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An Efficient Catalyst for the Conversion of Fructose into Methyl Levulinate

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Abstract The catalytic alcoholysis of fructose in methanol to methyl levulinate was performed by using phosphotungstic acid iron catalysts. The catalysts were characterized by powder X-ray diffraction, infrared spectroscopy, and X-ray fluorescence spectroscopy. The results showed that the exchanging of H^+ with Fe^{3+} ions could modify the acidity of $H_3PW_{12}O_{40}$ and introduce some Lewis acidity into the molecules. The highest yield of methyl levulinate was obtained over the Fe-HPW-1 catalyst. This catalyst showed 100 % fructose conversion with 73.7 % yield of methyl levulinate at 130 °C, 2 MPa for 2 h, and it could be reused at least five times without obvious loss of activity. The results suggest that the combination of Brønsted acidity with some Lewis acidity could effectively promote the conversion of fructose in methanol to methyl levulinate.

Keywords Fructose · Methyl levulinate · Methanol · Phosphotungstic acid salts

1 Introduction

With gradual diminishment of fossil fuel reserves and step-by-step depravation of environmental quality, the development of renewable biomass energy attracts extensive concerns [1]. In recent years, more and more researchers are keen to identify and study chemical or biological methods to convert biomass into biofuels and feedstock chemicals [2–4]. In contrast to other renewable energy resources (solar, thermal, tidal, wind, hydro, etc.), biomass is the only renewable energy resources of fixed carbon, which is essential for the production of liquid hydrocarbon fuels and chemicals [5–7]. In this connection, the conversion of fructose to value-added chemicals is a key transformation. Fructose, an ample and cheap six-carbon sugar molecule that is highly dependent on biomass, will be a renewable and alternative source toward this challenging goal [8]. It is well known that the dehydration of fructose leads to formation of 5-hydroxymethylfurfural (HMF) which can be rehydrated to levulinic acid in water. Levulinic acid has been recognized as an important bio-platform chemical [9]. While, levulinate esters e.g. methyl levulinate, ethyl levulinate, and butyl levulinate are suitable to be used as additives for gasoline and diesel of transportation fuels [10]. Levulinate esters can also either be used in the flavoring and fragrance industries or as substrates for various kinds of condensation and addition reactions [11]. Hence, the direct conversion of sugars or cellulose to levulinic acid or its esters has become of importance.

Up to now, several researchers have reported the conversion of biomass into levulinate esters using various acid catalysts e.g. mineral acids (especially sulfuric acid), Lewis acids (metal chlorides), sulfonic acid-functionalized ionic liquids (SO_3H-ILS) and solid acid as catalysts [12–18]. For instance, Peng et al. [17] reported the catalytic conversion of cellulose to levulinic acid by using metal chlorides as catalysts, among which chromium chloride was uniquely effective and the yield of levulinic acid reached 67 % at 200 °C. The catalyst, however, decomposed to chromium oxide during the reaction. Saravanamurugan et al. [18]

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reported the catalytic transformation of fructose, glucose, and sucrose to ethyl levulinate with different SO_3H-ILS. It was found that ionic liquids based on the $[NTf_2]^-$ anion gave a higher yield of ethyl levulinate (77 %). The disaccharide sucrose was found to form 36 % of ethyl levulinate along with 33 % of another product, ethyl-D-glucopyranoside (EDGP). Glucose was converted into EDGP (63 %) with a lower yield of ethyl levulinate. Saravanamurugan and Riisager [19] also investigated various catalysts i.e. sulfuric acid functionalized SBA-15, sulfated zirconia, beta, Y, ZSM-5 and mordenite for the dehydration of sugars to ethyl levulinate in ethanol. They found that the SO_3H-SBA-15 catalyst showed a high catalytic activity for the selective conversion of fructose to ethyl levulinate (57 %) and glucose to EDGP (80 %) at 140 °C. Peng et al. [20] investigated a series of solid acid catalysts including SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, $SO_4^{2-}/ZrO_2–TiO_2$ and $SO_4^{2-}/ZrO_2–Al_2O_3$ for the conversion of glucose in ethanol; they found that with SO_4^{2-}/ZrO_2 as the catalyst an optimized ethyl levulinate yield of 30 % was obtained at 200 °C for 3 h. Tominaga et al. [21] presented an efficient catalyst system for the synthesis of methyl levulinate from cellulose and glucose by combining two different kinds of acids, a Lewis acid and a Brønsted acid, where the highest yield of methyl levulinate reached 75 %. Although the yield of methyl levulinate is high, the catalytic system of mixed acids is difficult to separate and recycle.

