Article

Direct Conversion of Carbohydrates into Ethyl Levulinate with Potassium Phosphotungstate as an Efficient Catalyst

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Abstract: A series of metal-modified phosphotungstates were prepared and performed for direct synthesis of ethyl levulinate from fructose in ethanol. Considering the cost of catalysts, catalytic activity of catalysts, and easy separation of catalysts together, K-HPW-1 was chosen as the most suitable catalyst for synthesis of ethyl levulinate from fructose. A high ethyl levulinate yield of 64.6 mol% was obtained at 150 °C within 2 h in ethanol. The introduction of low polar toluene as a co-solvent improved the yield of ethyl levulinate to 68.7 mol%. The recovered catalyst remained high activity with the yield of ethyl levulinate converted from fructose above 50 mol% after being used five times. Moreover, the generality of the catalyst was further demonstrated by glucose, sucrose, inulin, and cellulose with ethyl levulinate yielding 14.5, 35.4, 52.3, and 14.8 mol%, respectively.

1. Introduction

With the gradual diminishment of fossil fuel reserves and increased environmental concerns, it is quite necessary to develop and utilize renewable resources. Carbohydrates derived from biomass are one of the most abundant renewable resources and possess a great potential as raw materials to product fuels and bulk chemicals [1,2]. Among those bio-based products, levulinic acid has been listed as one of the 12 most important building blocks, which can be used for the production of various high-value organic chemicals, such as resin, polymers, pharmaceutical compounds, and flavor substances [3–5]. Therefore, much effort has been devoted to the research for the synthesis of levulinic acid from carbohydrates in the past decades [6–10].

In the recent years, there has been growing interest in the synthesis levulinate esters including methyl, ethyl, and *n*-butyl levulinate. Among these, ethyl levulinate, obtained by esterification of levulinic acid, is a versatile chemical compound and has been widely applied in food industry, as solvents and plasticizers. Besides, it can be used as an additive for transportation fuels, which shows excellent performance [11,12]. It is reported that furfuryl alcohol also can be converted into ethyl levulinate in the presence of an acid catalyst [13]. However, both levulinic acid and furfuryl alcohol need to be prepared from carbohydrates or biomass firstly, and then need to be purified for synthesis of ethyl levulinate. In addition, there is a third route for synthesis of ethyl levulinate that is to be converted from carbohydrates or biomass directly [14–17]. This route provides a convenient one-pot reaction to produce ethyl levulinate. Compared with the former two routes, this route has some advantages, like easy purification, minimized wastewater, and time saving [18]. The three reaction routes are shown in Figure 1.
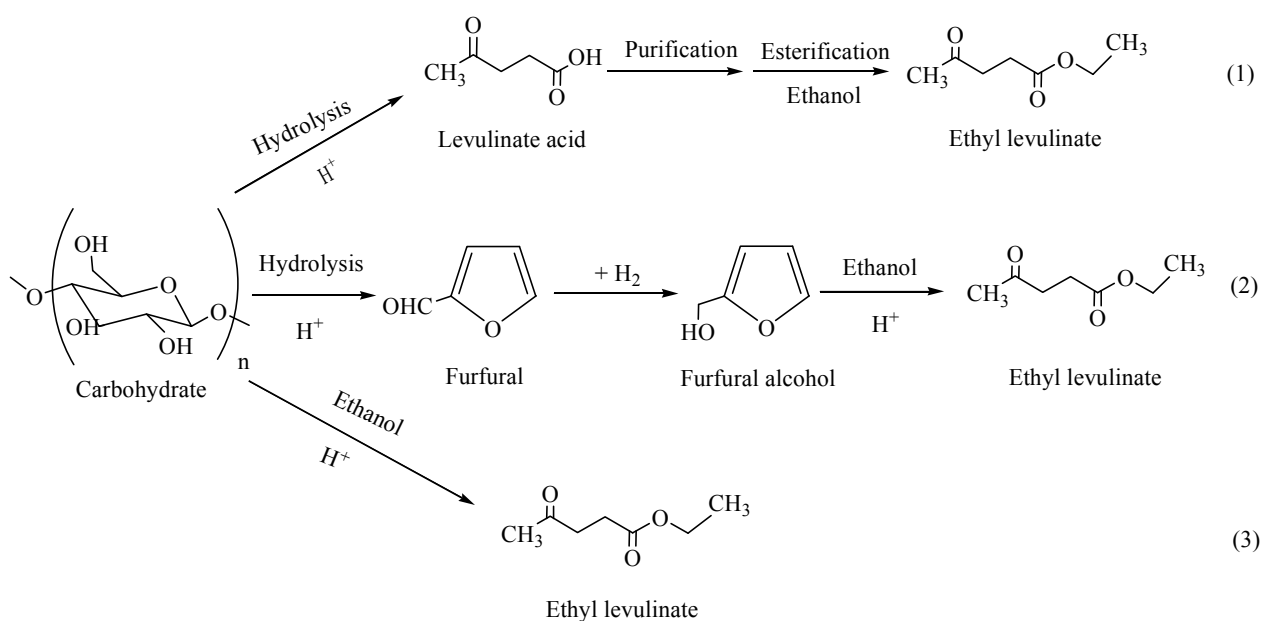

Figure 1. The routes of synthesis of ethyl levulinate.

