

# Synthesis of fructose over dealuminated USY supported heteropoly acid and its salt catalysts

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## Abstract

12-Phosphotungstic acid (PW) and cesium salt of PW supported on dealuminated ultra-stable Y zeolite (DUSY) with various loadings were prepared by impregnation method, and their physicochemical properties were characterized by X-ray powder diffraction (XRD), N<sub>2</sub> adsorption, solid state <sup>31</sup>P and <sup>29</sup>Si MAS NMR, Hammett indicator and SEM techniques. Their catalytic performances were evaluated in the liquid-phase acetalization of ethyl acetoacetate with ethylene glycol to fructose. The catalytic stability was tested using water treatment, in which the concentration of heteropoly compound was measured by ultraviolet–visual spectrophotometer. A high catalytic activity was found over the supported heteropoly compound catalysts. However, for the supported PW catalysts, a severe leaching of heteropoly anions into water was observed, leading to their poor reusability. By contrast, the Cs salt of PW catalyst supported on DUSY exhibited very high catalytic activity with high water-tolerance and reusability. The conversion of ethyl acetoacetate of 98.7% with the selectivity of fructose above 97% could be obtained over the DUSY supported sample containing 30% of Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> by weight at the optimal reaction conditions, and a considerable catalytic activity still could be achieved after five times of reaction cycle.

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**Keywords:** Heteropoly acid; 12-Phosphotungstic acid; Cs salt of PW; Ethyl acetoacetate; Acetalization; Fructose

## 1. Introduction

Fructose (2,4-dimethyl-2-ethyl acetate-1,3-dioxane) is a flavoring material with apple scent, and its synthesis usually involves the condensation reaction of ethylene glycol with carbonyl compounds in the presence of homogeneous catalysts, such as H<sub>2</sub>SO<sub>4</sub>, *p*-toluenesulfonic acid, pyridinium salts, etc. [1–3]. But these homogeneous catalysts are toxic, corrosive and often hard to be recovered from the reaction solution. To overcome these limits, various heterogeneous catalysts, such as zeolite [4], functionalized zeolite [5], Ti-exchanged clay [6], alumina [7] and silica functionalized by sulphonic acid groups [8] have been employed for the synthesis of 1,3-dioxolane from carbonyl compounds and ethylene glycol. However, most of these

procedures suffer from a high catalyst/substrate molar ratio and a long reaction time. In addition, the activities are still comparatively low.

Heteropoly acids (HPAs) have proved to be the alternative of traditional acid catalysts, such as sulfuric acid and aluminum chloride, due to their strong acidity and environmental benignity. But pure HPAs used as heterogeneous catalysts are hindered by their low surface area and high solubility in polar reaction systems, which thus results in separation problems. Salts of HPAs were prepared by partially exchanging protons of the parent HPAs with large cations, such as Cs<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, which could be water-insoluble and present a rather high surface area (exceeding 100 m<sup>2</sup> g<sup>-1</sup>) [9,10]. Attempts to improve the catalytic efficiency were also made by supporting HPAs on various carriers. Among them, amorphous silica [11,12] and mesoporous molecular sieve, such as MCM-41 [13–15] and SBA-15 [16] were widely studied. Recently, Y and modified Y zeolite were also introduced as the support for HPAs [17–20].

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12-Phosphotungstic acid (PW) simply impregnated onto porous carriers leads to severe leaching of active species in a polar reaction medium. Thus, efforts have been made to prepare the water-tolerant supported PW catalysts. Rao et al. found that alumina grafting silica supported PW showed no leaching in methanol solution [21]; Pizzio et al. revealed that PW supported on SiMCM-41 and functionalized SiMCM-41 exhibited low or negligible solubility in the mixture of ethanol and water [14]; Izumi et al. [12] and Kukovec et al. [22] found the occlusion of PW in the pore of silica by a sol–gel procedure prevented its leaching; Sulikowski et al. encapsulated PW in the supercage of Y zeolite by a “ship-in-the-bottle” method and the catalyst acted as the solid acid in the liquid phase [17]. On the other hand, the solid acid catalyst  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  was found to be water-tolerant [23] and silica-included  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  could be reused in the hydrolysis of ethyl acetate [12].

