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One-pot oxydehydration of glycerol to value-added compounds over metal-doped SiW/HZSM-5 catalysts: Effect of metal type and loading

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HIGHLIGHTS

- Glycerol conversion to acrylic acid is done over metal-doped supported SiW catalysts.
- V-SiW/HZSM-5 exhibits the highest glycerol conversion and acrylic acid yield.
- Rate of glycerol conversion is explained by a pseudo-first order reaction.
- The Eley–Rideal model provides the best fit with the experimental results.

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ABSTRACT

A one-pot oxydehydration of glycerol to value-added compounds was carried out over metal-doped SiW/HZSM-5 catalyst at low temperature (90 °C) and ambient pressure. Effects of metal types (Co, Ce, Ni and V) and loadings (0–8 wt.%) on catalyst properties and catalytic activity were explored. Doping different types of metal and loading on the surface of SiW/HZSM-5 catalyst affected surface chemistry and textural chemistry as well as the catalytic activity for glycerol conversion and product yield distribution. The V at 6% loading most effectively enhanced the activity of SiW/HZSM-5 for a one-pot oxydehydration of glycerol to value-added compounds. The presence of V6-SiW/HZSM-5 catalyst can enhance the glycerol conversion up to 99.67% with the yields of glycolic acid, formic acid, acetic acid, acrolein, acrylic acid, and propionic acid of 19.45%, 12.03%, 23.62%, 0.25%, 36.23% and 7.06%, respectively with less than 1.5% of glycerol converting to some undesired products. The kinetic studies of a one-pot oxydehydration of glycerol over this catalyst (V6-SiW/HZSM-5) showed the rate of glycerol conversion depended upon the glycerol concentration according to the pseudo-first order kinetic rate and about the zero order with respect to the H_2O_2 concentration. The Eley–Rideal model, assuming the reaction between a non-dissociative adsorption of H_2O_2 and glycerol molecule provided the best fit with the experimental results.

1. Introduction

Acrylic acid is recognized as a platform molecule being used as building block to produce plastics and polymers, which are used in surface coatings, sealants, paint, finishing, adhesives, polymer additives, textiles, inks, leather, as well as in paper treatment and electronic manufacturing processes [1,2]. Besides, it can be used as a chemical intermediate [3]. In 2009, the global acrylic acid consumption was 4 million tons and is expected to be rising to about 5 million tons per year by 2014 [1]. Classically, acrylic acid is produced via two sequential oxidation steps starting from propylene over Pd giant clusters [4]; vanadyl pyrophosphate (VPO) catalyst [5]; MoV(Nb)TeO-based catalysts [6] or from propene over Mo-based oxide [7–9].

Alternatively, acrylic acid can be produced directly from glycerol, the main by-product of biodiesel production, via the oxydehydration. By this reaction, the glycerol is first dehydrated to acrolein and subsequent acrolein oxidation to acrylic acid. Then, the oxydehydration is carried out either in the integrated dehydration–oxidation bed system with different functionalized-catalysts in separated bed [10,11] or in a single reactor in the presence of a bi-functional catalyst [12–17]. The former approach allows the possibility to match up the reaction conditions of both dehydration and oxidation to get the complete glycerol conversion and high product selectivity. In addition, it feeds glycerol with high water

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content. Then, the product effluent would be acrylic acid solution that can be used directly. However, this approach requires a more proper design such as fluidized or moving bed reactor [10]. Thus, the latter approach is more economically interesting because of the reduction of engineering investment. In addition, the heat balance may be reached with the endothermic character of dehydration and exothermic character of oxidation [18].

In a single reactor, several bi-functional catalysts having both acidic and oxidative functions were used to enhance the glycerol conversion and selectivity of acrylic. By using mixed oxide catalysts, the $FePO_4$ catalyst was active and selective to obtain acrolein but not to acrylic acid [18]. Adding oxygen in the feed stream can modify the mechanism of glycerol dehydration and further oxidation. Using the MoVTeNbO catalysts led to achieve a high yield of acrylic acid (28.4%), but also a high yield of acetic acid (23%). By using W–V–O bronze, approximately 25% acrylic acid yield was obtained by using a feed containing 2 mol% glycerol, 4% oxygen and 40% steam at the V/W ratios in the bronze between 0.1 and 0.2 [14]. High V content in oxygen-rich feed led to the formation of a high oxidative activity compound, V_2O_5, which can further oxidize acrylic acid to CO and CO_2 [14,17]. The addition of Nb in the tri-component bronze structure enhanced a higher yield of acrylic acid up to 34% at 290 °C because the incorporation of Nb resulted in a lower surface density of acid sites but higher fraction of stronger acid sites compared to both WO_3 and the bi-component W–V–O system [15]. The oxygen played an important role in accelerating the oxidation of the acrolein into acrylic acid, by allowing a greater concentration of the oxidizing V^{5+} sites [19]. After a precise control of oxygen pressure, a yield to acrylic acid as high as 50.5% were achieved with an increase of more than one order of magnitude in productivity over W–V–Nb catalyst. The addition of phosphoric acid (H_3PO_4) to W–V–Nb–O catalyst for direct conversion of glycerol to acrylic gave acrylic acid yield of 59.2% [20]. This is because H_3PO_4 can increase the acid amount and the Brönsted acidity of W–V–Nb–O catalyst. By using vanadium-impregnated zeolite beta, an acrylic acid is formed up to 20% selectivity at 548 K [21]. The heavier products were especially formed over the zeolite with higher vanadium content. By using the W/V catalysts, the $W_1V_{0.25}$ catalyst provided an almost complete conversion of glycerol to glyceric acid in gas phase system at 300 °C with acrylic acid yield of 25.7% [17]. More cations (ex. Mo^{5+}, W^{5+}, V^{4+}) presented in the bimetal oxide catalysts gave high catalytic oxidation activity [17].