To improve the direct synthesis of ethyl levulinate from carbohydrates derived from biomass, efficient acid catalysts have been developed, especially heterogeneous acid catalysts. Among various heterogeneous catalysts, Keggin-type heteropolyacid $H_3PW_{12}O_{40}$ (HPW) with a strong Brønsted acidity has attracted much attention [19], but its application was limited due to the high solubility in water and

polar solvents. The substitution of H^+ of HPW by large monovalent cations such as Cs^+, NH_4^+, K^+ and Ag^+ could modify the acidity of HPW and form a range of insoluble solid acid catalysts. Currently, little research on levulinate production from carbohydrates catalyzed by metal-modified phosphotungstates has been reported. Liu has reported that fructose can be efficiently converted into methyl levulinate with the catalysis of Fe-HPW-1, and the methyl levulinate yield of 73.7% was obtained at 130 °C for 2 h [20]. However, Fe-HPW-1 is soluble in the methanol medium, and has to be extracted by diethyl ether for the next use. Herein, it is necessary to develop metal-modified phosphotungstates with high catalytic activity and easy recovery.

In this study, various metal-modified phosphotungstates were prepared to convert ethyl levulinate from fructose in ethanol medium. Among these catalysts, insoluble K-HPW-1 showed highest catalytic activity for direct conversion of fructose into ethyl levulinate with a yield of 64.6 mol%. Meanwhile, toluene as a co-solvent showed a good performance on direct synthesis of ethyl levulinate from fructose. Moreover, the catalytic system was extended to various carbohydrates. This recycling study showed that K-HPW-1 relative to HPW could be facile to separate from reaction mixture by centrifugation and be reused with good catalytic activity.

2. Results and Discussion

2.1. Synthesis of Ethyl Levulinate from Fructose over Various Catalysts

A series of metal-modified phosphotungstates prepared were firstly performed for direct synthesis of ethyl levulinate from fructose in ethanol, and the results are presented in Figure 2. It was reported that insoluble Cs-HPW-2.5 and Cs-HPW-1 have porous structures, relatively high surface areas, and strong acid sites [21], but they did not show good performance for alcoholysis of fructose to ethyl levulinate. The yield of ethyl levulinate decreased with K^+ instead of H^+ in HPW gradually, and this is due to the decrease of Brønsted acidity of potassium phosphotungstates. Compared with other prepared phosphotungstates, Ag-HPW-1, Fe-HPW-1, and K-HPW-1 showed high catalytic activity in terms of synthesis of ethyl levulinate from fructose with yield of 58.1, 52.4, and 50.8 mol%, respectively. However, it was found that Fe-HPW-1 can be dissolved in ethanol, and high volatile and flammable diethyl ether has to be used to recover it [20]. Although ethyl levulinate yield obtained catalyzed by Ag-HPW-1 was a little higher than that of K-HPW-1, $AgNO_3$ that was used to synthesize Ag-HPW-1 was much more expensive than KCl used to synthesize K-HPW-1. Moreover, homogeneous HPW showed the highest activity and remarkably highest selectivity with ethyl levulinate yield of 64.9 mol%. But, HPW is soluble in ethanol medium and is not easy to separate from ethanol. Thus, considering the cost of catalyst, yield of ethyl levulinate, and easy separation of catalyst together, K-HPW-1 was chosen as the suitable catalyst for synthesis of ethyl levulinate from fructose in the subsequent exploration.
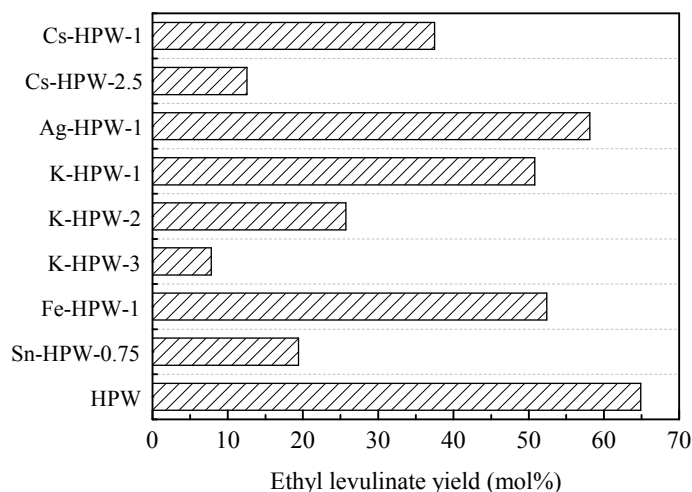
Figure 2. Effect of various catalysts on ethyl levulinate yield. Reaction conditions: fructose 0.8 g, catalyst 0.4 g, ethanol 40 mL, temperature 130 °C, reaction time 2 h.

