Direct Production of Ethyl Levulinate from Carbohydrates Catalyzed by H-ZSM-5 Supported Phosphotungstic Acid

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A series of supported phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) catalysts, including HPW/β, HPW/Sn-β, HPW/H-Y, HPW/H-ZSM-5, HPW/USY, HPW/ReUSY, and HPW/SBA-15, were prepared using an impregnation method for alcoholysis of fructose to ethyl levulinate in ethanol. Among these catalysts, HPW/H-ZSM-5 showed the highest catalytic activity, and the yield of ethyl levulinate from fructose increased with increasing phosphotungstic acid loading. The yield of ethyl levulinate reached 43.1% at 160 °C for 2 h over 20 wt.% HPW/H-ZSM-5, and the solid catalyst could be reused at least three times. EL yields of 19.1%, 27.3%, 37.4%, and 8.7% could be obtained from glucose, sucrose, inulin, and cellulose, respectively. Furthermore, the catalysts were characterized by BET surface area, X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. HPW/H-ZSM-5 showed good catalytic activity for the direct production of ethyl levulinate from fructose.

Keywords: Ethyl levulinate; Carbohydrates; H-ZSM-5; Phosphotungstic acid

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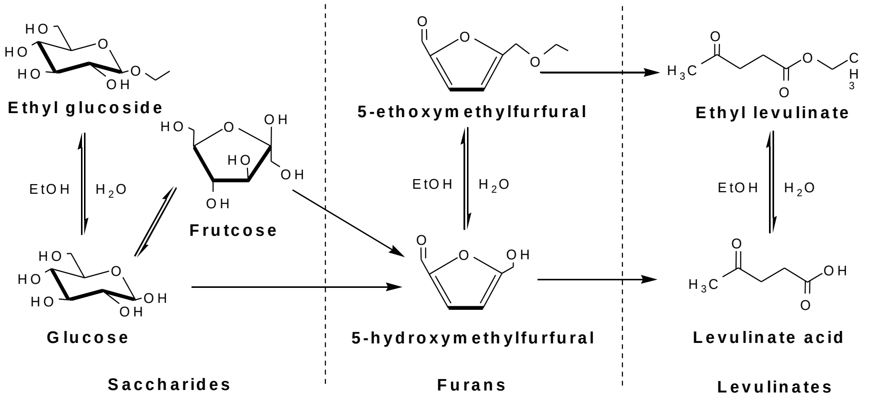
INTRODUCTION

Because of the depletion of fossil resources and increased environmental concerns, the development and utilization of renewable biomass resources has become an object of concern for countries around the world. Biomass can be converted into biofuels and feedstock chemicals that can replace fossil-based chemicals (Bridgwater 2012; Gallezot 2012; Deveci and Kar 2013). Currently, one of the most attractive and promising approaches is to convert biomass into ethyl levulinate (EL), a versatile chemical feedstock. EL can be used as an intermediate in the synthesis of more complex commercial products, as an oxygenate additive in fuels, in the flavoring and fragrance industry, or as a blending component in biodiesel (Joshi *et al.* 2011; Windom *et al.* 2011; Yadav and Yadav 2014).

Production of levulinate esters directly from biomass or biomass-based sugars is a typical acid-catalytic reaction. There have been several reports on the production of levulinate esters using acid catalysts such as liquid acids, ionic liquids, and solid acids (Garves 1988; Peng *et al.* 2011; Saravanamurugan *et al.* 2011; Chang *et al.* 2012; Yan *et al.* 2013; Chen *et al.* 2014b; Zhu *et al.* 2014). For instance, Chang *et al.* (2012) reported production of EL by direct conversion of wheat straw over sulfuric acid. Peng *et al.* (2012) reported that glucose can be directly converted to methyl levulinate using an extremely low concentration of sulfuric acid as the acid catalyst. This is efficient and economical for biomass conversion. Although the acid concentration of extremely low sulfuric acid is lower than 0.01 M, it is still harmful to the environment and corrosive to equipment to some extent. Saravanamurugan *et al.* (2011) synthesized different sulfonic acid-functionalized ionic liquids to catalyze conversion of carbohydrates into EL. However, the cost of ionic liquids is high and the reaction time is quite long. Saravanamurugan and Riisager (2013) presented the transformation of carbohydrates to methyl levulinate and EL over various zeolites and found that one of them (H-USY) gave the highest yield of methyl levulinate and EL. Solid acid catalysts are generally preferable in catalysis because of their easy separation, recyclability, and lack of equipment corrosion (Peng *et al.* 2011). Several researchers have prepared levulinate esters as raw materials from levulinic acid, furfural, and furfuryl alcohol (Lange *et al.* 2009; Fernandes *et al.* 2012; Chen *et al.* 2014a).

