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Catalytic dehydration of glycerol to acrolein over $M_{2.5}H_{0.5}PW_{12}O_{40}$ (M = Cs, Rb and K) phosphotungstic acids: Effect of substituted alkali metals

Sharifah Bee Abd Hamid [a,*], Nur Atiqah Daud [a], Durga Devi Suppiah [a], Wageeh Abdulhadi Yehya [a], Putla Sudarsanam [b], Suresh K. Bhargava [b]

[a] Nanotechnology and Catalysis Research Centre (NANOCAT), University of Malaya, Kuala Lumpur, Malaysia
[b] Centre for Advanced Materials and Industrial Chemistry (CAMIC), School of Science, RMIT University, Melbourne, VIC 3001, Australia

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ABSTRACT

Catalytic conversion of glycerol into value-added chemicals, particularly acrolein via acid-catalyzed dehydration route has received much attention due to the potential uses of acrolein. This work reports the synthesis of various alkaline metal substituted phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) catalysts, namely $M_{2.5}H_{0.5}PW_{12}O_{40}$ (M = Cs, Rb and K) using a controlled precipitation method. A systematic structural, morphology, and chemical characterization were conducted using various analytical techniques. XRD studies revealed that the incorporation of alkaline metals in $H_3PW_{12}O_{40}$ leads to decreased crystallite size and enhanced lattice strain. N_2 adsorption–desorption studies show that the specific surface area of $H_3PW_{12}O_{40}$ is significantly improved from 5 to 82 ($K_{2.5}H_{0.5}PW_{12}O_{40}$), 103 ($Rb_{2.5}H_{0.5}PW_{12}O_{40}$), and 94 m^2/g ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$). XRD, Raman, and FT-IR studies confirm the Keggin structure of all the alkaline metal substituted HPW catalysts. The acidity strengths estimated by NH_3-TPD analysis were obtained in the following order: H_3PW (2654.91 μmole/g) > $K_{2.5}H_{0.5}PW$ (1060.10 μmole/g) > $Rb_{2.5}H_{0.5}PW$ (762.08 μmole/g) > $Cs_{2.5}H_{0.5.5}PW$ (461.81 μmole/g). Although alkaline metal substituted $H_3PW_{12}O_{40}$ catalysts exhibit higher specific surface area and smaller crystallite size compared to parent $H_3PW_{12}O_{40}$ low glycerol conversions were found for substituted $H_3PW_{12}O_{40}$ catalysts. As well, the parent $H_3PW_{12}O_{40}$ catalyst shows an excellent acrolein selectivity (95%) which is much higher than that of $Cs_{2.5}H_{0.5.5}PW$ (81.9%) and very close to the selectivities obtained over $Rb_{2.5}H_{0.5}PW$ (95.1%) and $K_{2.5}H_{0.5.5}PW$ (95.6%) catalysts. The catalytic performance of $H_3PW_{12}O_{40}$ and $M_{2.5}H_{0.5}PW_{12}O_{40}$ materials is directly proportional to their acidic strengths, indicating that the catalyst acidity is a key factor for achieving better results in glycerol dehydration.

1. Introduction

The transformation of renewable energy feedstocks, especially biomass into valuable chemicals and fuels is currently a hot research topic due to the potentiality of biomass-derived products for replacing fossil fuel-derived products in chemical industry [1]. Glycerol is one of the most valuable biomass-derived molecules that can be largely obtained as the main by-product during biodiesel production via transesterification of vegetable oils and animal fats with ~10 wt% of the total biodiesel synthesized [2,3]. Therefore, the surplus production of glycerol offers great opportunities for researchers to use glycerol as a bio-renewable source for the synthesis of value-added chemicals and fuels.