There have been several reports about the production of levulinate esters in near-critical alcohols from carbohydrates biomass feedstocks, such as cellulose, sucrose, glucose, fructose, etc. [22–24]. Rataboul and Essayem [22] studied that the conversion of microcrystalline cellulose using $Cs_xH_{3-x}PW_{12}O_{40}$ or sulfated zirconia solid acid catalysts in supercritical MeOH and MeOH-H_2O (90/10) mixtures at 300 °C, 10 MPa, and 1 min. Up to 20 % yield of methyl levulinate was obtained. Wu et al. [23] investigated the alcoholysis of cellulose in near-critical methanol using H_2SO_4 as catalyst. A high yield of up to 55 % methyl levulinate was achieved at 190 °C for 5 h.

Obviously, the yields of levulinate esters are still unsatisfied. Moreover, the consumption of alcohols e.g. methanol, ethanol during reactions was not mentioned in most studies. Whereas, excessive consumption of alcohols to diether is one of the substantial obstacles for the development of the process to synthesize levulinate esters [25, 26]. Therefore, seeking an efficient and environmental benign catalyst with high yields of levulinate esters and low consumption of alcohols is essential for economical conversion of those biomass feedstocks.

Phosphotungstic acid salts as water tolerant acid catalysts with both Brønsted and Lewis acidities have attracted much attention [27–29]. They can be recycled and separated easily and have been broadly applied to catalyze isomerization, dehydration, cracking, alkylation, esterification, acylation, etc. [30, 31]. In the present work, we found that the iron salt of phosphotungstate could effectively catalyze the conversion of fructose into methyl levulinate. This catalyst could be used repeatedly at least five times without obvious loss of activity.

2 Experimental

2.1 Materials

Fructose (≥98 %), glucose (≥98.0 %), sucrose (≥98.0 %), phosphotungstic acid hydrate (≥98.5 %), methanol (≥99.5 %) n-butanol (99.0 %) and $FeCl_3·6H_2O$ (≥99.0 %) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). N_2 (>99.99 %) was supplied by the Xi'an MESSER Gas Company.

2.2 Catalysts Preparation and Characterization

Phosphotungstic acid hydrate ($H_3PW_{12}O_{40}·xH_2O$) was dried in an oven at 110 °C for 6 h, and the resultant sample was denoted HPW. The detailed synthesis procedure of the other catalysts is as follows: 4 mmol $H_3PW_{12}O_{40}·xH_2O$ was dissolved in 10 ml distilled water and then 4 mmol $FeCl_3·6H_2O$ was added into the above solution under vigorous stirring at 30 °C for 3 h. Finally, the solution was cast onto a glass substrate and then transferred into an oven for evaporation of water at 110 °C for 6 h. The resultant sample was denoted Fe-HPW-1. A similar procedure was used for preparing other catalysts with different iron contents. The resultant samples were denoted Fe-HPW-2 and Fe-HPW-3, respectively.

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded with a BRUKER D8 Advance X-ray diffractometer with a Cu Kα radiation source operated at 40 kV and 40 mA. Data was collected from 5 to 80° with a step of 0.02° at a scanning speed of 10 °/min. Infrared spectra were recorded on a Bruker EQUINX55 FTIR spectrometer using KBr disc technique. The concentration of the sample in KBr was 1.0 wt%, and 0.2 g of KBr was used in the preparation of the reference and sample disks. The relative contents of Fe, P and W in the catalysts were determined by a Shimadzu XRF-1800 X-ray fluorescence spectrometer.

2.3 Reaction Test and Product Analysis

The experiments were performed in a 35 ml stainless steel autoclave equipped with a mechanical stirrer. In a typical experimental, 0.75 g fructose, 24 g methanol, and 0.48 g catalyst were loaded into the reactor. The autoclave was purged three times and then pressurized to 2.0 MPa with N_2 at room temperature. The autoclave was heated to the desired temperature and left for the desired time with a stirring speed of 600 rpm. After completion of the reaction, the reactor was cooled in an ice-water mixture to room temperature before collecting the samples.