In recent years, heteropolyacids have been widely used in acid-catalyzed reactions because of their strong Brønsted acidity, high proton mobility, and the ability to accept and release electrons (Kozhevnikov 1998; Yang *et al.* 2012a; Wang *et al.* 2013). However, some of the major problems limiting the application of phosphotungstic acid in industry include their low surface areas and difficulty of separation from reaction mixtures (Sawant *et al.* 2007; Maheria *et al.* 2013). Recently, Chen *et al.* (2014b) reported that a high EL yield was obtained from fructose by making use of ionic liquid-based polyoxometalat salts; however, the cost of the catalyst was quite expensive, which may limit its industrial application. Immobilizing soluble acids on an insoluble support is a strategic way to transform the high performance of soluble acids into heterogeneous solid catalysts. H-ZSM-5 is commercially available at a low cost and has a large surface area, so it may appropriately act as an inorganic support for the immobilization homogeneous catalysts to prepare various heterogeneous catalysts. To date, the study of the direct production of EL from carbohydrates catalyzed by supported phosphotungstic acid over zeolites has rarely been reported. The reaction pathway for alcoholysis of saccharides to ethyl levulinate was shown in Scheme 1 (Yang *et al.* 2012b). In this paper, $H_3PW_{12}O_{40}$/H-ZSM-5 (HPW/H-ZSM-5) was prepared and exhibited higher activity in the synthesis of EL directly from carbohydrates in ethanol than those of the other supported phosphotungstic acid catalysts.



Scheme 1. Reaction pathway for alcoholysis of saccharides to ethyl levulinate

EXPERIMENTAL

Materials

Ethyl levulinate, used for calibration, with a purity of over 99%, was obtained from Aladdin Reagent (Shanghai, China). SBA-15 was purchased from Nanjing XFNANO Materials Technology (Nanjing, China). Zeolites β, H-ZSM-5, USY, ReUSY, and H-Y were purchased from Nankai University (Tianjin, China). Ethanol, fructose, and phosphotungstic acid hydrate were purchased from Kermel Chemical Reagent (Tianjin, China). All reagents were of analytical grade and were used without further purification. De-ionized water was used for all experiments.

Methods

Catalyst preparation

A series of supported phosphotungstic acid catalysts was prepared using a wet impregnation method. Typically, phosphotungstic acid hydrate ($H_3PW_{12}O_{40}{\cdot}xH_2O$) was dried at 110 °C for 6 h. Afterwards, a desired amount of HPW (*e.g.*, 0.4 g for 20 wt.%) was dissolved in 20 mL of a 1:1 (v/v) mixture of ethanol and water, and 1.6 g of H-ZSM-5 was added to this solution with stirring at room temperature overnight. The mixture was dried at 120 °C for 12 h and calcined at 350 °C for 4 h. The 20 wt.% HPW supported over the H-ZSM-5 zeolite was designated 20 wt.% HPW/H-ZSM-5. Sn-β was prepared as per the procedure reported by Dijkmans *et al.* 2013. HPW/β, HPW/SBA-15, HPW/USY, HPW/ReUSY, HPW/H-Y (all 20 wt.% loading), 10 wt.% HPW/H-ZSM-5, and 30 wt.% HPW/H-ZSM-5 were prepared similarly.

Catalytic reaction procedure

The experiments were performed in a 12-mL cylindrical, stainless steel, pressurized reactor. For each experiment, fructose (120 mg), anhydrous ethanol (6 mL), and a given weight of solid acid catalyst were added to the reactor. The reactor was then brought to the desired temperature using external heating. Time zero was recorded when the set temperature was reached. After running the reaction for a desired duration, the reactor was cooled down in a cool water bath to terminate the reaction. The product and solid acid catalyst were separated by filtration. The recovered catalyst was washed with water and ethanol three times each and dried at 120 °C overnight. Then, it was calcined at 350 °C for 4 h before being reused in a new experiment under the same reaction conditions.

Products analysis

Ethyl levulinate was determined using a gas chromatograph equipped with a flame ionization detector (FID). EL was separated on an FFAP capillary column (30 m × 0.32 mm × 0.33 μm) at a programmed temperature range of 90 to 210 °C with nitrogen as the carrier gas. The amount of ethyl levulinate was calculated using standard curves based on 1-octanol as an internal standard.

Catalyst characterization

X-ray powder diffraction patterns of the samples were determined using a BRUKER X-ray diffractometer (D8 Advance, Bruker, Germany) with a Cu Kα radiation source operated at 40 kV and 40 mA. Data were collected from 2θ between 10^o and 80^o with a step of 0.02^o at a scanning speed of 3 degrees/min. Fourier transform infrared (FT-

IR) spectra were obtained using a spectrometer (Nicolet 6700, Thermo Fisher Scientific, USA) at a spectral resolution of 4 cm^{-1} in the wave number range of 4000 to 400 cm^{-1}. The porous properties of the samples were analyzed using nitrogen adsorption-description isotherms that were obtained using a Micromeritics analyzer (Tristar II 3020, Micromeritics, USA) at 77 K. The Brunaer-Emmett-Teller (BET) and Barrett-Johner-Halendar (BJH) theories were used for surface area determination and pore size distribution calculation, respectively. X-ray photoelectron spectroscopy (XPS) was conducted on a system (Escalab 250, Thermo Fisher Scientific, USA) with an Al Kα radiation source. The binding energies for each spectrum were calibrated with a C 1s spectrum of 284.6 eV. Survey spectra for each sample over a binding energy range of 0 to 1100 eV were recorded at pass energy of 160 eV and resolution of 0.05 eV per step.

