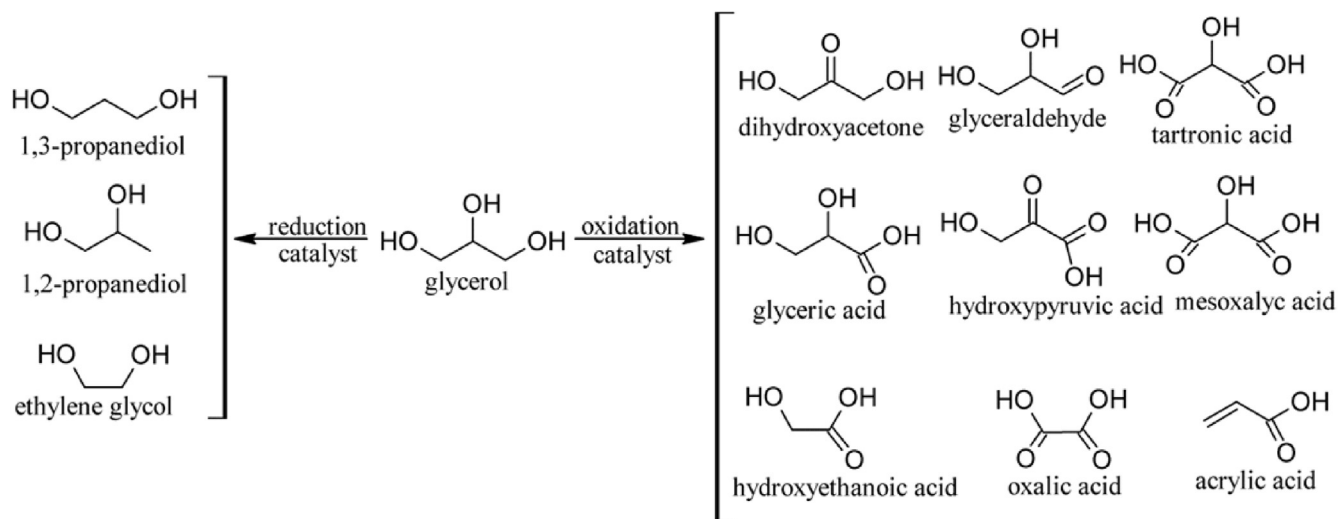
etherification, oligomerization, and polymerization, as reviewed elsewhere [2,3]. Glycerol oxidation or reduction is achieved by means of a complex pathway of reactions that can lead to a large number of useful intermediate substances or value-added chemicals (Scheme 1).

Acrylic acid is one of the many value-added molecules prepared by the catalytic conversion of glycerol. This molecule is attractive from economic and environmental perspectives, and is used in a number of industrial applications. The primary use of acrylic acid, accounting for approximately 67% of the total production, is as a raw material for the manufacture of acrylic esters and resins used in coatings and adhesives. 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 [4]. Hence, it is 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.

Heterogeneous catalysts based on vanadium oxides are well known as active and selective oxidation catalysts, due to their

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Scheme 1. Value-added products obtained from the oxidation and reduction of glycerol.

capacity to adopt multiple oxidation states and the ability to achieve dynamic changes in vanadium oxidation states during catalytic reaction according to the Mars-van Krevelen mechanism [5]. There have been several investigations of efficient multifunctional catalysts capable of performing the oxidative hydration of glycerol in a single step [6–9]. López Nieto et al. [10,11] described the use of vanadium pyrophosphate for this reaction, while Ueda et al. [8] studied different transition metal oxides [oxides, V/W mixed oxides with hexagonal tungsten bronze structure, and V/W/Nb mixed oxides]. Until now, the best result was the conversion of 100% of glycerol into 50% of acrylic acid using V–W–Nb mixed oxides [10].

Several factors can play a role in the selective oxidation achieved by heterogeneous catalysts based on vanadium oxides. These include: (a) vanadium lattice oxygen, (b) vanadium–oxygen bond strength, (c) host structure and the ordering and environment of oxygen atoms, (d) dynamic redox cycles between multiple oxidation states of the metal, (e) multi-functionality of the active sites, (6) spatial isolation of active sites, and (f) phase cooperation. The V–Mo–Te–Nb oxides are good examples of catalysts that present all these properties [8].

The use of zeolite-based catalysts containing vanadium with the specific aim of producing value-added products using glycerol as raw material has not been widely reported in the literature. The first study was published in 2013, describing the production of acrylic acid by glycerol oxidative hydration using vanadium impregnated on an acid zeolite with BEA topology [12], although only a few aspects of catalyst performance were explored. In 2015, Martins et al. [13] reported the catalytic behavior of bifunctional V_2O_5 /MFI catalysts with acidic and oxidizing properties for the gas-phase oxidative hydration of glycerol. One of the main reaction products was acrylic acid, formed by dehydration of glycerol to acrolein at an acidic site and subsequent oxidation at a redox site, but the selectivity of the reaction was very low (17%). Hunsom et al. [14] reported the one-pot oxidative hydration of glycerol to value-added compounds using metal-doped SiW/HZSM5-5, with 99.7% conversion and 36.23% selectivity to acrylic acid. Mairelles-Torres et al. [15] described the dehydration of glycerol to acrolein using solid vanadium–phosphorus catalysts supported on a mesoporous zirconium SBA-15 silica. However, no direct conversion of glycerol to acrylic acid was observed and the selectivity to acrolein was around 40%. Therefore, apart from zeolites of the BEA and MFI families, no other zeolites impregnated with vanadium oxides have

been reported as being capable of performing one-pot catalytic conversion of glycerol to acrylic acid.

AM-6 is a large-pore vanadosilicate containing hexacoordinated vanadium, whose structure is similar to that of the ETS-10 titanosilicate. It was first reported by Rocha et al. [16], who synthesized it in the presence of ETS-10 seeds [16]. The synthesis of AM-6 in the absence of seeds, but using structure directing agents (SDAs) such as TMAOH and chiral organic molecules derived from decahydroquinoline, 2,6-dimethyl-piperidine, 3,5-dimethylpiperidine, and (S)-sparteine has been reported by Sacco et al. [17] and Paula et al. [18].

AM-6 vanadosilicate catalysts have been employed as heterogeneous catalysts for the highly selective dehydration of *t*-butanol to isobutene [19], as a solid support for enzyme immobilization in transesterification reactions [20], and for the photocatalytic oxidation of ethylene [21]. However, they have not yet been used specifically for the catalytic oxidative hydration of glycerol to value-added products (Scheme 1). In a previous study, investigation was made of microporous vanadosilicate ETS-10-like materials produced using different organic templates derived from piperidinium cations [18]. Systematic catalytic studies were performed with the aim of identifying their possible applications as heterogeneous catalysts for the production of biofuels and value-added products derived from glycerol. Here, we present the best catalytic results obtained with vanadosilicate catalysts prepared using 1,1,3,5-tetramethyl-piperidinium cation derivatives.

2. Experimental section

2.1. Synthesis of organic templates derived from 3,5-cis-trans-dimethylpiperidine

Scheme 2 shows a schematic illustration of the SDAs synthesized using the following procedure. One mol of 3,5-dimethylpiperidine (Aldrich, mixture of isomers) and 1.5 mol of base (potassium bicarbonate) were added to 170 mL of methanol. Dropwise addition was made of 1 mol of the alkyl dihalide or 2 mol of the halide to the solution over a 10–15 min period, followed by refluxing for 48 h. The reaction mixture was cooled to room temperature and the methanol was evaporated. The white solid remaining was extracted with 250 mL of chloroform and the precipitated solid was filtered. The chloroform fraction was

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