



## Role of acidity over rare earth metal ion-exchanged heteropolytungstates during oxidation of alcohols



Xiaoxiang Han<sup>a,\*</sup>, Yingying Kuang<sup>a</sup>, Kai Ouyang<sup>a</sup>, Renjun Kan<sup>a</sup>, Xiujuan Tang<sup>b</sup>,  
Chin-Te Hung<sup>c</sup>, Li-Li Liu<sup>c</sup>, Pei-Hao Wu<sup>c</sup>, Shang-Bin Liu<sup>c,d,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Zhejiang Gongshang University, Hangzhou 310018, China

<sup>b</sup> College of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310018, China

<sup>c</sup> Institute of Atom and Molecular Sciences, Academic Sinica, Taipei 10617, Taiwan

<sup>d</sup> Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan

### ARTICLE INFO

#### Article history:

Received 6 June 2016

Revised 14 September 2016

Accepted 12 October 2016

Available online 21 November 2016

#### Keywords:

Tungstophosphoric acid

Rare earth metal

Acid synergy

Oxidation of alcohols

Response surface methodology

Reaction kinetic

### ABSTRACT

A series of Brønsted-Lewis acidic catalysts, denoted RE-TPA ( $M_yH_{3-3y}PW_{12}O_{40}$ ;  $M = La, Ce, Pr, Nd, Sm$ ;  $y = 1/3, 2/3, 1$ ), prepared by incorporating rare earth (RE) metal cations as Lewis centers onto the superacidic tungstophosphoric acid (TPA), were characterized by XRD, FT-IR, TGA-DTA and NMR. In particular, their acidic properties were studied by Pyridine-IR and solid-state  $^{31}P$  NMR of adsorbed phosphorous probe molecule. The high catalytic activity for the RE-TPAs was found to invoke Brønsted-Lewis acid synergy. Among various catalysts examined for oxidation of benzyl alcohol (BzOH) with hydrogen peroxide, the  $Ce_{1/3}H_2PW_{12}O_{40}$  was utilized to optimize the reaction conditions while nearly full BzOH conversion, and excellent benzaldehyde yield (98.2%) and selectivity (98.4%) could reach by response surface methodology (RSM). Additional recyclability and kinetic studies revealed that the RE-TPA catalysts are robust, reusable, and highly efficient for alcohols oxidation reaction with an apparent order of 2.5 and an active energy of 37.3 kJ/mol.

© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

### 1. Introduction

Carbonyl compounds are vital reliance as intermediates in organic and pharmaceutical synthesis and have been widely exploited in diverse fields of chemical industry, for examples, perfumes, dyestuffs, and agro-processing. Some of the most important carbonyl compounds, such as aldehydes (RCOH) and ketones (RCOR'), are commonly produced through catalytic oxidations of primary and secondary alcohols, respectively, invoking viable oxidants [1–4]. Nevertheless, while the oxidations of alcohols represent a facile and economic route for the production of aldehydes and ketones, the radical reactions are difficult to control due to the higher oxidation potential required. In general, compounds of transition metals, e.g., Cr or Mn are used as oxidants while utilizing precious metals such as Ru, Pd, and Au as catalysts during these oxidation reactions [5]. However, there are various drawbacks to using these reagents, including high cost and environmental concerns, which largely limit their industrial applications. Moreover, these oxidative systems are rather aggressive, thus require immod-

erate conditions (e.g., temperature, acidity, etc.) and may yield unwanted and difficult-to-remove by-products, which further jeopardize their applications. Thus, there is clearly a demand to develop innovative catalyst systems which may activate molecular oxygen effectively while retaining the high selectivity and mild conditions prerequisite for practical industrial applications.

In this context, polyoxometalates (POMs), polyatomic ions with three-dimensional framework structure consisting of several types of transition metal oxanions which are linked together through shared oxygen atoms, have attracted considerable attentions especially as oxidation catalysts. In particular, the POM/ $H_2O_2$  system, is known to be an efficient, environmental benign, as well as cost-effective catalyst system for oxidation reactions [6–13]. Hydrogen peroxide is a widely used green oxidant, which is easy to handle and commonly applied under mild reaction conditions. On the other hand, POMs are known to exhibit fast and reversible multi-electron redox behaviors under mild conditions, thus, are promising catalysts for the oxidation of alkanes, aromatics, olefins, alcohols [14,15]. However, being soluble in most polar solvents, bulk POM catalysts are adverse for separation and recycling. In addition, their inherent low specific surface areas (typically,  $<10\text{ m}^2/\text{g}$ ) are also unfavorable for molecular diffusion and mass transport. To circumvent this problem, modified POM catalysts