RESULTS AND DISCUSSION

Effect of Various Supported Phosphotungstic Acid Catalysts on EL Yield

A series of supported phosphotungstic acid catalysts, including HPW/β, HPW/Sn-β, HPW/H-Y, HPW/H-ZSM-5, HPW/USY, HPW/ReUSY, and HPW/SBA-15 (all 20 at wt.% loading), was first employed for the production of EL from fructose in ethanol, and the results are shown in Fig. 1. HPW/H-ZSM-5 had the highest catalytic activity, and the highest EL yield was 40.6%. Thus, H-ZSM-5 was chosen as a suitable supporter for HPW.

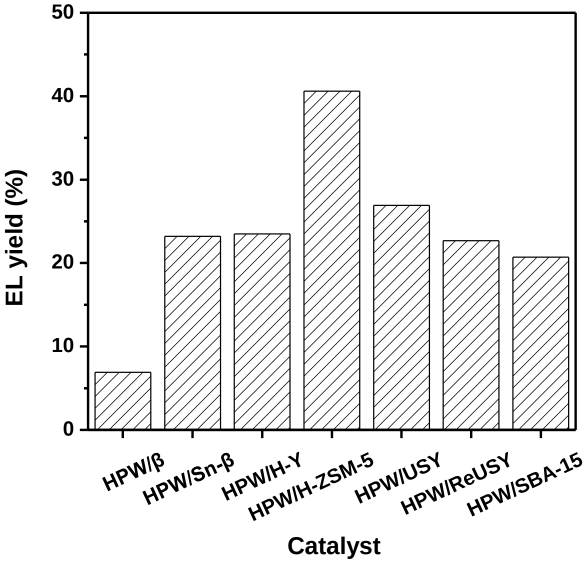


Fig. 1. Effect of HPW supported over different zeolites on the synthesis of EL from fructose. Reaction conditions: fructose, 120 mg; catalyst, 120 mg; ethanol, 6 mL; temperature, 160 °C; time, 2 h.

Catalyst Characterization and Performance of Different HPW Loadings

The structural features of catalysts with various HPW loadings are listed in Table 1. The surface areas of catalysts decreased with increasing HPW loading, possibly because of the coverage of the pore structure by HPW. Hence, pore volume and pore diameter also decreased with increasing HPW loading.

Table 1. Structural Features of Catalysts with Different HPW Loadings

Entry	Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
1	H-ZSM-5	251.77	0.137	2.18
2	10 wt.% HPW/H-ZSM-5	205.63	0.107	2.09
3	20 wt.% HPW/H-ZSM-5	195.52	0.099	2.03
4	30 wt.% HPW/H-ZSM-5	183.75	0.093	1.92

XRD diffractograms of H-ZSM-5, HPW/H-ZSM-5, and HPW samples are shown in Fig. 2. Diffraction peaks of HPW appeared at 10.2°, 25.4°, and 34.6°, similar to results reported by Chai *et al.* (2008). Weak diffraction peaks at 10.2°, belonging to HPW, were detected on the catalyst when the loading was 10 wt.%. When HPW loading reached 20 wt.% and 30 wt.%, the characteristic diffraction peaks of HPW appeared at 2θ = 10.2°, 25.4°, and 34.6°, indicating that HPW was successfully immobilized on H-ZSM-5. Moreover, the characteristic diffraction peaks at 2θ = 22° to 25° for H-ZSM-5 and HPW/H-ZSM-5 samples were indicative of the presence of the H-ZSM-5 structure, demonstrating that this structure was not destroyed during catalyst preparation.

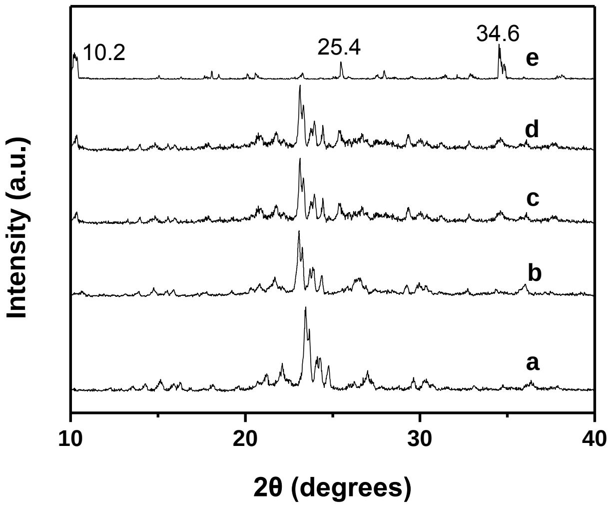


Fig. 2. Powder X-ray diffraction patterns: (a) H-ZSM-5; (b) 10 wt.% HPW/H-ZSM-5; (c) 20 wt.% HPW/H-ZSM-5; (d) 30 wt.% HPW/H-ZSM-5; (e) HPW

Typical FT-IR spectra with different loadings of HPW over H-ZSM-5 are shown in Fig. 3. There were four main absorption bands assigned for the Keggin structure of HPW, at 1082 cm^{-1} (P-O_a), 992 cm^{-1} (W-O_d), 889 cm^{-1} (W-O_b), and 800 cm^{-1} (W-O_c) (Ghanbari-Siahkali *et al.* 2000). The bands were ascribed to asymmetric bond stretching vibration.