Methyl levulinate, methyl formate, methanol and 5-methoxymethylfurfural in the reaction products were analyzed on a GC (Agilent 6820 instrument) equipped with a HP-FFAP capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector. *n*-Butyl alcohol was added in the liquid products as an internal standard. Fructose was quantified using a HPLC coupled with a RID detector and an Inertsil ODS-SP column. A solution of methanol was used as the mobile phase with a volumetric of 0.30 ml min^{-1} at room temperature. Product identification was confirmed by using a Shimadzu GC–MS QP202S.

The conversion of fructose was calculated using the following equation:

$$\text{Fructose conversion } (\%) = \frac{C_{0F} - C_F}{C_{0F}} \times 100$$

Methyl levulinate yield was calculated as follows:

$$\text{Methyl levulinate yield } (\%) = \frac{C_{ML} \times M_F}{C_{0F} \times M_{ML}} \times 100$$

where C_{0F} and C_F were denoted as the initial and post-reaction concentration of fructose, respectively. C_{ML} is the concentration of methyl levulinate in the products; M_F and M_{ML} are the molecular weight of fructose and methyl levulinate, respectively.The conversion of methanol was calculated using the following equation:

$$\text{Methanol conversion } (\%) = \frac{C_{0M} - C_M}{C_{0M}} \times 100$$

Methyl formate yield was calculated as follows:

$$\text{Methyl formate yield } (\%) = \frac{C_{MF} \times M_M}{C_{0M} \times M_{MF}} \times 100$$

where C_{0M} and C_M were denoted as the initial and post-reaction concentration of methanol, respectively. C_{MF} is the concentration of methyl formate in the products; M_M and M_{MF} are the molecular weight of methanol and methyl formate, respectively.

3 Results and Discussion

3.1 Catalyst Characterization

The relative contents of Fe, P and W in the catalysts were analyzed by an X-ray fluorescence spectrometer and the results are summarized in Table 1. The phase structures of the catalysts were characterized by powder X-ray diffraction, and the results are shown in Fig. 1. The Fe-HPW samples show similar XRD patterns with the HPW with numbers diffraction lines at 2θ = 10.1, 14.3, 17.6, 20.4, 22.9, 25.1, 29.2 and 34.4°, which are assigned to a cubic system. These results confirm that the modification with Fe^{3+} cation does not change the local structure of Keggin anion and the secondary structure of Keggin-type heteropolyacid. No XRD signals due to oxides or hydroxide of Fe were observed in XRD pattern of Fe-HPW. With the addition of Fe in HPW, the intensity of diffraction lines decreases.

Table 1 The relative content of Fe, P, W in the catalysts determined by X-ray fluorescence

Catalyst	Fe (%)	P (%)	W (%)
HPW	–	2.36	97.53
Fe-HPW-1	0.38	2.46	97.16
Fe-HPW-2	0.62	2.60	96.78
Fe-HPW-3	0.98	2.16	96.86

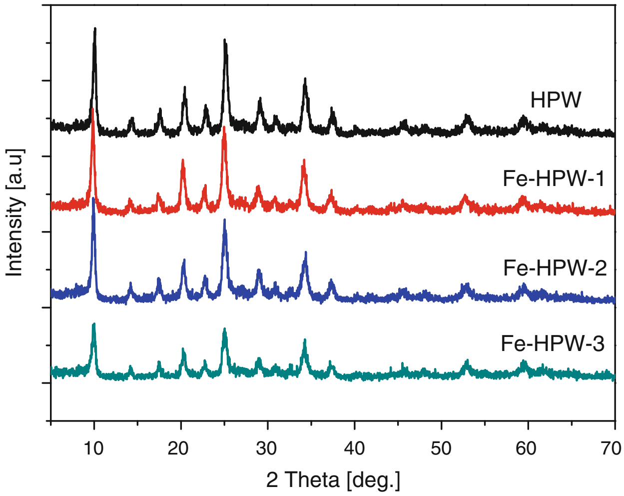

Fig. 1 Powder X-ray diffraction patterns of catalysts

The Keggin anion of HPW is composed of a tetrahedral PO_4 surrounded by 12 octahedral WO_6, sharing edges in W_3O_{13} triads and corners with other triads through bridging oxygens [32]. The FT-IR spectra of the catalysts (see Fig. 2) show absorption peaks in the range from 800 to 1100 cm^{-1}, which are assigned to $[PW_{12}O_{40}]^{3-}$ structural vibrations. It could be distinguished easily at 1080, 984, 880 and 808 cm^{-1}, which are attributed to the asymmetry vibrations P–O_a (internal oxygen connecting P and W), W–O_d (terminal oxygen bonding to W atom), W–O_b (edge-sharing oxygen connecting W) and W–Oc (corner-sharing oxygen connecting W_3O_{13} units), respectively. Moreover,