2.2. Catalyst Characterization

XRD patterns of HPW, K-HPW-1, K-HPW-2, and K-HPW-3 are displayed in Figure 3a. HPW showed typical cubic secondary structure of Keggin anion with characteristic diffraction peaks at 10.2°, 21.3°, 25.3°, and 34.4° [22]. K-HPW-1, K-HPW-2, and K-HPW-3 showed similar XRD patterns to that of HPW and present cubic secondary structure. The results indicated that Keggin structure was not destroyed during catalyst preparation in case of introduction of potassium. Moreover, the intensity of diffraction peaks decreased with the addition of potassium in HPW.
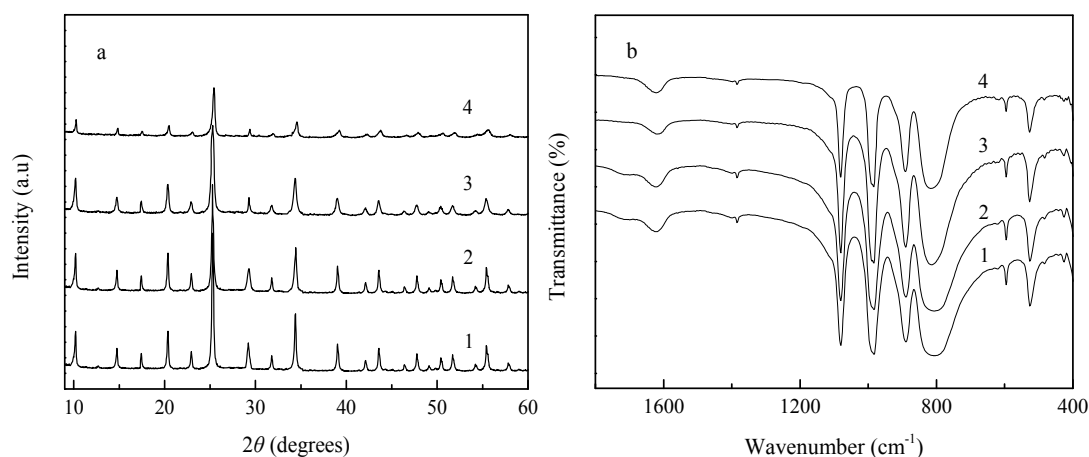

Figure 3. XRD patterns (**a**) and FT-IR spectra (**b**) of HPW, K-HPW-1, K-HPW-2, and K-HPW-3. 1. HPW; 2. K-HPW-1; 3. K-HPW-2; 4. K-HPW-3.

HPW, K-HPW-1, K-HPW-2, and K-HPW-3 were further characterized by FT-IR, and the results are shown in Figure 3b. As reported that Keggin structure is composed of a PO_4 tetrahedron, surrounded by four W_3O_9 groups formed by edge sharing octahedral [23]. The FT-IR spectra of the catalysts shows characteristic peaks of Keggin structure in the range from 700 to 1200 cm^{-1} in Figure 3. Four types of atoms in keggin are the asymmetry vibrations P-O_a (1080 cm^{-1}), W-O_d (983 cm^{-1}), W-O_b (889 cm^{-1}),

and W-O$_c$ (808 cm^{-1}), respectively, which coincides with those referred in the literature [24]. The results further indicated that Keggin structure remained in case of introduction of potassium.

2.3. Effects of Reaction Parameters on Ethyl Levulinate Yield

Effect of reaction temperature varying from 130 to 180 °C on the fructose conversion and product distributions catalyzed by K-HPW-1 is shown in Figure 4a. It can be seen that almost all the fructose has been converted in the process. Meanwhile, ethyl levulinate yield gradually increased with the increase of reaction temperature from 130 to 150 °C. When the reaction temperature was above 150 °C, ethyl levulinate yield began to decrease. This result suggested that higher temperature is unfavorable for alcoholysis of fructose to ethyl levulinate, which is in accordance with our previous report [14]. Moreover, more humins can be observed as the reaction temperature is increased, which means unwanted side reactions were enhanced in the process. Thus, the optimum temperature for ethyl levulinate formation from fructose was 150 °C in this study. In addition, 5-ethoxymethylfurfural and levulinic acid can be detected in the reaction liquid. 5-ethoxymethylfurfural is considered as the intermediate in the formation of ethyl levulinate via cleavage of the aldehyde group on the furfural intermediate, and levulinic acid is the end product of the hydrolysis of 5-hydroxymethylfurfural. Both of them are considered as main products in the reaction process. As shown in Figure 4a, the yield of 5-ethoxymethylfurfural was obviously lower, which means most of them were converted to ethyl levulinate and other products. Moreover, the yield of 5-ethoxymethylfurfural decreased from 8.2 to 1.4 mol% when the temperature increased from 130 to 180 °C, suggesting that high temperature is unfavorable for the production of 5-ethoxymethylfurfural. Meanwhile, the levulinic acid yield was also very low (less than 3.5 mol%) at different temperature. This result suggested that levulinic acid cannot be produced efficiently in ethanol medium.

Effect of catalyst amount ranging from 0.1 to 1.0 g on ethyl levulinate yield was further studied, and the catalyst amount also showed significant effect on ethyl levulinate yield (Figure 4b). It can be seen that ethyl levulinate yield increased from 34.9 to 64.6 mol% when the catalyst amount was increased from 0.1 to 0.6 g. However, ethyl levulinate yield gradually decreased when the catalyst amount was more than 0.6 g, indicating that the increase of catalyst amount cannot improve the ethyl levulinate yield efficiently. The reason may be more catalysts can enhance the side reactions of the process, which results in the decrease of the ethyl levulinate yield. In the experiments, 0.6 g of K-HPW-1 was found to be an ideal amount for the synthesis of ethyl levulinate from fructose in ethanol. Meanwhile, 5-ethoxymethylfurfural yield decreased gradually with the increase of catalyst amount, and levulinic acid yield was almost kept in a low level.