Figure 3(a) shows a typical broad band around 1300 to 1000 cm^{-1} that was assigned to the Si-O-Si asymmetric stretching vibration of H-ZSM-5. The characteristic bands of HPW in the catalysts were observed at 992 and 889 cm^{-1} in Fig. 3(b), (c), and (d), indicating that the Keggin structure remained with HPW loading on H-ZSM-5.

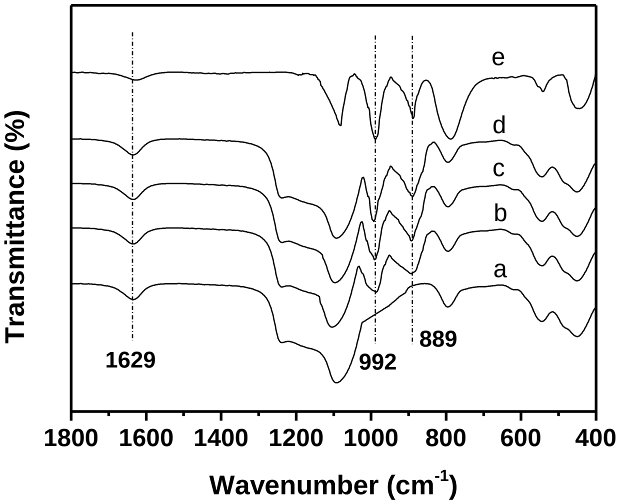


Fig. 3. FT-IR spectra: (a) H-ZSM-5; (b) 10 wt.% HPW/H-ZSM-5; (c) 20 wt.% HPW/H-ZSM-5; (d) 30 wt.% HPW/H-ZSM-5; (e) HPW

The effect of HPW loading over H-ZSM-5 on the EL yield was investigated further. As shown in Table 2, EL yield increased with increasing HPW loading. When support H-ZSM-5 was used as a catalyst, the EL yield was only 1.4%. This result suggested that the acidity of H-ZSM-5 was lower for alcoholysis of fructose. When 10 wt.% HPW/H-ZSM-5, 20 wt.% HPW/H-ZSM-5, and 30 wt.% HPW/H-ZSM-5 were used as catalysts, EL yields of 18.3%, 40.6%, and 35.7% were obtained, respectively. For comparison, the homogeneous HPW was also used to catalyze alcoholysis of fructose to EL, and its amount was equal to that of 20 wt.% HPW/H-ZSM-5. The results showed that the highest EL yield was 49.8%. Although HPW showed higher catalytic activity, it was difficult to separate from the reaction medium. Considering its high EL yield and easy separation of catalyst, 20 wt.% HPW/H-ZSM-5 was chosen as the catalyst for alcoholysis of fructose in subsequent exploration.

Table 2. Synthesis of EL from Fructose using Various HPW Loadings over H-ZSM-5

Entry	Catalyst	Catalyst amount (mg)	EL yield (%)
1	H-ZSM-5	120	1.4
2	10 wt.% HPW/H-ZSM-5	120	18.3
3	20 wt.% HPW/H-ZSM-5	120	40.6
4	30 wt.% HPW/H-ZSM-5	120	35.7
5	HPW	24	49.8

Reaction conditions: fructose, 120 mg; ethanol, 6 mL; temperature, 160 °C; time, 2 h

Effect of Reaction Temperature on EL Yield

The effect of reaction temperatures varying from 140 to 180 °C on EL yield, using a 20 wt.% HPW/H-ZSM-5 catalyst, was studied. It can be seen from Fig. 4 that reaction temperature plays an important role in the reaction. When the temperature was 140 °C, the EL yield increased quickly at the beginning of the reaction. After 2 h, the EL yield increased slowly as the reaction time was prolonged. At 160 °C, a similar EL yield trend can be observed, but the EL yield was noticeably higher than that at 140 ^{o}C because of the increase in temperature. However, when the reaction was performed at 180 ^{o}C, it was found that the EL yield peaked earlier, at 1 h. After this point, the EL yield began to decrease gradually as time increased, indicating that higher temperatures are unfavorable for increasing EL yield. This is due to the conversion of EL into γ-valerolactone and 3-(1-ethoxyethoxy)-2-methylbutanal, which were detected by GC-MS.