The dehydration of glycerol to acrolein is one of the most promising routes of glycerol valorization. Acrolein is an important intermediate for the production of acrylic acid, acrylic acid esters, adhesive, detergents, and polymers [1]. As well, it is a valuable ingredient in the production of quinoline, pentaerythritol, glutaraldehyde, 1,2,6-hexanetriol, and oil-well derivatives [4]. Acrolein is currently obtained from the partial oxidation of petrochemical-derived propene [5]. It is understandable that the production of acrolein from a cheap and abundant biomass-derived glycerol can provide a more economical and sustainable alternative route [1].

Various types of solid acid catalysts have been developed for the dehydration of glycerol to acrolein. The Keggin type

* Corresponding author.
E-mail address: sharifahbee@um.edu.my (S.B.A. Hamid).

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heteropolyacids (HPAs), which possess strong Brønsted acidity than the zeolites, metal oxides, and concentrated H_2SO_4, have been widely used in various acid-catalyzed reactions, including glycerol dehydration [6]. Their chemical composition is typically described as $XM_{12}O_{40}^{x-8}$ where X is the central atom (Si^{4+}, P^{5+}, etc.), x is its oxidation state, and M is the metal ion (Mo^{6+} or W^{6+}). However, the application of HPAs is greatly limited in a number of acid-catalyzed reactions due to their various drawbacks, such as low surface area (<10 m^2/g), low thermal stability and high polar solubility [1]. Various strategies have been developed to improve the physicochemical, acidic, and catalytic properties of HPAs, including exchange of its protons (H^+) with various metal ions and/or dispersing them on suitable supports [7,8]. Particularly, the incorporation of alkaline metals (e.g., K, Rb, and Cs) into HPAs can improve the specific surface area, water-tolerance ability, and simultaneously adjust the acidity, resulting in enhanced catalytic performance and catalysts' stability [9]. It has been demonstrated that the synthesis of non-stoichiometric K^+ or Cs^+ salts of $H_3PW_{12}O_{40}$ with a replacement ratio between two and three protons leads to improved specific surface areas. The highest activities in acid-catalyzed esterification of isoamyl alcohol were achieved upon substitution of 2.5 proton equivalents by Cs ion [5].

Therefore, this research work aims to investigate the potential of alkaline metals, such as K, Rb, and Cs to tune physicochemical, textural, and acidic properties of phosphotungstic acid ($H_3PW_{12}O_{40}$) which could replace the corrosive sulfuric acid in glycerol dehydration to acrolein. Various spectroscopic and non-spectroscopic analytical techniques, such as XRD, BET surface area, FT-IR, pyridine adsorbed FT-IR, SEM, NH_3-TPD, and Raman were used to understand the properties of alkaline metal ion exchanged phosphotungstic acids. The catalytic application of developed acid catalysts was tested for the dehydration of glycerol under liquid-phase conditions.

2. Experimental

2.1. Catalyst synthesis

Various alkaline metal ion exchanged phosphotungstic acids ($M_{2.5}H_{0.5}PW_{12}O_{40}$, where M = K, Rb and Cs) were prepared by a controlled precipitation method that has been reported elsewhere [8,10–12]. In a typical synthesis procedure, the predetermined amounts of aqueous solution of Cs_2CO_3 (Cs^+: 0.25 mol dm^{-3}) or Rb_2CO_3 (Rb^+: 0.25 mol dm^{-3}) or K_2CO_3 (K^+: 0.25 mol dm^{-3}) are added to a 0.08 mol dm^{-3} solution of H_3PW at a rate of 1 mL min^{-1} at 30 °C. The white precipitates formed in the solution were aged for 16 h at 30 °C. The solutions were then filtered off and dried in the oven at 100 °C to remove access liquid. The solid precursor was then calcined at 350 °C for 4 h under inert atmosphere conditions.