Figure 4c showed the effect of reaction time in terms of the direct synthesis of ethyl levulinate from fructose in ethanol at 150 °C. The ethyl levulinate yield increased during the first 2 h of the reaction process, and then leveled off after 2 h. Meanwhile, the amount of insoluble humins augmented with the increase of the reaction time. Therefore, 2 h was taken as the optimal reaction time for ethyl levulinate production. The yield of 5-ethoxymethylfurfural was 8.2 mol% at 0 h, and then decreased with the prolonging of the reaction time. This is because longer reaction time can result in further conversion of 5-ethoxymethylfurfural to ethyl levulinate [25]. Similarly, the yield of levulinic acid was very low in the

whole process. Therefore, it can be concluded the catalytic system is not adaptable for the synthesis of levulinic acid.
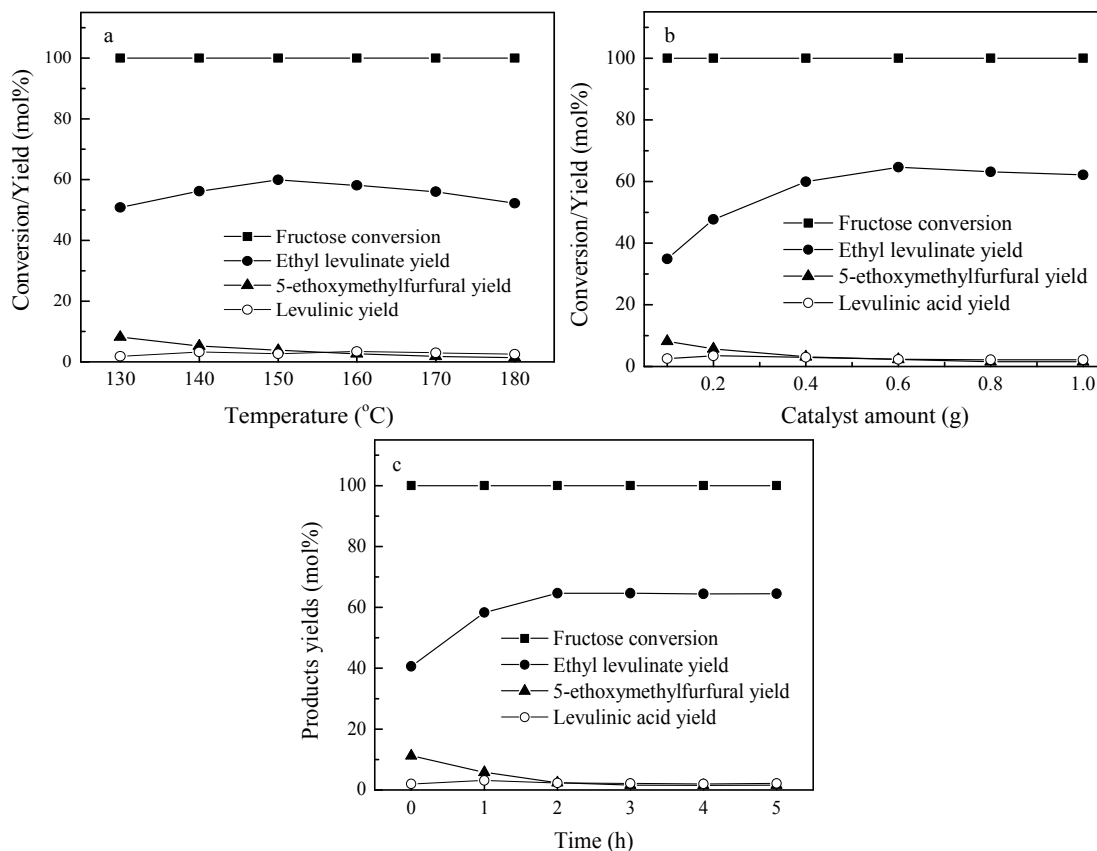

Figure 4. Effect of reaction parameters on product yields. (**a**) effect of temperature. Reaction conditions: fructose 0.8 g, K-HPW-1 0.4 g, ethanol 40 mL, reaction time 2 h; (**b**) effect of catalyst amount. Reaction conditions: fructose 0.8 g, ethanol 40 mL, temperature 150 °C, reaction time 2 h; (**c**) effect of reaction time. Reaction conditions: fructose 0.8 g, K-HPW-1 0.6 g, ethanol 40 mL, temperature 150 °C.

In order to obtain the optimal process conditions for alcoholysis of fructose to ethyl levulinate, an orthogonal experiment was further carried out based on the discussion above. The arrangements of orthogonal experiments with three factors (temperature, catalyst amount, and time) and the analysis results are listed in Table 1. It can be seen that the maximum ethyl levulinate yield is 64.6 mol% under the condition of temperature 150 °C, time 2 h, and catalyst amount 0.6 g, while the lowest ethyl levulinate is 42.3 mol% for temperature 140 °C, time 1 h, and catalyst amount 0.4 g. The most significant influencing among the three factors on ethyl levulinate yield was found to be temperature, followed by time, and catalyst amount. To obtain each factor, the intuitive analyses were performed as shown in Figure 5, based on statistical calculation using the data in Table 1. In summary, the optimization results for high ethyl levulinate production were temperature of 150 °C, time of 2 h, and catalyst amount of 0.6 g.