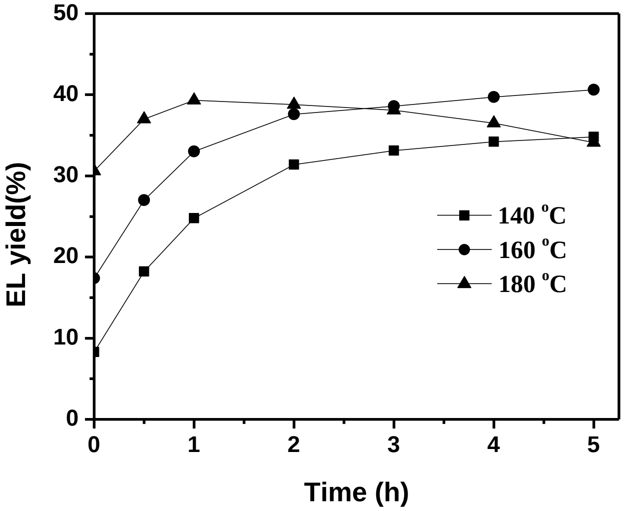


Fig. 4. Effect of reaction temperature on EL yield. Reaction conditions: fructose, 120 mg; 20 wt.% HPW/H-ZSM-5, 120 mg; ethanol, 6 mL

Effect of Catalyst Amount on EL Yield

Using 20 wt.% HPW/H-ZSM-5 as the acid catalyst, the effect of catalyst amounts ranging from 60 mg to 180 mg on EL yield was investigated. It can be seen from Fig. 5 that increasing catalyst amounts will increase the EL yield at 160 °C. When the catalyst amount was 60 mg, the EL yield increased slowly as time increased, and it required a longer reaction time to reach a higher level due to the lower acidity. When the catalyst amount was increased to 120 mg, the EL yield increased significantly and the yield also increased gradually as the reaction time was prolonged. As expected, the EL yield increased further when the catalyst amount was raised to 180 mg. The highest EL yield for this amount (43.1%) was obtained at 2 h. After that, it was almost constantly maintained. As time increased, the EL yield obtained with the 120 mg catalyst was close to that obtained using the 180 mg catalyst.

Conversion of Various Carbohydrates

Carbohydrates such as glucose, sucrose, inulin, and cellulose were also used as raw materials for the direct production of EL over a 20 wt.% HPW/H-ZSM-5 catalyst (Fig. 6). It was found that the yield of EL from glucose was 19.1%, which was much lower than that from fructose, suggesting fructose is rather easier to synthesize EL with than is glucose. Sucrose, consisting of one glucose and one fructose unit, was converted into EL with a medium yield of 27.3%. The EL yield from inulin, consisting of fructose units, was 37.4%, which was similar to the EL yield from fructose. Furthermore, the yield of EL from cellulose was only 8.7% at 220 °C, which was the lowest yield among the carbohydrates. This is because cellulose consists of D-anhydroglucopyranose units joined together in long chains by β-1,4-glycosidic bonds and the structure is quite stable because of the tight hydrogen-bonding network and van der Waals interactions (Dadi *et al.* 2006; Watanabe 2010). In addition, the insolubility of cellulose in ethanol may also resulted in the low yield. Consequently, cellulose was more difficult to convert into EL compared with the other carbohydrates.

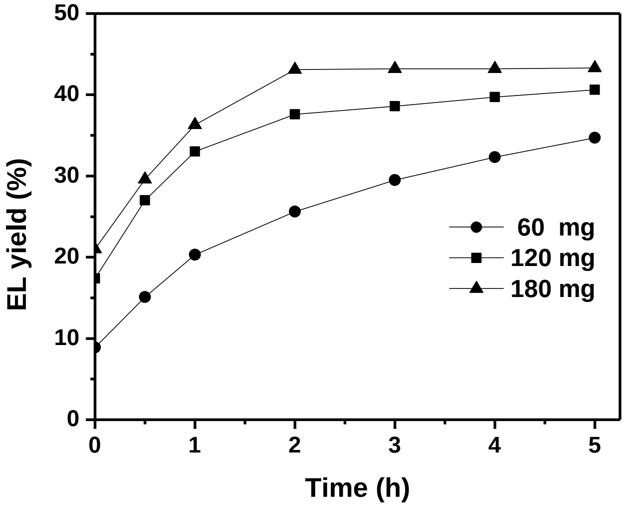


Fig. 5. Effect of catalyst amount on EL yield using 20 wt.% HPW/H-ZSM-5. Reaction conditions: fructose, 120 mg; ethanol, 6 mL; reaction temperature, 160 ^{o}C