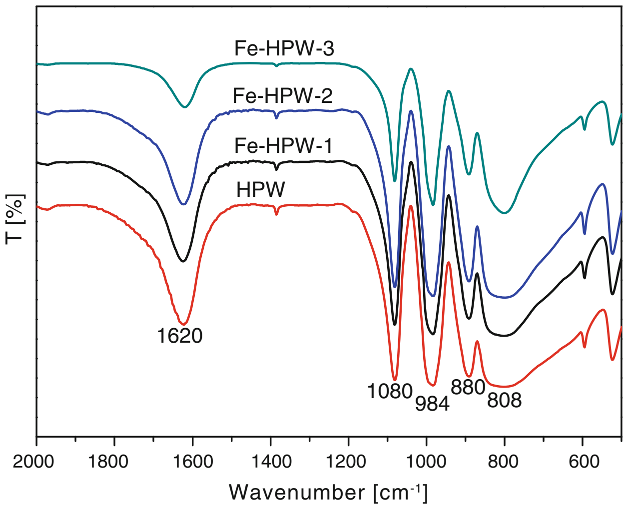

Fig. 2 FT-IR spectra of catalysts

the peak at 1620 cm^{-1} is due to $H_5O_2^+$ ($H_2O\cdots H^+\cdots OH_2$) [30]. The intensity of this band for Fe-HPW is lower than that for HPW and decreases with increasing the content of Fe^{3+} cations in the Fe-HPW samples, suggesting that some part of protons present in the form of $H_5O_2^+$ are exchanged by Fe^{3+} cations [29], which may results in the decrease of Brøsted acidity in the catalysts.

3.2 Catalytic Activity

The alcoholysis of fructose in methanol was performed by using different catalysts. The results are presented in Table 2. As shown in Table 2, at 100 °C, the conversion of fructose is 20.1 % with 2.3 % yield of methyl levulinate when using $FeCl_3\cdot 6H_2O$ as a catalyst. For the HPW catalyst, 95.5 % fructose conversion, 23.4 % yield of methyl levulinate and 19.2 % yield of 5-methoxymethyl-furfural were obtained. The Fe-HPW-1 catalyst shows the best catalytic performance, giving 98.7 % fructose conversion, 25.0 % yield of methyl levulinate and 20.8 % yield of 5-methoxymethyl-furfural. The catalytic activity of Fe-HPW-2 is inferior to that of Fe-HPW-1, but it is appreciably better than that of Fe-HPW-3. The conversion of fructose, yields of methyl levulinate and 5-methoxymethyl-furfural on Fe-HPW-2 are 93.4, 21.8 and 16.7 %, respectively. For Fe-HPW-3, the conversion of fructose is 90.1 %, and the yields of methyl levulinate and 5-methoxymethyl-furfural are 19.8 and 13.4 %, respectively. When the reaction temperature was increased to 130 °C under identical other conditions, fructose was converted completely, the yields of methyl levulinate for $FeCl_3\cdot 6H_2O$, HPW, Fe-HPW-1, Fe-HPW-2, and Fe-HPW-3 are 2.3, 60.4, 73.7, 65.9, and 60.3 %, respectively. The Fe-HPW-1 catalyst again shows the best catalytic performance. Over this catalyst, the conversion of methanol at 130 °C is 8.8 %, the yield of methyl formate is 4.6 %, indicating that most converted methanol was transformed into other by products such as dimethyl ether, etc.

It is known that $H_3PW_{12}O_{40}$ heteropolyacid as a Brøsted acid has the highest acid strength and has higher acidity than H_2SO_4 [33]. Exchanging of H^+ with metal cations can modify the acidity strength of $H_3PW_{12}O_{40}$ and introduce some Lewis acidity into the molecule [32–34]. Lewis acidity of salts of metal cation (M^{n+}) and $PW_{12}O_{40}{}^{3-}$ ($M_{3}/nPW_{12}O_{40}$) originates from the metal cation as electron pair accepters; while Brøsted acidity is generated from dissociation of coordinated water under the polarizing effect of the cation [27, 28]. The Fe-HPW-1 catalyst shows the maximum yield of methyl levulinate in the present cases, suggesting that the combination of Brønsted acidity with Lewis acidity could effectively promote the conversion of fructose in methanol to methyl levulinate. Previous research has confirmed that both Brønsted and Lewis acid sites can catalyze the alcoholysis of fructose to ethyl levulinate esters [18, 35]. However, the exact roles of Brønsted and Lewis acids in the reaction need to be classified further.