Table 1. The results of orthogonal experiments.

Entry	Temperature (°C)	Catalyst Amount (g)	Time (h)	Ethyl Levulinate Yield (mol%)
1	140	0.4	1.0	42.3
2	140	0.6	1.5	52.5
3	140	0.8	2.0	53.1
4	150	0.4	1.5	55.8
5	150	0.6	2.0	64.6
6	150	0.8	1.0	54.3
7	160	0.4	2.0	58.1
8	160	0.6	1.0	54.6
9	160	0.8	1.5	57.8
k_1	49.3	52.1	50.4	-
k_2	58.2	57.2	55.4	-
k_3	56.8	55.1	58.6	-
Range	8.9	5.1	8.2	-

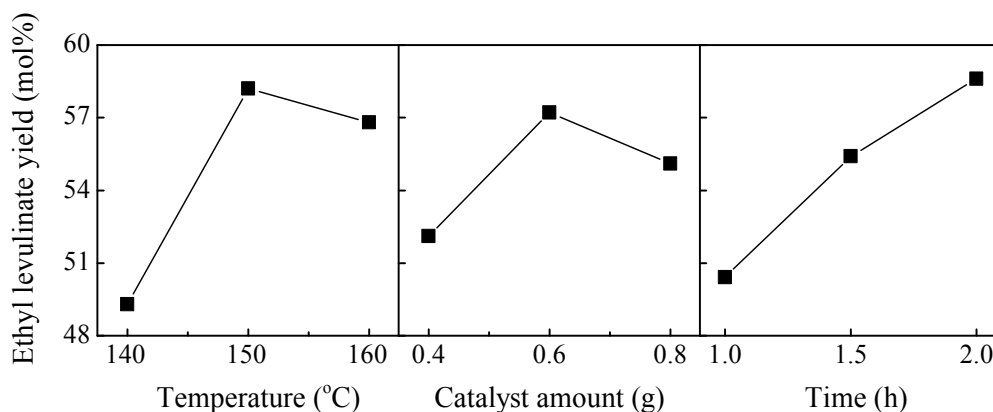Note: k_i, the mean of ethyl levulinate yield at each level; *Range* = $k_{max} - k_{min}$.

Figure 5. Intuitive analysis of the relationship between process conditions (temperature, catalyst amount, and time) and ethyl levulinate yield.

2.4. Effect of Co-Solvents on Synthesis of Ethyl Levulinate from Fructose

To investigate the effect of low-polar organic solvents on ethyl levulinate yield, six organic solvents including n-hexane, toluene, methyl isobutyl ketone (MIBK), acetonitrile, tetrahydrofuran (THF), and 1,4-dioxane were added as co-solvent in ethanol medium, and the results are shown in Figure 6a. It was reported that the introduction of low-polar co-solvent in ethanol may improve the ethyl levulinate yield [26]. However, different solvents show different effects on the yield. As shown in Figure 6a, the addition of *n*-hexane, THF, and 1,4-Dioxane resulted in slightly decreased yield. In comparison, the yield of ethyl levulinate was the lowest when acetonitrile was used as co-solvent, which has the highest polarity. Clearly, toluene showed the best performance on the selectivity of ethyl levulinate with a yield of 61.1 mol%. This is most likely because toluene acted as an effective extracting agent for separating ethyl levulinate and avoiding its further degradation [27]. Thus, toluene can be chosen as a suitable co-solvent in the following exploration.
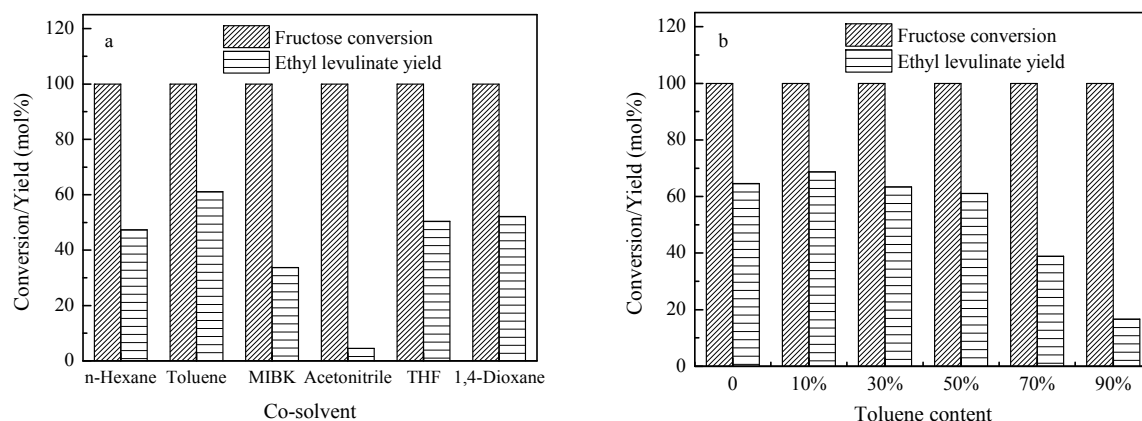
Figure 6. Effect of co-solvents (**a**) and toluene content (**b**) on synthesis of ethyl levulinate from fructose. Reaction conditions: fructose 0.8 g, K-HPW-1 0.6 g, temperature 150 °C, reaction time 2 h, ethanol 20 mL, co-solvent 20 mL (**a**) or ethanol/toluene 40 mL (**b**).

