



Design of a highly active silver-exchanged phosphotungstic acid catalyst for glycerol esterification with acetic acid



Shanhui Zhu^{a,b}, Xiaoqing Gao^c, Fang Dong^{a,b}, Yulei Zhu^{a,c,*}, Hongyan Zheng^c, Yongwang Li^{a,c}

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

^b Graduate University of Chinese Academy of Sciences, Beijing 100039, PR China

^c Synfuels China Co. Ltd., Taiyuan 030032, PR China

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ABSTRACT

A series of highly active, selective, and stable silver-exchanged phosphotungstic acid (AgPW) catalysts were prepared, characterized, and evaluated for bio-derived glycerol esterification with acetic acid to produce valuable biofuel additives. The structures, morphologies, acidities, and water tolerance of these samples were determined by FTIR, Raman, XRD, SEM-EDX, FT-IR of pyridine adsorption, and H₂O-TPD. Several typical acidic catalysts were also performed for comparison. Among them, partially silver-exchanged phosphotungstic acid (Ag₁PW) presented exceptionally high activity, with 96.8% conversion within just 15 min of reaction time and remarkable stability, due to the unique Keggin structure, high acidity as well as outstanding water-tolerance property. A plausible reaction mechanism was also proposed. In addition, this Ag₁PW catalyst exhibited universal significance for esterification, holding great potential for a wide range of other acid-catalyzed reactions.

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1. Introduction

As a consequence of the diminishing fossil resources, significant efforts have been taken worldwide to convert renewable biomass into fuels and value-added compounds [1,2]. In this context, biodiesel derived from the lipid fraction of biomass is currently attracting considerable attention for its sustainability, reduced toxicity and carbon neutral alternative of fossil fuels [2,3]. Biodiesel is manufactured by the transesterification of triglycerides with methanol or ethanol, which concurrently yields large amounts of glycerol equivalent to about 10 wt% of the total biodiesel production [3]. With the steady growth of biodiesel industry, tremendous surplus of glycerol has been produced, and evidently, a glycerol “lake” is being formed, which makes its commercial value depreciate sharply. Due to its nontoxic, edible, biodegradable properties as well as multifunctional structure, glycerol holds the potential of being an extremely important building block for the biorefinery. Consequently, a variety of catalytic processes have been envisaged for the valorization of glycerol by hydrogenolysis, reforming, etherification, esterification, oxidation, dehydration, and so on [4–9]. As such, one of the most promising potential approaches is catalytic esterification of glycerol with acetic acid to the formation of

monoacylglycerol (MAG), diacylglycerol (DAG), and triacylglycerol (TAG) because of their versatile uses as biofuel additives directly or as precursors in the synthesis of polyesters [10].

The esterification of alcohols with organic acids is a conversion of both environmental and industrial importance, being employed extensively in the synthesis of various esters from bio-derived feedstocks. Among them, the selective esterification of glycerol with acetic acid is probably one of the most studied processes in the literature of esterification, and so can be taken as a model reaction in this type of catalysis [11]. Conventionally, the esterification of glycerol with acetic acid is performed in the presence of mineral acids catalysts. However, the inherent disadvantages related with homogeneous system lie in separation and purification of the products, resulting in the environmental problems and economical inconveniences. In order to tackle these problems, a great number of heterogeneous solid acid catalysts have been developed in recent works, such as hydroxylated magnesium fluorides [12], sulfated activated carbon [13], SO₃H-functionalized ionic liquids [14], mesoporous silica with sulfonic acid groups [15], zeolites [16], Amberlyst-15 [17], and heteropolyacids [18–20]. Despite the relative efficiency of these catalysts in glycerol esterification, many of them have low densities of effective acid sites, tedious preparation protocols, and rapid loss of catalytic activity. Furthermore, the unavoidable generation of water as a byproduct of esterification can have a serious impact on the catalytic performance of some solid acid catalysts such as supported heteropolyacids (HPAs)

* Corresponding author at: State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China. Fax: +86 351 7560668.