2.2. Catalyst characterization

The crystalline properties of the catalysts were analysed using powder X-ray diffraction (Bruker D8) theta/2theta goniometer (model D8) equipped with a Cu Kα monochromatized radiation source and a scintillation counter detector. The data sets were collected in reflection geometry in the range of $2° \leqslant 2\theta \leqslant 80°$ with a step size of $\Delta 2\theta = 0.02°$ analysed using High Score Plus software to determine the crystal phases and phase purity. The Keggin structure of the catalysts was confirmed by a Fourier transform infrared (FT-IR) spectroscopy (Bruker, Model IFS 66v/s) using KBr pellet technique with the resolution of 4 cm^{-1}. Pyridine adsorbed FT-IR experiments were conducted using a Perkin Elmer spectrum 400. Approximately, 50 mg of catalyst was dried in an oven at 100 °C for 1 h. Few drops of pyridine (~0.5 ml) were contacted directly with the sample. The sample was then dried in a vacuum oven at 120 °C for 1 h. The sample was then stored in a desiccator and allowed to cool to room temperature prior to analysis. The spectra were recorded in the range of 1400–1900 cm^{-1} using ATR method. Raman spectroscopic investigations were carried out with a Renishaw inVia Raman microscope using a 50× objective lens using 785 nm laser source with instrument grating 1200 1/mm.

The morphology of the catalysts was estimated using Hitachi S-520 scanning electron microscope (SEM) at an accelerated voltage of 5 kV. Specific surface area, pore volume, and pore size distribution of the catalysts were determined using N_2 adsorption–desorption analysis on Sorptometric 1990 instrument. The acidic properties of the catalysts were determined by ammonia temperature-programmed desorption analysis (NH_3-TPD) using TPDRO 1100 series instrument (Thermo Finnigan). All the samples were pre-treated in nitrogen (30 min, 50 °C) followed by ammonia treatment (30 mL/min). The samples were the continued to be treated with nitrogen (30 min, 50 °C) followed by ammonia desorption from 30 to 900 °C under He flow.

2.3. Catalyst activity test

The catalytic performance of alkaline metal ion exchanged phosphotungstic acids was conducted for the dehydration of glycerol using a 200 mL high-pressure autoclave reactor (Top Industries). For each experiment, 1 mol of glycerol (Friendienmann Schmidt, ⩾99.8%) and 0.1 g catalyst were loaded into the reactor. The sealed reactor was purged with pure N_2 at room temperature to evacuate air. The reactor was then pressurized with N_2 to 1 bar, followed by heating to the reaction temperature. After reaching the required reaction temperature, time and stirring (300 rpm) were initiated. After each reaction, the reactor was cooled to room temperature and liquid samples were collected for analysis.

Analysis of the products was done by Agilent GC 6890 N equipped with two types of detector; flame ionization detector (FID) and thermal conductivity detector (TCD). Three different columns; 30 m × 0.53 mm × 5.00 μm DB1 column, 30 m × 0.32 mm × 20 μm HP-Plot Q and 30 m × 0.53 mm × 40 μm Molesieve (MS) column were used for product separation.

3. Results and discussion

3.1. 1 Structural analysis

The crystalline structure and phase integrity of pure HPW and alkaline metal ion exchanged (Cs^+, Rb^+, K^+) HPW catalysts were evaluated using XRD analysis. Fig. 1 shows the characteristic reflections of the parent HPW acid at $2\theta = 20.8°$, 23.3°, 25.5, 29.5°, 34.7° and 37.9°, which can be assigned to the (211), (220), (222), (400), (332) and (431) planes of face-centered cubic structured phosphotungstic acid, respectively (PDF-File 00-050-0304). Table 1 shows the main diffraction peaks with the corresponding d-spacings and relative intensities for the parent phosphotungstic acid.

The most intense peak observed at 25.5° (hkl 222) for the parent $H_3PW_{12}O_{40}$ acid has been marked as the signature peak representing the Keggin structure of phosphotungstic acid. This peak was also observed in the XRD patterns of all the alkaline metal substituted HPW catalysts; however it is shifted to higher angles (Fig. 1 and Table 2). Lattice strain and crystallite size of the catalysts were calculated using Scherrer equation [13] and the values were listed in Table 2. Substitution of protons by metal ions with different ionic radius causes a rearrangement of the secondary structure which also affects the crystallite size [14]. It was found