On this basis, effect of toluene content on the synthesis of ethyl levulinate from fructose was further studied and the results are shown in Figure 6b. When the toluene content was 10%, the yield of ethyl levulinate in the ethanol/toluene media was 68.7 mol%, which was higher than that of 64.6 mol% in pure ethanol media. In this reaction, 10% volume fraction of toluene may protect ethyl levulinate and suppress the side reactions during the reaction process. However, the yield of ethyl levulinate decreased with further increase of the toluene content, and it was found that the formation of humins was also increased. Therefore, 10% volume fraction of toluene can be chosen as the optimum content.

2.5. Catalyst Recycling

Recycling experiments for K-HPW-1 were carried out for the conversion of fructose to ethyl levulinate in ethanol/toluene medium under identical experimental conditions. Figure 7 shows the results from recycling K-HPW-1 for five consecutive runs. In the first run, the yield of ethyl levulinate was 68.7 mol%. With the increasing numbers of catalyst recycling, the yield of ethyl levulinate decreased gradually. After being used for five runs, the yield of ethyl levulinate was still above 50 mol%, indicating K-HPW-1 has a long lifetime for the conversion of fructose.
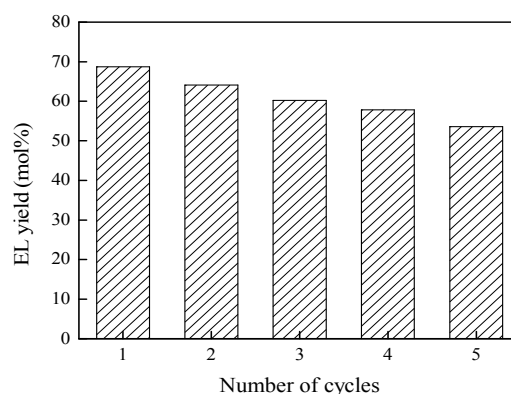

Figure 7. Catalyst recycling experiments with the insoluble K-HPW-1 catalyst. Reaction conditions: fructose 0.8 g, K-HPW-1 0.6 g, toluene 4 mL, ethanol 36 mL, temperature 150 °C, reaction time 2 h.

The surface structures of fresh and recycled K-HPW-1 catalysts were characterized by XRD, FT-IR and SEM, respectively. In Figure 8, characteristic diffraction peaks of HPW on the recycled catalyst still appeared at 2θ = 10.2°, 21.3°, 25.3°, and 34.4°. Figure 8b also show the characteristic bands of HPW in the catalysts were observed at 1080, 992, 889, and 808 cm^{-1} in Figure 8b. Both of them indicated the Keggin structure remained in the recycled catalyst K-HPW-1. Besides, the surface morphologies of the fresh and recycled K-HPW-1 catalysts were also observed by SEM, and the results are shown in Figure 9. Figure 9a presented the distinguishable and homogeneous morphology of the fresh K-HPW-1 catalyst at the levels of 20,000 times magnification, and Figure 9b showed a ruleless and fuzzy morphology of the recycled catalyst after five runs. Besides, the color of the catalyst was changed from white to dark gray. These morphology and color differences are attributed to the carbon deposition caused by degradation of products.
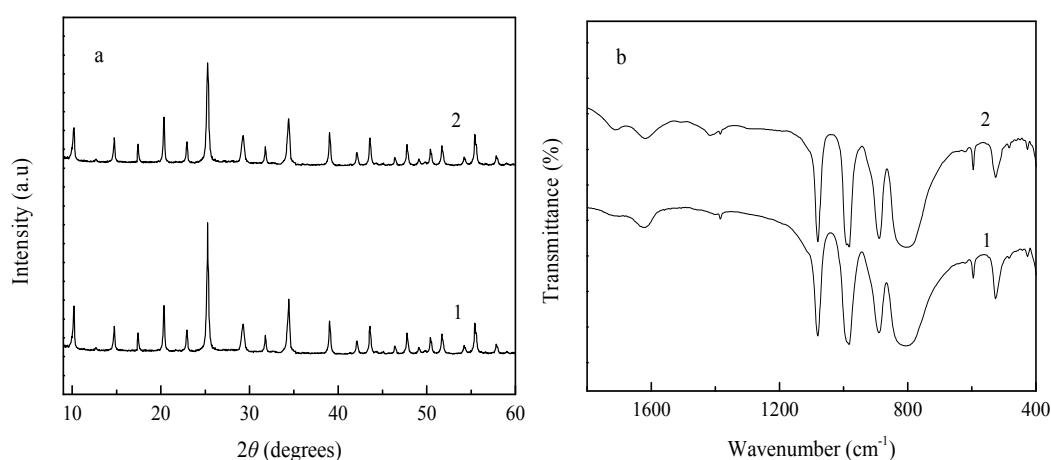