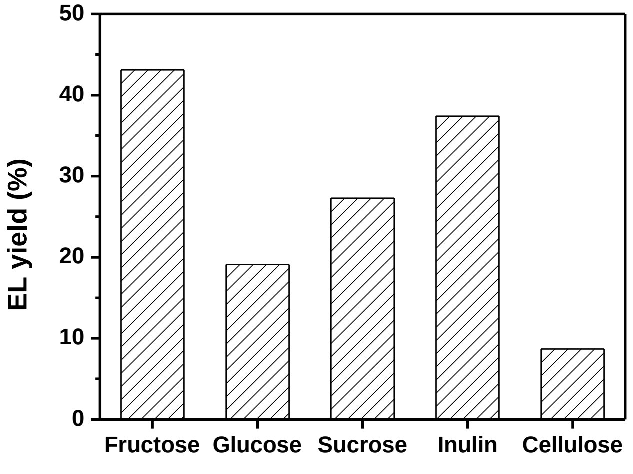


Fig. 6. Effect of various carbohydrates on EL yield. Reaction conditions: carbohydrate amount, 120 mg; 20 wt.% HPW/H-ZSM-5, 180 mg; ethanol, 6 mL; reaction temperature, 220 °C (cellulose) and 160 °C (other carbohydrates); reaction time, 2 h

Catalyst Recycling

The reusability of 20 wt.% HPW/H-ZSM-5 was studied for four cycles under identical experimental conditions. The catalyst was filtered, washed, and calcined at 350 °C for 4 h after completing each reaction. As can be seen in Fig. 7, activity decreased with increasing numbers of catalyst recycling. An EL yield of 32.8% was obtained after calcination in the second run, indicating that the catalyst activity had not recovered. This may be due to partial loss of HPW in the catalyst dissolved in the reaction mixture. In the third and fourth run, the yields of EL were 26.2% and 23.3%, respectively, showing that catalyst activity gradually decreased.

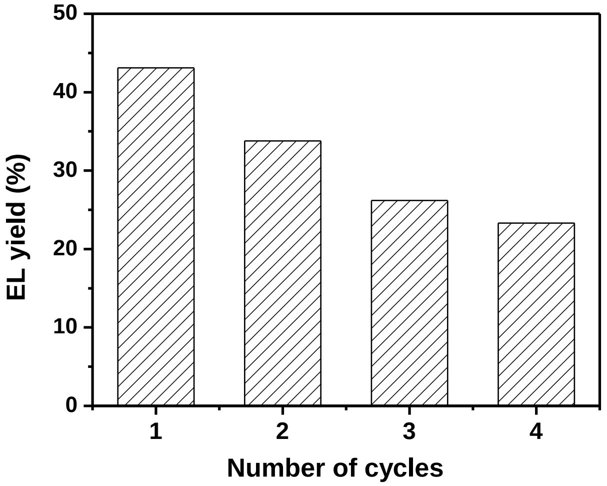


Fig. 7. Catalyst recycling experiments with 20 wt.% HPW/H-ZSM-5. Reaction conditions: reaction temperature, 160 °C; fructose, 120 mg; ethanol, 6 mL; reaction time, 2 h

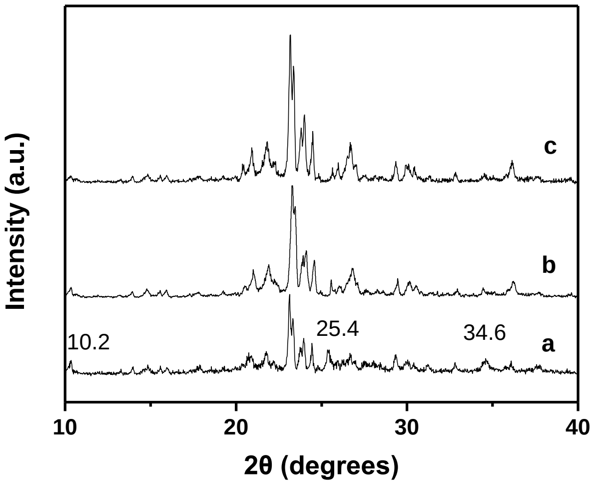


Fig. 8. Powder X-ray diffraction patterns of catalysts: (a) fresh; (b) after first use; (c) after fourth use

The surface structures of fresh and recycled 20 wt.% HPW/H-ZSM-5 catalysts were further characterized by XRD, FT-IR, and XPS, respectively. It can be observed clearly from Fig. 8 that characteristic diffraction peaks of HPW on the recycled catalysts still appeared at 2θ = 10.2^o, 25.4^o, and 34.6^o. Moreover, the two characteristic diffraction peaks were weak after increasing numbers of catalyst recycling, which corresponds with the EL yield results (Fig. 7). The diffraction peaks of H-ZSM-5 increased with catalyst recycling time. Figure 9 shows that the intensity of bands assigned to the Keggin structure of HPW over H-ZSM-5 at 992 and 889 cm^{-1} became weaker with increasing catalyst recycling. Table 3 lists the experimental elemental compositions of the catalysts as confirmed from the XPS spectra analysis. With increasing numbers of catalyst recycling, the content of P and W decreased, indicating that catalyst activity decreased due to the loss of HPW.