The results in Table 2 reveal that Fe-HPW-1 is the most effective catalyst for the alcoholysis of fructose to methyl levulinate among all the catalysts. Therefore, in the following studies Fe-HPW-1 was chosen as the catalyst to investigate the influences of process parameters on the alcoholysis of fructose.

3.2.1 *Effect of Catalyst Amount*

Catalyst dosage determines the availability of the acidic sites that catalyze both the production of the desirable products and undesirable byproducts. Thus, the competition between the production of desirable methyl levulinate and undesirable byproducts at different catalyst dosages was investigated in the methanol medium. Figure 3 shows the effect of catalyst dosage on the fructose conversion and the product distributions. It can be found that with increasing catalyst dosage from 0.12 to 0.48 g, the yield of methyl levulinate increases from 58.6 to 73.7 %. With further increasing catalyst dosage to 0.6 g, the yield of methyl levulinate decreases due to additional side-reactions. Taking the cost and the efficiency into consideration, 0.48 g catalyst was chosen as an optimal content in subsequent experiments.

3.2.2 *Effect of Reaction Temperature*

The results of fructose conversion and product distributions as a function of reaction temperature are depicted in Fig. 4. The conversion of fructose increases from 98.7 to 100 % with increasing the reaction temperature from 100 to 130 °C, and the methyl levulinate yield increases from 25.3

Table 2 The conversion of fructose to methyl levulinate using various catalysts

Catalysts	Temp. (°C)	Fructose conversion (%)	Methanol conversion (%)	Methyl levulinate yield (%)	5-Methoxymethyl-furfural yield (%)	Methyl formate yield (%)
HPW	130	100	9.5	60.4	0	3.50
	100	95.5	8.7	23.4	19.2	1.54
Fe-HPW-1	130	100	8.8	73.7	0	4.61
	100	98.7	7.2	25.0	20.8	1.95
Fe-HPW-2	130	100	7.8	65.9	0	4.57
	100	93.4	6.9	21.8	16.7	1.63
Fe-HPW-3	130	100	7.1	60.3	0	4.67
	100	90.1	6.5	19.8	13.4	1.72
$FeCl_3$	130	87.3	1.2	2.3	0	1.38
	100	20.1	0.8	0	1.2	0

Reaction conditions methanol 24 g, fructose 0.75 g, catalyst 0.48 g, 2 MPa, 130 °C, 2 h, stirring speed 600 rpm

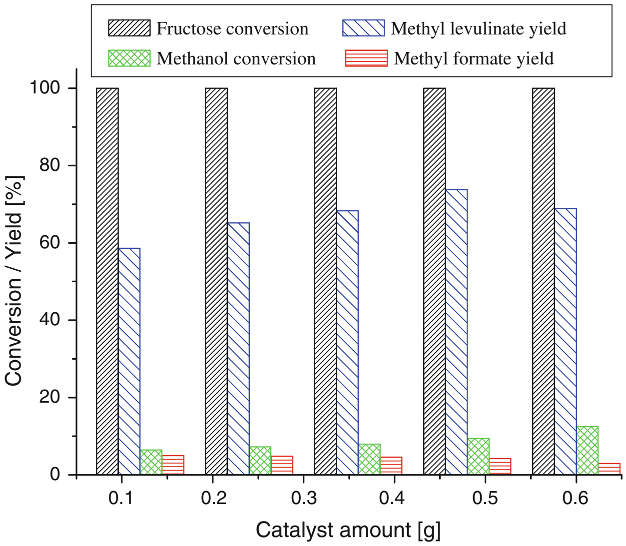

Fig. 3 Effect of catalyst amount on the conversion of fructose. *Reaction conditions* methanol 24 g, fructose 0.75 g, 130 °C, 2 MPa, 2 h, stirring speed 600 rpm