E-mail address: zhuyulei@sxicc.ac.cn (Y. Zhu).

because of their extremely hydrophilic nature. Consequently, how to design a highly active, inexpensive, robust, and water-tolerant heterogeneous solid acid catalyst that can be employed by simple preparation protocol is still a great challenge.

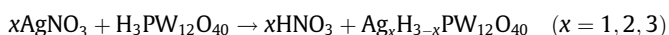
HPAs, possessing characteristics of strong Brønsted acidity and easily tunable acidity, have been demonstrated to display outstanding catalytic performance in a wide range of acid-catalyzed reactions [21–24]. However, the lack of thermal stability and high solubility in polar media of HPAs has limited their further applications in heterogeneous acid-catalyzed reactions. In contrast to grafting HPAs onto porous supports, it is more effective to exchange protons of HPAs with different cations (e.g., K^+ , Cs^+ , Ag^+) to form insoluble salts, which can tune and amplify HPAs reactivity or even result in the appearance of bifunctional or multifunctional catalysis [25]. Such a conceptual strategy would lead to offer a new class of tunable and recoverable HPA salts catalysts with high efficiency and heterogeneity, providing versatile applications in sustainable chemistry. Recently, Borghèse et al. [26] have developed a series of exceedingly effective and reusable silver-exchanged silicotungstic acid catalysts for the rearrangement of alkyloxiranes to furans. Compared to $H_4SiW_{12}O_{40}$ and other HPAs such as $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$ (HPW) presents stronger Brønsted acidity and thermal stability, because of the weak interaction between acidic protons and large Keggin anion. Thereby, in this work, we have focused on designing silver modified HPW catalysts prepared by an ion-exchanged method, exhibiting unprecedented catalytic activity and superior stability for glycerol esterification. To the best of our knowledge, this is the first report on the catalytic performance of heterogeneous silver-exchanged HPA catalysts for the esterification.

Accordingly, in the present investigation, Ag-exchanged HPW catalysts with varying Ag contents were prepared, characterized, and evaluated for glycerol esterification with acetic acid. The catalyst features were characterized using various spectroscopy techniques and correlated with the observed catalytic performance of glycerol esterification. The esterification of different alcohols with organic acids was performed to check the scope of this catalyst.

2. Experimental

2.1. Catalyst preparation

All the chemicals were obtained commercially and used without any further purification. $H_3PW_{12}O_{40} \cdot xH_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). $AgNO_3$ was supplied by Tianjin Damao Chemical Co., Ltd. Prior to the preparation, the water content of $H_3PW_{12}O_{40} \cdot xH_2O$ was checked by TG-MS. The Ag-exchanged HPW catalysts were synthesized by an ion-exchanged method, according to the procedure described previously [26,27]. Firstly, 10.25 g HPW was dissolved in 20 ml deionized water at room temperature under vigorous stirring. Then, the appropriate amount of $AgNO_3$ (0.1 mol/L) aqueous solution was added dropwise to the former solution with continuous stirring. The resultant mixture was aged 2 h at room temperature, and the excess water was evaporated in a rotary evaporator. The remaining powder was dried at 80 °C overnight and then calcined at 250 °C in static air for 4 h. Analogously, the number of Ag atom, i.e., x in $Ag_xH_{3-x}PW_{12}O_{40}$ ($x = 1, 2, 3$), can be conveniently controlled by varying the amount of $AgNO_3$ aqueous solution. These as-prepared catalysts are designated as Ag_1PW , Ag_2PW , and Ag_3PW , wherein the number implies the number of Ag ions exchanged. The formation of $Ag_xH_{3-x}PW_{12}O_{40}$ reaction undergoes based on the following equations:



