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# Continuous synthesis of ethyl levulinate over Cerium exchanged phosphotungstic acid anchored on commercially silica gel pellets catalyst

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## ABSTRACT

Cerium salt of phosphotungstic acid (CeTPA) supported on commercially silica gel pellets (SGP) catalysts were prepared for continuous synthesis of ethyl levulinate in a fixed-bed reactor. The characterization of the catalysts obtained from N<sub>2</sub> sorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) revealed that the heteropolyacid salts basically kept its Keggin structure and Ce was present in the presence of Ce<sup>3+</sup> on the catalyst, the catalytic activity are related to acidity and the dispersion of CeTPA on SGP. The catalyst with 30% CeTPA/SGP showed high catalytic activity with about 98.5% levulinic acid conversion and 99.5% selectivity for ethyl levulinate for 50 h of Time on stream at the optimum conditions.

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## 1. Introduction

Nowadays, the catalytic synthesis of value-added biomass platform chemicals has attracted much attention [1–3]. Among of these biomass based platform compounds, ethyl levulinate (EL) maintained high chemical activity due to a carbonyl and an ester group in its molecular structure. Nowadays, EL are widely used in medicine and health, perfumes, elasticizers and other industries. In addition, EL was also used as a novel form of liquid fuel additive, which would dramatically reduce the depletion of fossil energy [4–6].

The conventional method for production of EL is esterification of levulinic acid (LA) with ethanol accompanied with acid catalyst, such as HCl, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> and so on [7–9]. These catalysts have been phased out because they gradually appeared environmental problems, and sulfated metal oxides, ion exchange resins, zeolites, supported heteropoly acids, etc were extensively applied to this reaction [10–16]. Among of these solid acid catalysts, Keggin type heteropoly acids (HPAs) has been the focus of considerable attention due to its tunable acidity as well as the uniform strong acidic sites [16,17]. Although HPAs are useful acid catalysts, the low specific surface area, high solubility in polar solvents and difficult to separate from polar media limit its potential catalytic performance

[17]. Exchange of HPAs's protons (H<sup>+</sup>) with metal ions to form HPAs salt and grafting it onto porous support is often used to enhance its surface area, acidity and decrease its solubility in polar solvents [18]. Thus, the metal ions and support play an important role on the catalytic performance of the final catalyst. Very recently, several kinds metal cations were used to exchange the protons of HPAs to form HPAs salts [18,19]. Among of these HPAs salts, Cs salt of phosphotungstates are well-known for its high thermal stability (≥500 °C) and water tolerance [20]. However, the tendency to form milky colloid in polar solvent resulting them hard to be anchored on suitable supports. Thus it is still of great interest to exploit an efficient kind of metal salt of HPAs. Cerium is one of the most used rare earth element to be used as catalysis material, and Ce salt of HPAs has been applied for various reactions [21,22]. Generally, the powder forms of ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> have been used to supported the HPAs salts and displayed well performance [20,23,24]. However, if these powder catalysts were to be used in the industrial scale, it must be pelletized with a binder, which can produce a remarkable influence on the overall acidic properties of the catalyst and thus the final catalytic performance [25].

Up to now, the synthesis of ethyl levulinate has been extensively described in flask or autoclave [8–10]. However, this batch process is a tedious process with high energy consumption, much waste of labor and thus hard to be used in an industrial process. These results encouraged us to built a continuous process for the synthesis of EL.

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So far, the continuous synthesis process for EL in fixed-bed reactor based on shaped catalyst was seldom reported.

Among various HPAs, phosphotungstic acid (TPA) was selected in the present studies due to its strong acidic sites and higher water tolerance. Aim to establish a continuous synthesis process for EL in fixed-bed reactor, commercially silica-gel pellets were applied as support and Cerium salt of TPA catalysts were developed. The relationship of physicochemical properties and catalytic activity were investigated and the reaction parameters were optimized. Finally, the time on stream performance of the obtained catalyst was tested under the optimum reaction conditions.

## 2. Experimental

### 2.1. Catalyst preparation

Phosphotungstic acid was purchased from Xiya Reagent (Shandong, China), levulinic acid and cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) were supplied by Macklin (shanghai, China), ethanol was provided from Iron Pagoda Reagent (Shandong, China). The above chemicals used were of A.R. grade. Silica gel pellets (SGP) was obtained from Hailang Silica-gel Dryer Factory (Qingdao, China).

CeTPA supported on SGP was prepared by the method described below. 1.0 mmol of TPA was dissolved in 20 mL distilled water at room temperature and the cerium ion precursor 1.0 mmol of  $\text{Ce}(\text{NO}_3)_3$  was added to the former solution under continuous stirring.  $[\text{Ce}]^{3+} : [\text{PW}_{12}\text{O}_{40}]^{3-}$  molar ratio was adjusted to 1:1, corresponding to the stoichiometry of the Ce salt. After the solution of Ce salt was stirred for 1 h, the excess water was removed on water bath. 10.0 mL of aqueous solution of CeTPA (0.2 g) was added drop wise to support SGP (2.0 g). After impregnating for 4 h, the catalysts was filtered and dried at 110 °C for 6 h. Then, the catalyst was impregnated with the aqueous solution residue for 4 h again, next dried at 110 °C for 6 h. Finally the catalyst was calcined at 400 °C for 4 h. The catalysts were represented as x% CeTPA/SGP, where x represents the weight percentage of CeTPA on the catalyst.