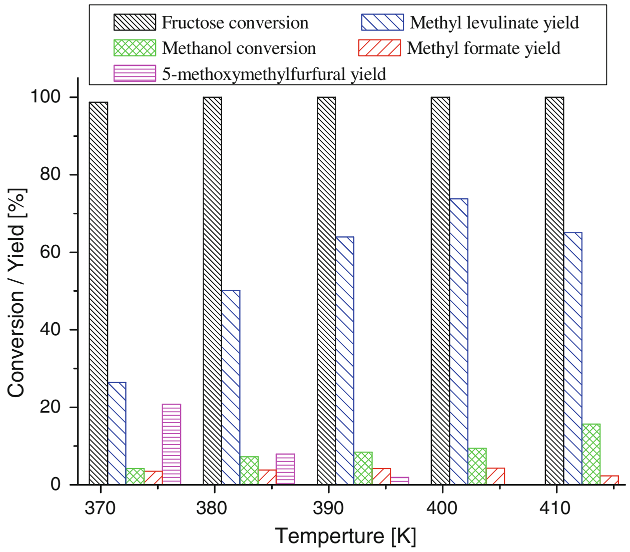

Fig. 4 Effect of reaction temperature on the conversion of fructose. *Reaction conditions* methanol 24 g, fructose 0.75 g, catalyst 0.48 g, 2 MPa, 2 h, stirring speed 600 rpm

to 73.6 %; whereas, the yield of 5-methoxymethylfurfural decreases from 20.8 % to zero, indicating that 5-methoxymethylfurfural should be the intermediate which can readily transform into methyl levulinate through rehydration and methanol addition at higher temperatures. Further increasing reaction temperature led to the reaction solution becoming brown gradually, and the yield of methyl levulinate decreased to 66.4 % at 140 °C. This may be due to the fact that at higher temperatures side-reactions may occur, bringing about numerous polymers and humin matters. In addition, methyl levulinate could be decomposed to some extent at higher temperatures [24]. The results suggest the reaction temperature could be a crucial parameter for formation of methyl levulinate, and 130 °C is the optimum reaction temperature for the alcoholysis of fructose.

3.2.3 *Effect of Reaction Pressure and Time*

The effect of reaction pressure on the yield of methyl levulinate is shown in Fig. 5. As can be seen, with increasing pressure from 0 to 2 MPa the yield of methyl levulinate increases from 58.5 to 73.7 %; however, further increasing pressure to 3 MPa, the yield of methyl levulinate decreases to 68.6 %.

We also investigated the influence of reaction time (see Fig. 6) and found that under the conditions of 130 °C and 2 MPa, with increasing reaction time the yield of methyl

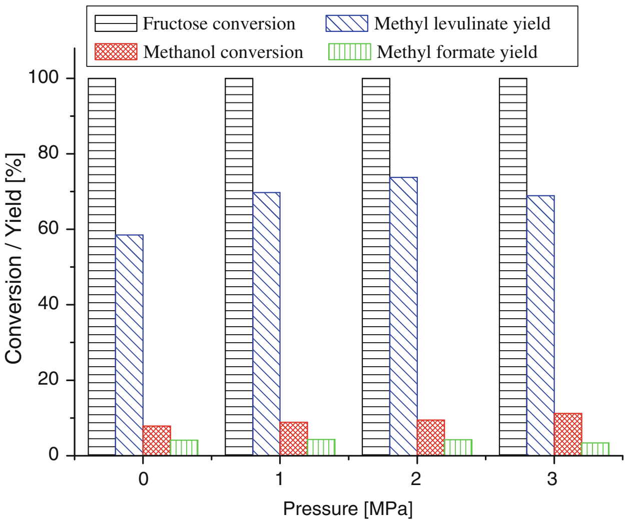

Fig. 5 Effect of reaction pressure on the conversion of fructose. *Reaction conditions* methanol 24 g, fructose 0.75 g, catalyst 0.48 g, 130 °C, 2 h, stirring speed 600 rpm