Wet ion-exchanged resins Amberlyst-15 (30 nm of average pore diameter, $50 \text{ m}^2 \text{ g}^{-1}$) and Amberlyst-30 (30 nm of average pore diameter, $53 \text{ m}^2 \text{ g}^{-1}$) were dried overnight at 110 °C prior to the catalytic tests. ZSM-5 ($Si/Al = 25$, 0.56 nm of average pore diameter, $50 \text{ m}^2 \text{ g}^{-1}$) was activated at 500 °C in static air for 4 h before the test. ZrO_2 ($59.7 \text{ m}^2 \text{ g}^{-1}$) supplied from Jiangsu Qianye Co., Ltd was used as the support. MoO_3/ZrO_2 , WO_3/ZrO_2 , Nb_2O_5/ZrO_2 , and SO_4^{2-}/ZrO_2 were prepared by incipient wetness impregnation method by using $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (SCRC), $(NH_4)_6W_7O_{24} \cdot 6H_2O$ (SCRC), $Nb(OH)_5$ (King-Tan Tantalum Industry Ltd.), H_2SO_4 (SCRC) as precursors. Specifically, these catalysts were prepared by impregnation of ZrO_2 with the calculated amount of aqueous solution of desired precursors and then dried overnight at 110 °C followed by calcination at 600 °C in static air for 4 h. Appropriate amount of oxalic acid dehydrate (SCRC) was added to the solution of $Nb(OH)_5$ to improve the solubility during the preparation of Nb_2O_5/ZrO_2 . The nominal loadings of acid components (MoO_3 , WO_3 , Nb_2O_5 , and SO_4^{2-}) in the corresponding catalysts were 15%. Cs-exchanged HPW catalyst ($Cs_{2.5}PW$) was prepared with the same procedure as the aforementioned Ag_1PW , wherein 2.5 protons in one HPW molecule can be replaced by Cs atoms.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on D2/max-RA X-ray diffractometer (Bruker, Germany) using $Cu K\alpha$ radiation at 30 kV and 10 mA. The measurements were obtained in the step of 0.04° with account time of 0.5 s and in the 2θ range of 5–90°.

Raman spectroscopy was obtained on a Renishaw-UV-vis Raman System 1000 equipped with a CCD detector at room temperature. The air-cooled frequency doubled Nd-Yag laser operating at 532 nm was employed as the exciting source with a power of 30 MW.

Scanning Electron Microscopy (SEM) was conducted on a Quanta 400F microscope. EDX spectra were obtained using 20 kV primary electron voltages to determine the composition of the samples.

The IR spectra were measured on a Vertex 70 (Bruker) FT-IR spectrophotometer, equipped with a deuterium triglycine sulfate (DTGS) detector. The powder samples were mixed with KBr (2 wt%) and pressed into translucent disks at room temperature. The spectra were recorded in the range of 400–4000 cm^{-1} .

IR spectra of adsorbed pyridine (Py-IR) were recorded with the same apparatus as above. The samples were pressed into self-supporting wafers, degassed in a vacuum at 300 °C for 1 h, and subsequently exposed to the pyridine vapor after cooling down to 30 °C. The Py-IR spectra were then recorded at 200 °C after applying vacuum for 30 min. The quantification of acidity was calculated by Lambert-Beer equation,

$$A = \frac{\varepsilon \cdot W \cdot c}{S}$$

where A is the absorbance (area in cm^{-1}), ε the extinction coefficient (m^2/mol), W the sample weight (kg), c the concentration of acid (mol/kg or mmol/g) and S is the sample disk area (m^2).

The amount of Brønsted and Lewis acid sites was estimated from the integrated area of the adsorption bands at ca. 1540 and 1450 cm^{-1} , respectively, using the extinction coefficient values based on the previous report [28].

H_2O -TPD was performed in an Auto Chem.II 2920 equipment (Mircromeritics, USA). Prior to each run, 0.3 g catalyst was first pretreated in flowing He at 250 °C for 1 h and then cooled to 50 °C followed by saturating with water using pulse model until saturation. After being purged with He for 30 min, the catalyst

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