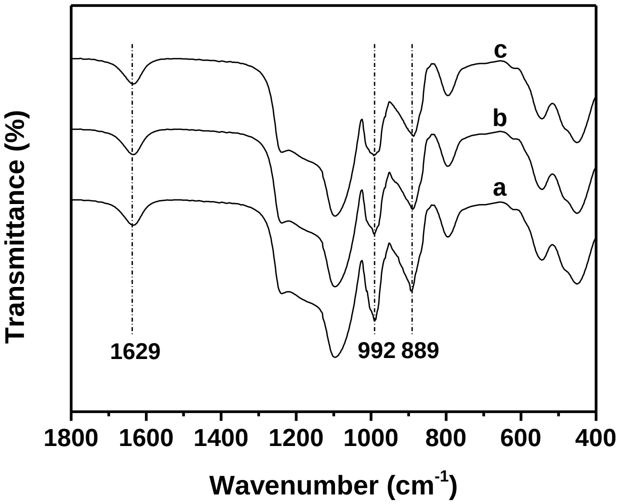


Fig. 9. FT-IR spectra of catalysts: (a) fresh; (b) after first use; (c) after fourth use

Table 3. Experimental Elemental Compositions by XPS Analysis for Fresh and Recycled Catalysts

Catalyst	P (%)	W (%)	O (%)	Si (%)	Al (%)
fresh	0.24	1.66	74.85	21.57	1.68
after first use	0.19	1.29	74.98	21.90	1.64
after fourth use	0.13	0.91	74.52	2.79	1.65

CONCLUSIONS

1. Among all the supported phosphotungstic acid catalysts, 20 wt.% HPW/H-ZSM-5 exhibited the highest catalytic activity in the direct production of EL from fructose in ethanol.
2. EL could be obtained with a high yield of 43.1% at 160 °C for 2 h with fructose as a raw material. Carbohydrates such as glucose, sucrose, inulin, and cellulose were also used as raw materials for the direct production of EL, with yields of 19.1%, 27.3%, 37.4%, and 8.7%, respectively.
3. The catalyst could be easily separated from the reaction mixture by filtration and was further recovered by calcination. Moreover, it could be reused at least three times.

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REFERENCES CITED

Bridgwater, A. V. (2012). "Review of fast pyrolysis of biomass and product upgrading," *Biomass Bioenerg.* 38, 68-94. DOI: 10.1016/j.biombioe.2011.01.048

Chai, S. H., Wang, H. P., Liang, Y., and Xu, B. Q. (2008). "Sustainable production of acrolein: Gas-phase dehydration of glycerol over 12-tungstophosphoric acid supported on ZrO_2 and SiO_2," *Green Chem.* 10(10), 1087-1093. DOI: 10.1039/b805373a

Chang, C., Xu, G. Z., and Jiang, X. X. (2012). "Production of ethyl levulinate by direct conversion of wheat straw in ethanol media," *Bioresour. Technol.* 121, 93-99. DOI: 10.1016/j.biortech.2012.06.105

Chen, B. F., Li, F. B., Huang, Z. J., Lu, T., Yuan, Y., and Yuan G. Q. (2014a). "Integrated catalytic process to directly convert furfural to levulinate ester with high selectivity," *ChemSusChem* 7(1), 202-209. DOI: 10.1002/cssc.201300542

Chen, J. Z., Zhao, G. Y., and Chen, L. M. (2014b). "Efficient production of 5-hydroxymethylfurfural and alkyl levulinate from biomass carbohydrate using ionic liquid-based polyoxometalate salts," *RSC Adv.* 4(8), 4194-4202. DOI: 10.1039/c3ra45632c

Dadi, A. P., Varanasi, S., and Schal, C. A. (2006). "Enhancement of cellulose saccharification kinetics using an ionic liquid pretreatment step," *Biotechnol. Bioeng.* 95(5), 904-910. DOI: 10.1002/bit.21047

Deveci, H., and Kar, Y. (2013). "Adsorption of hexavalent chromium from aqueous solutions by bio-chars obtained during biomass pyrolysis," *J. Ind. Eng. Chem.* 19(1), 190-196. DOI: 10.1016/j.jiec.2012.08.001

Dijkmans, J., Gabriëls, D., Dusselier, M., de Clippel, F., Vanelderen, P., Houthoofd, K., Malfliet, A., Pontikes, Y., and Sels, B. F. (2013). "Productive sugar isomerization with highly active Sn in dealuminated β zeolites," *Green Chem.* 15(10), 2777-2785. DOI: 10.1039/c3gc41239c

Fernandes, D. R., Rocha, A. S., Mai, E. F., Mota, Claudio, J. A., and da Silva, T. (2012). "Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts," *Appl. Catal. A* 425-426, 199-204. DOI: 10.1016/j.apcata.2012.03.020

Gallezot, P. (2012). "Conversion of biomass to selected chemical products," *Chem. Soc. Rev.* 41(4), 1538-1558. DOI: 10.1039/c1cs15147a

Garves, K. (1988). "Acid catalyzed degradation of cellulose in alcohols," *J. Wood Chem. Technol.* 8(1), 121-134. DOI: 10.1080/02773818808070674

Ghanbari-Siahkali, A., Philippou, A., Dwyer J., and Anderson, M. W. (2000). "The acidity and catalytic activity of heteropoly acid on MCM-41 investigated by MAS NMR, FTIR, and catalytic tests," *Appl. Catal. A* 192(1), 57-69. DOI: 10.1016/S0926-860X(99)00333-6