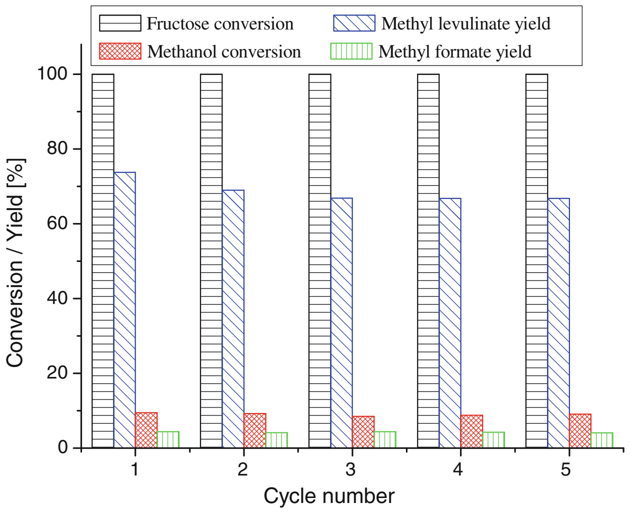

Fig. 7 The recycling of catalyst. *Reaction conditions:* methanol 24 g, fructose 0.75 g, catalyst 0.48 g, 130 °C, 2 MPa, 2 h, stirring speed 600 rpm

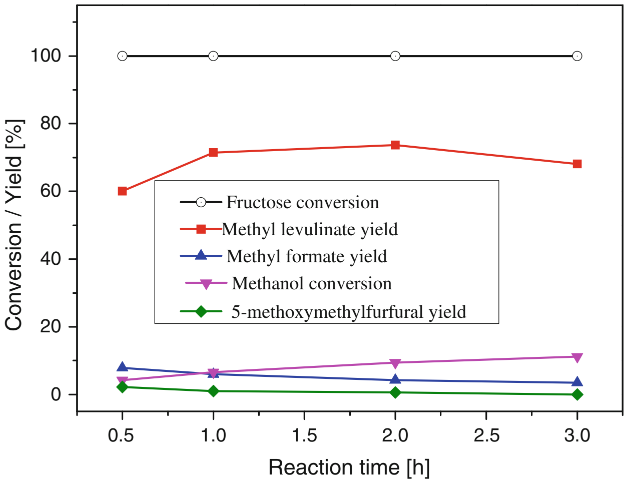

Fig. 6 Effect of reaction time on the conversion of fructose. *Reaction conditions* methanol 24 g, fructose 0.75 g, catalyst 0.48 g, 130 °C, 2 MPa, stirring speed 600 rpm

levulinate increased slightly, and then decreased slightly. The highest yield of methyl levulinate was obtained with 2 h reaction time.

3.2.4 Catalyst Recycles

The stability and reusability of catalysts are extremely important aspect for any industrial process to reduce production cost. After each run, methanol and other low boiling point products were evaporated under reduced pressure at 40 °C. Subsequently, the catalyst was extracted by with diethyl ether and followed by evaporation, and then used for the next run under the identical reaction conditions. From Fig. 7, it is found that the catalyst can be used repeatedly at least five times with slight loss of methyl levulinate yield. The decrease of activity was probably due to the lost of catalyst in the purification process.

3.2.5 Proposed Reaction Pathway for the Conversion of Fructose

During reaction, a variety of products were detected, namely methyl levulinate, methyl formate, 5-methoxymethylfurfural, and a trace amount of HMF at low temperature. Besides, a main gas-phase product of dimethyl ether was detected by GC, which was generated from the intermolecular dehydration of methanol. During the experiments, some dark-brown insoluble substances known as humins were also observed, which were formed by side reactions of the acid-catalyzed decompositions of reactant and/or certain products under the experimental conditions. Among the products, 5-methoxymethylfurfural was formed only at low reaction temperature; at 130 °C 5-methoxymethylfurfural was not detected in the products, suggesting that it is the intermediate. According to the experiment findings and the related literatures [18, 19], a plausible reaction pathway for the acid-catalyzed conversion of fructose to methyl levulinate in methanol medium was proposed, as summarized in Scheme 1. Firstly, fructose dehydrates to form HMF which then rapidly etherifies with methanol to form 5-methoxymethylfurfural. In the subsequent step, the intermediate product 5-methoxymethylfurfural is converted to methyl levulinate and methyl formate through rehydration and methanol addition.