Our previous work found that the glycerol oxydehydration required weak-strength acid catalyst with high oxidative ability [22]. Approximately 84% of glycerol converted to various valued-added compounds such as acrylic acid, glycolic acid, formic acid, acetic acid and acrolein in aqueous solution at 90 °C in the presence of H_2O_2 as oxidant via Al_2O_3-supported polyoxometalate (POM) catalysts. To enhance higher glycerol conversion and product yield, various types of POM catalyst as well as supports were explored. It was found that the SiW/HZSM-5 catalyst exhibited the highest glycerol conversion (85.54%) to acrylic acid (30.57%) and other valued-products in the presence of 2.74 mol L^{-1} at 90 °C. In this work, to increase the oxidative ability, various types of transition metals (Co, Ce, Ni and V) at different loadings were incorporated into the structure of SiW/HZSM-5 catalyst. The kinetic rate of a one-pot oxydehydration of glycerol over the highest catalytic activity via metal-doped SiW/HZSM-5 catalysts was also explored.

2. Experimental

2.1. Catalyst preparation and characterization

Various metal-doped SiW/HZSM-5 catalysts were prepared by the sequential-impregnation method. Initially, approximately of 2.14 g of SiW ($H_4SiW_{12}O_{40}{\cdot}xH_2O$, Sigma–Aldrich® Inc., USA) was dissolved thoroughly in 5 ml distilled water at room temperature. Then, a prescribed amount of 5 g of HZSM-5 (SiO_2/Al_2O_3 = 25, Zibo Xinhong Chemical Trade Co., Ltd.) was added slowly. The obtained slurry was stirred at constant rate of 200 rpm at room temperature for 1 h. The SiW/HZSM-5 catalyst was obtained after drying at 110 °C and calcination at 400 °C for 20 h. Consequently, four types of transition metals (Co, Ce, Ni and V) were added into the structure of SiW/HZSM-5 catalyst. Approximately 5 g of cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, Sigma–Aldrich® Inc., USA), cerium(III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, Sigma–Aldrich® Inc., USA), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, Sigma–Aldrich® Inc., USA) and sodium metavanadate ($NaVO_3$), Sigma–Aldrich® Inc., USA) were first dispersed in 50 ml of distilled water. To obtain the Ce-, Co-, Ni-, and V-SiW/HZSM-5 catalysts at identical loading of 4 wt.%, 5.16, 8.23, 8.25, and 3.99 ml of these solutions were mixed thoroughly with 4 g of SiW/HZSM-5 catalyst at room temperature. The slurry was stirred at constant rate of 200 rpm at room temperature for 1 h. The ready-to-use metal-doped SiW/HZSM-5 catalysts were obtained after drying at 110 °C for 20 h and calcine at 400 °C for 4 h.

The morphology of all obtained catalysts was characterized as the following. The BET surface area, pore volume, and average pore diameter of as-prepared catalysts were derived from N_2 adsorption isotherms measured at −196 °C (Micromeritics ASAP 2020). Prior the measurement, each sample was degassed at 200 °C for 4 h. The average pore diameter was calculated according to the BJH method. The crystal structures of the catalysts were determined by the X-ray diffraction patterns (XRD) of the catalysts on a Siemens PE-2004 X-ray diffractometer using CuKa (λ = 0.15406 nm) radiation operated at 40 kV and 20 mA. The content of added metal in the SiW/HZSM-5 catalysts was determined by the energy dispersive X-ray spectroscopy (EDX, JEOL, JSM-6400 and Link ISIS Series 300). The elemental analyses of catalysts were determined by X-ray fluorescence (XRF) patterns on Bruker AXS, Germany Model: S4 Pioneer Wavelength dispersive X-ray Fluorescence (WDXRF) Spectrometry. The tube voltage and the current were 60 kV and 50 mA, respectively. The data were collected in the range of 0.2–20 A (60–0.6 keV) with total resolution 3–100 eV and typical measurement time 2–10 s per element. The program was used SPECTRAPlus software of the Bruker with the Standardless Analysis. The acidities of all metal-doped SiW/HZSM-5 catalysts were determined by temperature-programmed desorption of ammonia (NH_3-TPD) in a fixed-bed continuous flow microreactor at atmospheric pressure equipped with TCD detector.

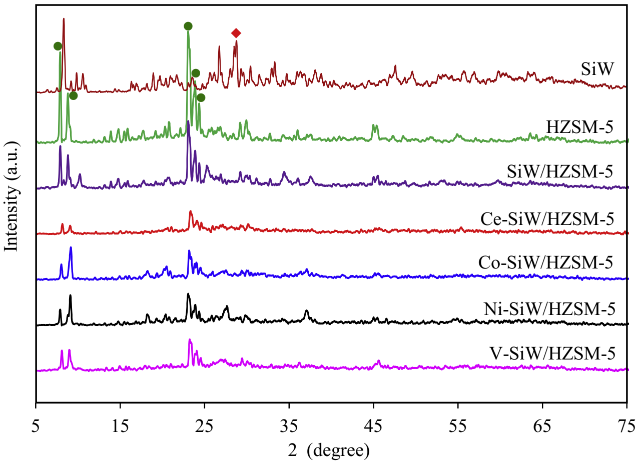

Fig. 1. XRD pattern of HZSM-5, SiW and metal-doped SiW/HZSM-5 at constant metal loading of 4 wt.% (●, HZSM-5 and ◆, SiW hexahydrate).