



Heteropolyacid-based ionic liquids as effective catalysts for the synthesis of benzaldehyde glycol acetal

Xiaoxiang Han^{a,*}, Wei Yan^a, Keke Chen^a, Chin-Te Hung^b, Li-Li Liu^{b,c}, Pei-Hao Wu^b, Shing-Jong Huang^d, Shang-Bin Liu^{b,c,*}

^a Department of Applied Chemistry, Zhejiang Gongshang University, Hangzhou 310035, China

^b Institute of Atom and Molecular Sciences, Academic Sinica, Taipei 10617, Taiwan

^c Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan

^d Instrumentation Center, National Taiwan University, Taipei 10617, Taiwan

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ABSTRACT

A series of environmental benign ionic liquid (IL) catalysts, synthesized by incorporating varied amounts of tungstophosphoric acid (TPA) and pyridinium propyl sulfobetaine (PPS) zwitterionic precursor, were exploited for homogeneous conversion of biomass. In particular, these water-soluble PPS-TPA IL ([PPSH]_xH_{3-x}PW₁₂O₄₀; x = 1.0–3.0) catalysts were evaluated for acetalization of benzaldehyde with glycol. The catalyst system revealed self-separation characteristics, which resulted in the formation of biphasic product/catalyst layers to render facile product separation and catalyst recycling. Among various PPS-TPA ILs examined, the [PPSH]₂HPW₁₂O₄₀ catalyst exhibited excellent durability and an optimal acetal yield over 85%, in good agreement with that predicted by factorial design of experiments and response surface methodology (RSM). The effects and correlations of different experimental variables such as reaction time, relative reactant concentration, amount of water-carrying agent, and amount of catalyst were addressed by the Box–Behnken design (BBD). The deduced optimal conditions lead to an acetal yield of 85.2%, which is consistent with experimental results and that predicted by the BBD model. The superior acetalization activities observed for the novel PPS-TPA IL catalysts are attributed to their highly acidic nature and weak mass transport resistance.

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1. Introduction

Acetals are commonly used as solvents, ingredients in perfumes or flavor chemicals, and intermediates or final products in petrochemicals, pharmaceuticals, and fine chemicals processes [1–3]. As carbonyl derivatives, acetals are excellent protection groups for carbonyl groups during multistep organic synthesis mainly due to their stability and lack of reactivity in basic media. Conventionally, acetalization reactions are catalyzed by liquid acids such as H₂SO₄, HCl, H₃PO₄, *p*-toluenesulfonic acid (in toluene), or acidic ionic liquids (ILs) [4–9], which are handicapped by undesirable environmental hazards due to their high corrosiveness and formidable recovery and reuse. In addition, acetalization carried

out over these acid catalysts also suffered from inherent problems such as highly susceptible to water and excessive amounts of by-products. As such, considerable efforts have been made in developing more durable solid acid catalysts for acetalization of aldehyde with alcohol, for examples, supported Lewis acid [10–12], zeolites [13,14], montmorillonites [5,15], and ion exchange resins [16–18]. Nonetheless, issues related to product selectivity, environmental safety, spent catalyst disposal, and catalyst recyclability remained as critical challenges for the design and fabrication of highly active catalysts for acetalization.

Heteropolyacids (HPAs), especially those of the Keggin series, have been widely used as catalysts in heterogeneous as well as homogeneous reactions for the synthesis of fine and/or special chemicals due to their unique structural, redox, and acidic properties [19–24]. However, despite of their strong acidic characteristics, HPAs are often limited by the low thermal stability, inferior solubility in polar solvents, and small surface area (<10 m²/g). The latter largely inhibits accessibility of internal active sites from reactants during the catalytic reaction. To circumvent this problem, modified catalysts such as HPAs supported on porous substrates have been

* Corresponding authors at: Academia Sinica, Institute of Atomic and Molecular Sciences, Taipei 10617, Taiwan. Tel.: +86 571 28008975/+886 2 23668230; fax: +86 571 2800 8900/+886 2 2362 0200.