Figure 8. XRD patterns (**a**) and FT-IR spectra (**b**) of fresh and recycled K-HPW-1. 1. Fresh catalyst; 2. Recycled catalyst after five runs.
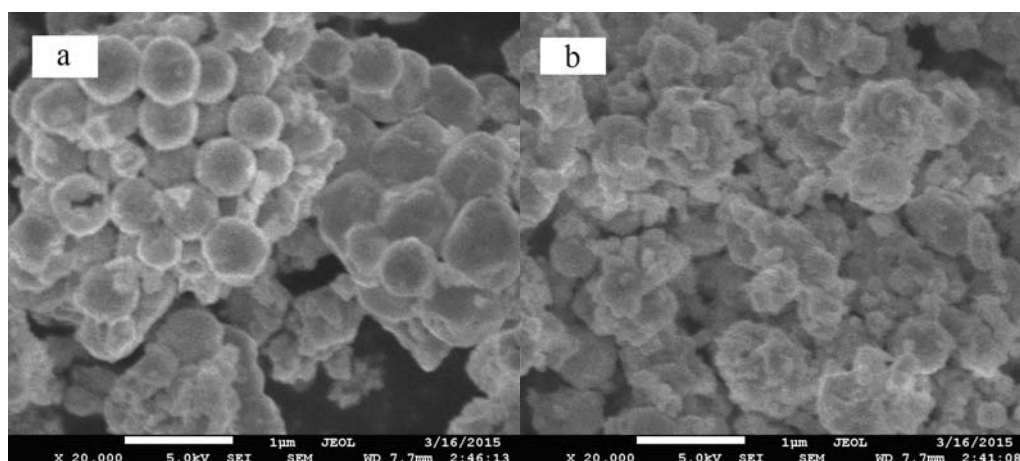

Figure 9. SEM images for fresh catalyst (**a**) and recycled catalyst after five runs (**b**).

2.6. Effect of Various Raw Materials on Synthesis of Ethyl Levulinate

In order to evaluate the generality of the catalyst for the synthesis of ethyl levulinate, the insoluble K-HPW-1 catalyst was further extended to the other carbohydrates such as glucose, sucrose, inulin, and

cellulose. As shown in Table 2. Fructose gave the highest yield of ethyl levulinate, while the yield of ethyl levulinate converted from glucose was only 14.5 mol%, which was far lower than that of fructose. Sucrose and inulin are two of the most abundant and renewable saccharides from biomass. When sucrose was used, a medium ethyl levulinate yield of 35.4 mol% was obtained. Whereas, 52.3 mol% of ethyl levulinate yield was obtained for inulin which consists of one molecule of glucose and 1–59 molecules of fructose. Furthermore, the yield of ethyl levulinate from cellulose consisted of glucose units, was 14.8 mol% at 220 °C. The results demonstrated that K-HPW-1 was an effective catalyst in terms of synthesis of ethyl levulinate from fructose units in carbohydrates.

Table 2. Effect of various raw materials on synthesis of ethyl levulinate.

Raw Meterials	Temperature (°C)	Conversion (%)	Ethyl Levulinate Yield (mol%)	5-Ethoxymethylfur-fural Yield (mol%)	Levulinic Acid Yield (mol%)
Fructose	150	100	68.7	3.5	2.1
Glucose	150	99.2	14.5	1.5	1.7
Sucrose	150	98.1	35.4	2.1	2.0
Inulin	150	>95	52.3	2.5	2.1
Cellulose	220	>95	14.8	1.2	1.4

Reaction conditions: carbohydrate 0.8 g, K-HPW-1 0.6 g, toluene 4 mL, ethanol 36 mL, reaction time 2 h.

For comparison, several related results about ethyl levulinate production from fructose catalyzed by different catalysts are shown in Table 3. The yields of ethyl levulinate were observably different due to the difference of the catalysts. Besides, the yields also depended on the reaction conditions. Saravanamurugan *et al.* [28] and Chen *et al.* [29] reported that high ethyl levulinate yields can be obtained with ionic liquids as catalysts, while it took longer time (more than 12 h) to reach the reaction equilibrium and the cost of catalysts was also quite high. In most studies, the yield of ethyl levulinate was lower than 60 mol%. However, the yield of ethyl levulinate can reach up to 68.7 mol% under the optimum conditions in this study, which means K-HPW-1 is an efficient catalyst for synthesis of ethyl levulinate from fructose.

Table 3. Comparison of different research on ethyl levulinate production from fructose.

Research	Catalyst	Medium	Reaction Conditions	Ethyl Levulinate Yield (mol%)
[9]	Amberlyst 70	Ethanol/water	175 °C 2 h	37
[15]	SO_4^{2-}/TiO_2	Ethanol	200 °C 2 h	59
[16]	H-USY(6)	Ethanol	150 °C 20 h	40
[28]	[NEt₃BSO₃H][HSO₄]	Ethanol	140 °C 24 h	77
[29]	IL-POMs [a]	Ethanol	120 °C 12 h	28–80
[30]	SO₃H-SBA-15	Ethanol	140 °C 24 h	57
This study	K-HPW-1	Ethanol/toluene	150 °C 2 h	68.7

[a] Ionic liquid-based polyoxometalate salts.