Joshi, H., Moser, B. R., Toler, J., Smith, W. F., and Walker, T. (2011). "Ethyl levulinate: A potential bio-based diluent for biodiesel which improves cold flow properties," *Biomass Bioenerg.* 35(7), 3262-3266. DOI: 10.1016/j.biombioe.2011.04.020

Kozhevnikov, I. V. (1998). "Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions," *Chem. Rev.* 98(1), 171-198. DOI: 10.1021/cr960400y

Lange, J. P., van de Graaf, W. D., and Haan, R. J. (2009). "Conversion of furfuryl alcohol into ethyl levulinate using solid acid catalysts," *ChemSusChem* 2(5), 437-441. DOI: 10.1002/cssc.200800216

Maheria, K. C. Kozinski, J., and Dalai, A. (2013). "Esterification of levulinic acid to n-butyl levulinate over various acidic zeolites," *Catal. Lett.* 143(11), 1220-1225. DOI: 10.1007/s10562-013-1041-3

Peng, L. C., Lin, L., Zhang, J. H., Shi, J. B., and Liu, S. J. (2011). "Solid acid catalyzed glucose conversion to ethyl levulinate," *Appl. Catal. A* 397(1-2), 259-265. DOI: 10.1016/j.apcata.2011.03.008

Peng, L. C., Lin, L., and Li, H. (2012). "Extremely low sulfuric acid catalyst system for synthesis of methyl levulinate from glucose," *Ind. Crop. Prod.* 40, 136-144. DOI: 10.1016/j.indcrop.2012.03.007

Saravanamurugan, S., and Riisager, A. (2013). "Zeolite catalyzed transformation of carbohydrates to alkyl levulinates," *ChemCatChem* 5(7), 1754-1757. DOI: 10.1002/cctc.201300006

Saravanamurugan, S., Van Buu, O. N., and Riisager, A. (2011). "Conversion of mono- and disaccharides to ethyl levulinate and ethyl pyranoside with sulfonic acid-functionalized ionic liquids," *ChemSusChem* 4(6), 723-726. DOI: 10.1002/cssc.201100137

Sawant, D. P., Vinu, A., Justus, J., Srinivasu, P., and Halligudi, S. B. (2007). "Catalytic performances of silicotungstic acid/zirconia supported SBA-15 in an esterification of benzyl alcohol with acetic acid," *J. Mol. Catal. A: Chem.* 276(1-2), 150-157. DOI: 10.1016/j.molcata.2007.07.001

Wang, H. L., Deng, T. S., Wang, Y. X., Qi, Y. Q., Hou, X. L., and Zhu Y. L. (2013). "Efficient catalytic system for the conversion of fructose into 5-ethoxymethyl-furfural," *Bioresour. Technol.* 136, 394-400. DOI: 10.1016/j.biortech.2013.02.110

Watanabe, H. (2010). "The study of factors influencing the depolymerisation of cellulose using a solid catalyst in ionic liquids," *Carbohydr. Polym.* 80(4), 1168-1171. DOI: 10.1016/j.carbpol.2010.01.039

Windom, B. C., Lovestead, T. M., Mascal, M., Nikitin, E. B., and Bruno, T. J. (2011). "Advanced distillation curve analysis on ethyl levulinate as a diesel fuel oxygenate and a hybrid biodiesel fuel," *Energy Fuels* 25(4), 1878-1890. DOI: 10.1021/ef200239x

Yadav, G. D., and Yadav, A. R. (2014). "Synthesis of ethyl levulinate as fuel additives using heterogeneous solid superacidic catalysts: Efficacy and kinetic modeling," *Chem. Eng. J.* 243, 556-563. DOI: 10.1016/j.cej.2014.01.013

Yan, K., Wu, G. S., Wen, J. L., and Chen, A. C. (2013). "One-step synthesis of mesoporous $H_4SiW_{12}O_{40}$-SiO_2 catalysts for the production of methyl and ethyl levulinate biodiesel," *Catal. Commun.* 34, 58-63. DOI: 10.1016/j.catcom.2013.01.010

Yang, Y., Abu-Omar, M. M., and Hu, C. W. (2012a). "Heteropolyacid catalyzed conversion of fructose, sucrose, and inulin to 5-ethoxymethylfurfural, a liquid biofuel candidate," *Appl. Energy* 99, 80-84. DOI: 10.1016/j.apenergy.2012.04.049

Yang, Y., Abu-Omar, M. M., and Hu, C. W. (2012b). "Conversion of glucose into furans in the presence of AlCl3 in an ethanol-water solvent system," *Bioresour. Technol.*116 190-194. DOI:10.1016/j.biortech.2012.03.126

Zhu, W. N., Chang, C., Ma, C., and Du, F. G. (2014). "Kinetics of glucose ethanolysis catalyzed by extremely low sulfuric acid in ethanol medium," *Chin. J. Chem. Eng.* 22(2), 238-242. DOI: 10.1016/S1004-9541(14)60049-5

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