\* Corresponding authors. Fax: +86 571 2800 8900\+886 2 2362 0200.  
E-mail addresses: [hxx74@126.com](mailto:hxx74@126.com) (X. Han), [sbliu@sinica.edu.tw](mailto:sbliu@sinica.edu.tw) (S.-B. Liu).

were developed and used. Their structural and acidic properties may also be manipulated through substitution of elemental compositions of the  $\text{PW}_{12}\text{O}_{40}^{3-}$  polyanions, by exchange of counter cation (*i.e.*,  $\text{H}^+$ ) with metal ions to form insoluble salts [16–20], by dispersing on porous solid supports such as carbons, alumina, zeolites, and mesoporous silicas [21–24]. For ion-exchanged POMs, the type of exchangeable counter cation normally has a strong influence on the tertiary structure and acidic properties of the inorganic salts, thus, greatly affect their catalytic performances. Alkali ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ , *etc.*) and transition metal ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ , *etc.*) ion-exchanged TPAs were found to exhibit high catalytic activity in acetylation and benzylation reactions [19]. Mono transition metal-substituted phosphomolybdate catalysts, namely  $\text{PMo}_{11}\text{M}$  ( $\text{M} = \text{Co}$ ,  $\text{Mn}$ ,  $\text{Ni}$ ) were also found to be highly active for oxidations of alcohols [20]. These novel catalysts offer an environmentally benign, solvent-free process for oxidation of alcohols without the drawbacks of waste production, equipment corrosion, and high cost, while facilitate easy catalyst recovery and recycling. Nonetheless, few reports are available on rare earth metal ion-exchanged POMs for application in oxidations of alcohols.

Herein, we focus on synthesis and applications of rare earth (RE) metal ion-exchanged TPAs (RE-TPAs) for oxidations of alcohols. A series of lanthanide metals ion-exchanged TPA catalysts, namely  $\text{M}_y\text{H}_{3-3y}\text{PW}_{12}\text{O}_{40}$  ( $y = 1/3, 2/3, \text{ or } 1$ ), were prepared by exchanging the ionic proton ( $\text{H}^+$ ) with  $\text{M}^{3+}$  cation ( $\text{M} = \text{La}$ ,  $\text{Ce}$ ,  $\text{Pr}$ ,  $\text{Nd}$ , and  $\text{Sm}$ ). The structural and chemical properties of these catalysts were characterized by different physicochemical techniques. Moreover, their catalytic performances were assessed and compared for selective oxidation of benzyl alcohol and detailed reaction process, product optimizations, as well as kinetic model of the reaction were also investigated for the  $\text{Ce}_{1/3}\text{H}_2\text{PW}_{12}\text{O}_{40}$  catalyst, which shows the optimal performance.

## 2. Experimental

### 2.1. Catalyst preparation

All the chemicals were analytical grade and were used without further purification unless stated otherwise. The inorganic catalysts were synthesized by first dissolving  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (14.4 g) in deionized water at room temperature while under vigorous stirring. Then, an appropriate amount of desirable lanthanide salts, namely  $\text{M}(\text{NO}_3)_3$  ( $\text{M} = \text{La}$ ,  $\text{Ce}$ ,  $\text{Pr}$ ,  $\text{Nd}$ , and  $\text{Sm}$ ), was added to the above solution at  $90^\circ\text{C}$  under continuous stirring. The individual product so obtained after removing the water was dried  $120^\circ\text{C}$  followed by a calcination treatment under vacuum at  $70^\circ\text{C}$  overnight. Accordingly, a series of lanthanide metals ion-exchanged TPA catalysts were prepared and denoted as  $\text{M}_y\text{H}_{3-3y}\text{PW}_{12}\text{O}_{40}$  ( $y = 1/3$  for  $\text{La}$ ,  $\text{Pr}$ ,  $\text{Nd}$ , and  $\text{Sm}$ ). For comparison, the cerium series samples, namely  $\text{Ce}_y\text{H}_{3-3y}\text{PW}_{12}\text{O}_{40}$ , were prepared by varying the amount of cerium nitrate ( $y = 0, 1/3, 2/3, \text{ and } 1$ ).