### 2.2. Catalyst characterization

$\text{N}_2$  sorption curves of the catalysts were measured at 77 K on Autosorb-IQ-C analyzer (Quantachrome, America). The elemental analysis of the samples was measured using an Optima-2000DV ICP atomic emission spectrometer. The XRD patterns of the catalysts were obtained by PERSEE XD3 diffractometer using CuK $\alpha$  radiation at 36 kV, 20 mA. X-ray photoelectron spectroscopy (XPS) was carried out on a ESCALAB 250Xi spectrometer. The fourier transform infrared (FT-IR) spectra were collected by a Thermo Nicolet 6700 FTIR spectrometer. Acidity of the catalysts was determined via temperature-programmed desorption of  $\text{NH}_3$  ( $\text{NH}_3$ -TPD) using an automatic multi-purpose adsorption instrument TP-5080.

### 2.3. Catalyst evaluation

The esterification of levulinic acid with ethanol was performed in a vertical fixed-bed reactor with stainless steel tube using 1.0 mL catalyst (30 mesh). The solution of levulinic acid in ethanol (the mole ratio of LA and ethanol 1:8) was swept into the reactor at flow rate of 0.1 mL/min. The reaction mixture was collected and analyzed without preliminary separation by offline gas chromatograph (GC) equipped with a SE-54 capillary column and FID detector.

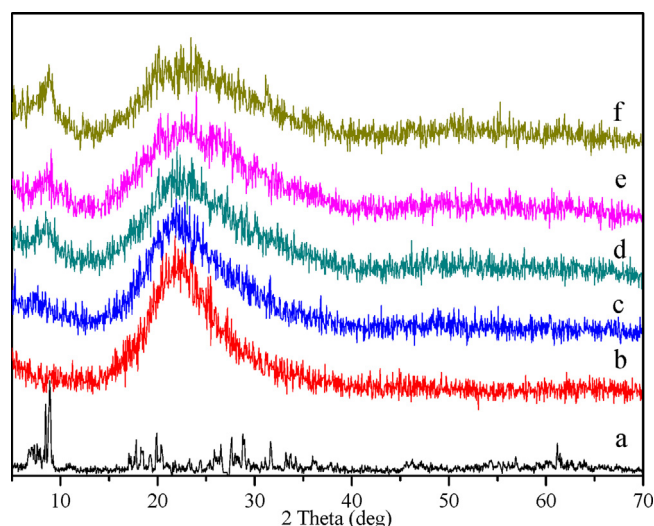


Fig. 1. XRD patterns of (a) TPA, (b) SGP, (c) 10% CeTPA/SGP, (d) 20% CeTPA/SGP, (e) 30% CeTPA/SGP, (f) 40% CeTPA/SGP.

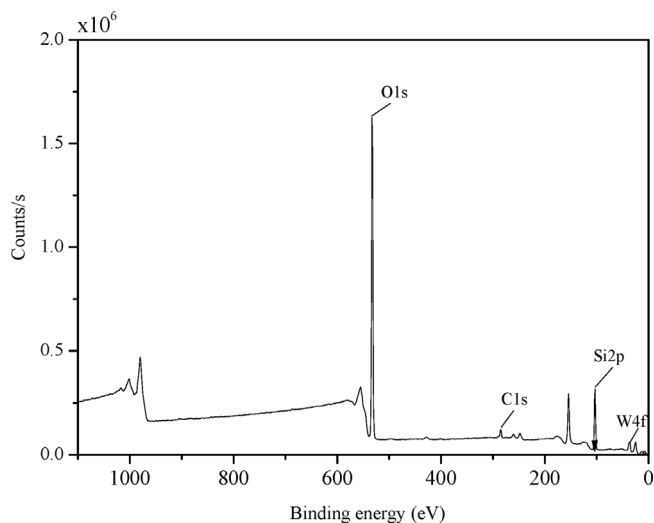


Fig. 2. Full XPS spectra of the 30% CeTPA/SGP.

## 3. Results and discussion

### 3.1. Catalyst characterization

The composition and textural properties CeTPA/SGP are listed in Table 1. The surface area of CeTPA/SGP catalysts are smaller than that of the parent support. And with the increase of the CeTPA content, the surface area of CeTPA/SGP catalyst are decreased slightly as well as the pore volume. The variation in the sorption properties of the catalysts may be due to the pore blockage by supported CeTPA according to previous studies [17–19].

Fig. 1. shows the XRD patterns of the parent support pure TPA, SGP and CeTPA supported catalysts. SGP support exhibits a broad peaks at  $2\theta$  range from 15° to 30°, demonstrated the amorphous behavior of the support, and the density of this diffraction peaks is reduced with the addition of CeTPA content. The diffraction peaks of Keggin ion of TPA can be observed on all the CeTPA supported catalysts at around 8.7°, demonstrated that the Keggin ion structure of TPA was kept unchanged in CeTPA/SGP catalysts [17–19].

Figs. 2–5 shows the XPS of Full XPS, W4f, P 2p and Ce 3d of 30% CeTPA/SGP catalyst. As can be found the Full XPS of CeTPA/SGP was similar with that of the pure TPA (Fig. S1). The W (VI) oxidation state

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