3. Experimental Section

3.1. Materials

$H_3PW_{12}O_{40} \cdot xH_2O$, anhydrous ethanol and KCl were purchased from Kermel Chemical Reagent (Tianjin, China), and the x value of $H_3PW_{12}O_{40} \cdot xH_2O$ was determined to be 10 by thermogravimetric method [31]. 5-hydroxymethylfurfural, levulinic acid, ethyl levulinate, and fructose with the purity of over 99% were purchased from Aladdin Chemical Reagent (Shanghai, China). 5-ethoxymethylfurfural (97%) was obtained from Sigma-Aldrich. Other chemicals were purchased from Kermel Chemical Reagent. All reagents were analytical grade and used without further purification.

3.2. Catalysts Preparation

The catalysts were prepared according to a reported procedure [30] as follows: an appropriate amount of metal salt (0.1 mol/L) aqueous solution was added dropwise into 20 mL HPW (0.08 mol/L) with vigorous stirring. Then the mixture was further stirred for another 2 h at room temperature. The catalyst was obtained by filtration and dried at 80 °C overnight. Finally, the catalyst was calcined at 300 °C for 4 h. These prepared catalysts are designated as Cs-HPW-1, Cs-HPW-2.5, Ag-HPW-1, K-HPW-1, K-HPW-2, K-HPW-3, and Sn-HPW-0.75 according to the stoichiometry. Fe-HPW-1 was prepared according to Liu's report [20].

3.3. Catalytic Reaction Procedure

The experiments of direct synthesis of ethyl levulinate from fructose in ethanol were performed in a 100 mL cylindrical pressurized reactor. In a typical run, fructose (0.8 g), ethanol (40 mL), and a given amount of solid acid catalysts were mixed in the reactor with a rotation speed of 600 rpm. Then, the reactor was brought to the desired temperature by external heating. Time zero was recorded when the set temperature was reached. After reaction, the reactor was cooled down in a cool water bath, and then the reaction mixture was diluted with anhydrous ethanol to 100 mL. The liquid was filtered with a 0.22 μm syringe filter prior to analysis by gas chromatography and high-performance liquid chromatography (HPLC). To test stability of the catalyst, K-HPW-1 was recycled by centrifugation after the reaction, and the recovered catalyst was washed with water and ethanol three times each and dried at 110 °C overnight. Then, it was calcined at 300 °C for 3 h before being reused in a new experiment under the same conditions.

3.4. Products Analysis

Ethyl levulinate was determined by a gas chromatography equipped with an FFAP capillary column (30 m × 0.32 mm × 0.33 μm) and flame ionization detector (FID). The amount of ethyl levulinate was calculated using standard curves based on 1-octanol as the internal standard. Fructose, 5-ethoxymethylfurfural and levulinic acid were quantified by HPLC equipped with a Waters 2412 Refractive Index detector (Milford, MA, USA) and a Bio-Rad HPX-87H column (Hercules, CA, USA) (300 mm × 7.8 mm) at 65 °C controlled with the column oven. 0.005 M H_2SO_4 with a flow rate of

0.6 mL/min was used as the mobile phase. The content of above components was calculated by external standard calibration curve method.

3.5. Catalysts Characterization

X-ray powder diffraction (XRD) patterns of the samples were carried out using a BRUKER X-ray diffractometer (D8 Advance, Bruker, Germany) with a Cu Kα radiation source operated. Data were collected from 2θ between 10° and 80° with a step of 0.02° at a scanning speed of 3°/min. Fourier transform infrared (FT-IR) spectra were conducted on a spectrometer (Nicolet 6700, Thermo Scientific, Waltham, MA, USA) at a spectral resolution of 4 cm^{-1} in the wave number range of 400 to 4000 cm^{-1}. A scanning electron microscope (SEM) (JSM-7500F, JEOL, Tokyo, Japan) was used to observe the surface morphology of the catalysts.

4. Conclusions

The H^+ of HPW substituted by K^+ could modify the acidity of HPW and form an efficient catalyst K-HPW-1 for synthesis of ethyl levulinate from fructose. The highest ethyl levulinate yield of 64.6 mol% was obtained at 150 °C within 2 h in ethanol. Six organic solvents were tested as co-solvents, and it was found toluene showed the best performance on the selectivity of ethyl levulinate. The introduction of toluene can improve the yield of ethyl levulinate to 68.7 mol%. Moreover, the recovered catalyst retained high activity with the yield of ethyl levulinate converted from fructose above 50 mol% after being used in five runs. The comparative research also showed K-HPW-1 is an efficient catalyst for synthesis of ethyl levulinate from fructose.

Acknowledgments

Author Contributions

Chun Chang, Guizhuan Xu, and Shiqiang Zhao contributed to the experimental design. Shiqiang Zhao, Shuqi Fang, Fengguang Du, and Ze Liu contributed to all the experimental data collection. Shiqiang Zhao wrote the first draft of the manuscript that was then extensively improved by Chun Chang and Guizhuan Xu.

Conflicts of Interest

The authors declare no conflict of interest.

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