E-mail addresses: hxx74@126.com (X. Han), sbliu@sinica.edu.tw, sbliu.iams@gmail.com (S.-B. Liu).

employed [25–27]. However, inevitable catalyst leaching usually takes place, especially for catalysts prepared by incorporating HPAs onto the supports by physisorption, leading to formidable problems in separation, recovery, and recycling of the catalyst. Thus, the development of durable HPA-based catalysts with facile recovery should be highly desirable; a task this study aims to explore.

Moreover, considerable R&D attentions have been paid in practical applications of ionic liquids (ILs) for organic reactions owing to their tailorable physicochemical properties, excellent thermal stability, and durability [9,28–30]. Consisting of an organic cation and an inorganic anion via ionic linkage, the structural properties of ILs may be modified by altering the inorganic anions [31], forming unique organic-inorganic hybrid materials [32]. Such materials are anticipated to possess high melting point, low solubility in common organic solvents, and high mass transfer resistance [33], which are favorable as designed acid catalysts for organic reactions [32,34–37].

We report herein the physicochemical and catalytic properties of a series of Keggin-type tungstophosphoric acid (TPA)-base IL salts prepared via ionic linkage of the polyanions of TPA with an imidazolium-based zwitterionic precursor, namely pyridinium propyl sulfobetaine (PPS), under varied composition ratios. The acid properties of the PPS-TPA IL catalysts so prepared were characterized by solid-state ^{31}P magic-angle-spinning (MAS) NMR using the adsorbed trialkylphosphine oxide (TMPO) as the probe molecule [38–45]. Moreover, their catalytic activities during acetalization of benzaldehyde with glycol were also investigated; the corresponding reaction process and product optimizations were accomplished by a factorial experimental design and response surface methodology (RSM) [46–48].

2. Experimental

2.1. Catalyst preparation

The PPS-TPAs IL catalysts were prepared following the procedures outlined in the literature (see Scheme S1; Supplementary data) [32,49]. In brief, known amounts of 1,3-propane sultone (12.2 g, 0.1 mol) was first mixed with pyridine (7.91 g, 0.1 mol) under stirring condition at 80 °C for about 6–12 h. Then, the solid zwitterion mass was filtered and washed thrice with ethyl acetate, followed by drying under vacuum (≤ 76 Torr). Subsequently, an aqueous solution of TPA ($\text{H}_3\text{PW}_{12}\text{O}_{40}$; 5.76 g in 50 mL H_2O) was added, and the mixture was stirred at 90 °C for 24 h. After removal of water, the final product was washed with diethyl ether, and then dried under vacuum. A series of PPS-TPA IL salts so prepared with varied PPS/TPA ratios are denoted as $[\text{PPSH}]_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$; $x = 1.0\text{--}3.0$. All research grade chemicals were used without further purification.

2.2. Catalyst characterization

All Fourier-transform infrared (FT-IR) spectra were recorded in 4000–400 cm^{-1} region on a Bruker IFS-28 spectrometer. A KBr disk was used to mount the sample. Thermogravimetric and differential thermogravimetric analysis (TGA-DTG) analyses were obtained on a TG-209 (Netzsch) apparatus. Typically, each sample was heated from room temperature (RT; 25 °C) to 600 °C at a heating rate of 10 K/min under dynamic N_2 atmosphere. All NMR spectra were acquired on an Avance III 500 (Bruker-Biospin) spectrometer using a single-pulse sequence and operating at a Larmor frequency of 500.13, 125.76, and 202.46 MHz for the ^1H , ^{13}C , and ^{31}P nucleus, respectively. All $[\text{PPSH}]_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($x = 1.0\text{--}3.0$) IL catalysts exhibited similar high-resolution (solution-state) ^1H and ^{13}C NMR spectra in D_2O . As an illustration, the NMR data obtained