Scheme 1 The conversion of fructose to methyl levulinate

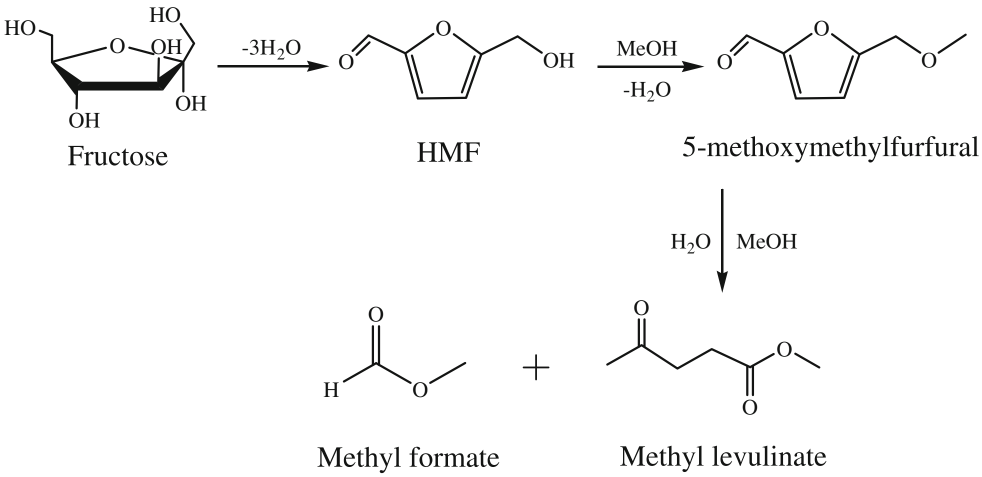

Table 3 Influences of different raw materials on the yield of methyl levulinate

Raw materials	Reaction temp. (°C)	Conversion (%)	Methanol conversion (%)	Methyl levulinate yield (%)	5-Methoxymethyl-furfural yield (%)	Methyl formate yield (%)
Glucose	130	97.5	7.92	13.8	0	0.97
Sucrose	130	86.5	8.02	44.3	0	3.07
Inulin[a]	130	–	8.72	92.3	0	4.08
Cellulose[a]	220	–	9.52	13.7	1.23	0.66

Reaction conditions methanol 24 g, catalyst 0.48 g, 2 MPa, 2 h, stirring speed 600 rpm

[a] Methyl levulinate yield (C-%) = (mol of methyl levulinate × 6)/(mol of carbon included charged substrates determined by CHNS analyzer) × 100

3.2.6 Conversion of Various Carbohydrates

To explore the applications of the catalyst for the production of methyl levulinate from other carbohydrates, glucose, sucrose, inulin, and cellulose were selected as substrates for the alcoholysis reaction and the results are summarized in Table 3. It can be noted that 13.8 % yield of methyl levulinate was obtained when using glucose as substrate, which is much lower than that from fructose. The distinct behavior of both hexoses might stem from the more stable ring structure of glucose, and the Fe-HPW-1 catalyst did not facilitate the required isomerisation of glucose to fructose to form methyl levulinate. Previously, it has been also found that glucose reacted preferentially with alcohol to form a cyclic product, alkyl-D-glycopyranoside rather than isomerization to fructose over various acid catalysts [18, 19]. The disaccharide sucrose, consisting of one fructose and one glucose unit, gave a medium amount of methyl levulinate (44.3 %) with 86.5 % conversion. Inulin, a mixture of oligo and ploysaccharrides, consisting of fructose units linked together by β linkages, gave 92.3 % yield of methyl levulinate. This value is higher than that when using fructose as a feed. It may be due to the fact that the alcoholysis of inulin conducts via different reaction routes with that in the alcoholysis of fructose. Similar phenomenon was also found in the hydrothermal conversion of glucose and cellulose to lactic acid using $Er(OTf)_3$ as a catalyst at 240 °C, 2 MPa for 30 min [36]. The yields of lactic acid are 48.2 and 62.8 %, respectively when using glucose and cellulose as raw materials. However, the detailed reaction mechanism needs to be investigated further. When cellulose was used as substrate, only 13.7 % yield of methyl levulinate was obtained at 220 °C.

4 Conclusions

The present study demonstrates that phosphotungstic acid iron catalysts are effective for the alcoholysis of fructose in methanol to methyl levulinate. Exchanging of H^+ with Fe^{3+} ions can modify the acidity of $H_3PW_{12}O_{40}$ and introduce Lewis acidity into the molecules. The highest yield of methyl levulinate was obtained in the catalytic conversion of cellulose in methanol over the Fe-HPW-1 catalyst. This catalyst showed 100 % fructose conversion with 73.7 % yield of methyl levulinate at 130 °C, 2 MPa for 2 h, and it could be reused at least five times without obvious loss of activity.

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