### 2.2. Catalyst characterization

All samples were characterized by a series of analytical and spectroscopic techniques, such as TGA, XRD, FT-IR, Py-IR, and solid-state  $^{31}\text{P}$  MAS NMR. FT-IR spectra were recorded on a Bruker IFS-28 spectrometer at room temperature. The XRD study was conducted on a Bruker D8 ADVANCE X-ray diffractometer equipped with a Ni-filtered  $\text{Cu K}\alpha$  radiation generated at 40 kV and 20 mA. The thermal stability of various catalysts was characterized by using a Netzsch TG209 thermal gravimetric analyzer. Typically, the TGA profiles were recorded from room temperature ( $25^\circ\text{C}$ ) to  $600^\circ\text{C}$  under  $\text{N}_2$  environment and a heating rate of  $10^\circ\text{C}/\text{min}$ . The acidic properties of various catalysts were examined by FT-IR of adsorbed pyridine as well as  $^{31}\text{P}$  solid-state NMR of adsorbed TMPO.

**Table 1**

List of symbols for various experimental variables and corresponding coded levels and ranges adopted in the experimental designs.

Variable (unit)	Symbol	Range and level		
		-1	0	1
BzOH/ $\text{H}_2\text{O}_2$ (mol/mol)	$x_1$	1:1	1:2	1:3
Reaction time (h)	$x_2$	3	4	5
Catalyst amount (wt%)	$x_3$	3	4	5
Water amount (mL)	$x_4$	15	20	25

Py-IR spectra were recorded at room temperature using the same apparatus described above. Each sample was pressed into a self-supporting wafer, degassed in a vacuum manifold at  $150^\circ\text{C}$  for 4 h, followed by exposing to pyridine vapor at room temperature at first, then, at  $100^\circ\text{C}$  for about 1 h before removing the physisorbed pyridine. The  $^{31}\text{P}$ -TMPO NMR approach has been known to be an important and reliable technique for characterizing the acidic properties of both solid and liquid acid catalysts [25,26]. The solid-state  $^{31}\text{P}$  MAS NMR measurements were carried out on a Bruker-Biospin Avance 500 spectrometer operating at a Larmor frequency of 202.46 MHz using a 4 mm double-resonance MAS probehead. The TMPO probe molecule was loaded onto the catalyst sample following a standard operation procedure described elsewhere [25–27].

### 2.3. Catalytic reaction

The catalytic performance of various catalysts was assessed by oxidation of benzyl alcohol (BzOH) with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). All reactions were performed with a 100 mL three-necked flask equipped with a reflux condenser. Desirable amounts of reactant (BzOH), oxidant ( $\text{H}_2\text{O}_2$ ), and water were added onto the  $\text{M}_y\text{H}_{3-3y}\text{PW}_{12}\text{O}_{40}$  catalyst ( $y = 0, 1/3, 2/3, \text{ or } 1$ ;  $\text{M} = \text{La}$ ,  $\text{Ce}$ ,  $\text{Pr}$ ,  $\text{Nd}$ , or  $\text{Sm}$ ) in the flask, then, refluxed at  $110^\circ\text{C}$  for 4 h in an oil bath. Chemical analysis of products was carried out by gas chromatography (Agilent 6890B) equipped with a flame ionization detector (FID) and a HP-5 capillary column. The BzOH conversion and benzaldehyde (BzH) product selectivity were calculated by means of the internal standard method using biphenyl as the standard.

### 2.4. Experimental design and mathematical model

Response surface methodology (RSM) with a confidence level of 95% was exploited for optimization of experimental parameters based on a Box-Behnken design (BBD). The design of experiments include four independent process variables, namely reactant/oxidant ratio ( $\text{BzOH}/\text{H}_2\text{O}_2$ ;  $x_1$ ), reaction time ( $x_2$ ), catalyst amount ( $x_3$ ), and water amount ( $x_4$ ), as specified in Table 1. Accordingly, a  $3^4$  full-factorial central composite design with three coded levels was used, leading to a total of 29 experimental sets (including 24 factorial points and 5 central points). As shown in Table 1, the four experimental variables were tested at levels coded with either a minus sign ( $-1$ ; low level), zero (0; center level), or a plus sign ( $+1$ ; high level). The coded values of these factors were obtained by the equation [28–31]:

$$x_i = \frac{X_i - X_0}{\Delta X_i} \quad (1)$$

where  $x_i$ ,  $X_i$ , and  $X_0$  ( $i = 1-4$ ) represents the coded, real, and central value of the independent variables, respectively. Whereas  $\Delta X_i = (\text{high level} - \text{low level})/2$  represents the step-change values of the associated variable.

A second-order model equation given by RSM was used to optimize the reaction process, to predict the yield of product (*i.e.*,

Download English Version:

<https://daneshyari.com/en/article/4998881>

Download Persian Version:

<https://daneshyari.com/article/4998881>

[Daneshyari.com](https://daneshyari.com)