from the $[\text{PPSH}]_{2.0}\text{HPW}_{12}\text{O}_{40}$ catalyst are listed below: ^1H NMR (500 MHz, D_2O); δ 2.482 (t, 2H), 2.982 (t, 2H), 4.825 (t, 2H), 8.220 (t, 2H), 8.705 (t, 1H), 8.878 (d, 2H) ppm; ^{13}C NMR (500 MHz, D_2O); δ 26.43, 47.29, 60.27, 129.04, 144.32, 146.42 ppm. On the other hand, detailed acid features, namely relative concentration and strength of Brønsted acidity in the PPS-TPA IL catalysts were studied by solid-state ^{31}P magic-angle-spinning (MAS) NMR of the adsorbed trimethylphosphine oxide (TMPO) as the probe molecule [38–45]. It has been demonstrated that a linear correlation between the observed ^{31}P NMR chemical shifts and the strengths of Brønsted acidity may be inferred [50,51] by means of such ^{31}P -TMPO NMR approach. Prior to the adsorption of TMPO, catalyst was first subjected to a thorough dehydration treatment at 150 °C for 24 h under vacuum ($< 10^{-5}$ Torr). Subsequently, a known amount of TMPO dissolved in anhydrous CH_2Cl_2 was introduced into a vessel containing the dehydrated solid sample in a glove box under N_2 environment. The sealed sample vessel was then connected to a vacuum manifold, followed by removal of the CH_2Cl_2 solvent by evacuation at 50 °C. To ensure a uniform adsorption of adsorbate probe molecules in the substrate, the sample was further subjected to thermal treatment at 120 °C for at least 24 h. Finally, the sealed sample vessel was placed in a N_2 glove box where the TMPO-loaded sample was transferred into a MAS rotor and then sealed by a gas-tight Kel-F cap. Typically, free induction decay (FID) signals were acquired using a single-pulse sequence (with a $\pi/6$ pulse-width of 1.5 μs and a recycle delay of 10 s) under a sample spinning rate of 12 kHz. The ^{31}P chemical shifts were referenced to 85% H_3PO_4 aqueous solution.

2.3. Catalytic reaction

The catalytic activities of the pristine TPA and various PPS-TPA IL catalysts were examined by acetalization of benzaldehyde with glycol. Typically, research grade benzaldehyde (10.6 g, 0.1 mol), glycol (11.16 g, 0.18 mol), and the PPS-TPA IL catalyst (0.53 g) were put in a three-neck flask equipped with a thermometer, a water segregator, a reflux condense, and a magnetic stirrer. The reaction mixture was heated to reflux for a desirable period of time in an oil bath under mechanical stirring, then, cooled to RT. Subsequently, owing to the self-separation characteristics of the reaction system, the precipitated IL catalyst may easily be separated, followed by filtering and washing (with diethyl ether) for later recycle use. Chemical analysis of the products was performed by a gas chromatograph (GC; Agilent 6890N) equipped with a FID detector and an HP-5 capillary column. Reactants and products were identified by comparing with authentic samples by using biphenyl as the internal standard. The yield was determined by the weight of acetal distilled at a specific temperature range of ca. 224–228 °C from the products.

2.4. Design of experiments and response surface methodology (RSM)

Response surface methodology (RSM) was employed to optimize the reaction process and product yield during acetalization of benzaldehyde with glycol over the PPS-TPA IL catalysts on the basis of a Box-Behnken experimental design [46]. The design of experiments include four experimental variables specified in Table 1, namely reaction time (x_1), alcohol/aldehyde reactant ratio (x_2), water-carrying agent amount (x_3), and catalyst amount (x_4). According, a 3^4 full-factorial central composite design with coded levels (see Table 1) was used, leading to a total of 29 experimental sets, which include 24 factorial points and 5 centering points. The aforementioned four experimental variables were tested at levels coded with either a minus sign (-1 ; lower value), zero (0; central value), or a plus sign ($+1$; higher value). The Design-Expert 6.0.5 (Stat-Ease, USA) software was used for the design of experiments

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