We have recently reported the PW and Cs salt of PW catalysts supported on dealuminated ultra-stable Y (USY) zeolite and observed their high catalytic activities in the hydroisomerization of *n*-heptane [19] and the esterification of *n*-butanol with acetic acid [24], respectively. In this work, we prepare PW and Cs salts of PW supported on dealuminated USY (DUSY), and observe a very high catalytic conversion, selectivity and stability of the supported cesium salts of PW catalyst in the synthesis of fructose by the acetalization of ethyl acetoacetate with ethylene glycol.

## 2. Experimental

### 2.1. Catalyst preparation

DUSY was prepared by a steam treatment of USY (Zhoucun Catalyst Factory, Si/Al=6) at 650 °C for 3 h, followed by the acid treatment in a 2 mol L<sup>-1</sup> HCl aqueous solution at 90 °C for 2 h. Supported PW ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ , Shanghai Chem. Reagent Co., AR) samples, PW/SP, where SP stands for DUSY, USY or silica gel ( $\text{SiO}_2$ , from Shanghai Silica Gel Factory,  $S_{\text{BET}} = 285 \text{ m}^2 \text{ g}^{-1}$ ), were prepared by the impregnation performed at room temperature with excess solution by contacting the corresponding support with the PW aqueous solution under constant stirring overnight, followed by evaporation at 70 °C and drying at 110 °C for 12 h. Supported Cs salts of PW,  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}/\text{DUSY}$  ( $x=1-3$ ), were obtained by sequential impregnation and in situ reaction on the support. Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) was supported onto DUSY by the incipient wetness impregnation, dried at 110 °C for 12 h and calcined at 500 °C for 4 h. Following this, the calculated amount of PW was introduced into the catalyst by the same procedure as that for PW/DUSY. The loading of PW and  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$  in catalyst was 10–40% by weight. The pure Cs salt of PW ( $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ) was prepared by adding the aqueous solution of  $\text{Cs}_2\text{CO}_3$  dropwise into the PW solution while stirring [25]. The resulting precipitate was dried at 110 °C overnight in vacuum and calcined at 200 °C for 3 h. The  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}/\text{DUSY}$  samples are abbreviated to be  $\text{Cs}_x\text{PW}$  and  $\text{Cs}_x\text{PW}/\text{DUSY}$ , respectively.

Before reaction, all catalysts were calcined in air at 200 °C for 3 h.

### 2.2. Catalyst characterization

X-ray powder diffraction (XRD) pattern was obtained on the Bruker D8 Advance diffractometer using the Ni-filtered Cu K $\alpha$  radiation at 40 kV and 30 mA. BET surface area was achieved by N<sub>2</sub> adsorption on the Coulter Omnisorp 100CX equipment. Pore size distributions and external surface area were determined at -195.8 °C using an ASAP 2020 M surface analyzer. Solid state MAS NMR spectra were recorded using a Bruker Avance 400D spectrometer with a spinning frequency of 9 and 4 kHz for <sup>31</sup>P and <sup>29</sup>Si, respectively. The acid strength of catalysts was measured with Hammett indicators, including anthraquinone ( $\text{p}K_{\text{a}} = -8.20$ ), *p*-nitrotoluene ( $\text{p}K_{\text{a}} = -11.35$ ), *p*-nitrochlorobenzene ( $\text{p}K_{\text{a}} = -12.70$ ), *m*-chloronitrobenzene ( $\text{p}K_{\text{a}} = -13.60$ ) and 2,4-dinitrofluorobenzene ( $\text{p}K_{\text{a}} = -14.52$ ).

Water treatment for supported catalysts (2.0 g) was carried out by stirring in water (50.0 g) to examine the amount of heteropoly species released from the support in the liquid phase by the Perkin-Elmer Lambda 35 UV–vis spectrophotometer. After stirred in water at room temperature for 1 h, the catalyst was recovered by filtering. This was repeated five times. The spectra from 200 to 400 nm were recorded for each filtrate with a built-in recorder, using quartz cells with 10 mm optical path. For the quantitative analysis, a calibration curve was created by using aqueous solution of PW, and the absorption band around 251 nm was used [23].

### 2.3. Synthesis of fructose

The catalytic activity of obtained samples was tested in the liquid-phase acetalization of ethyl acetoacetate (Shanghai Chem. Reagent Co., AR) with ethylene glycol (Shanghai Linfeng Chem. Reagent Co., AR) to synthesize fructose in a three-necked flask equipped with a magnetic stirrer, a water knockout vessel and a condenser. The typical reaction conditions were as follows: 70 °C of reaction temperature; 30 min of reaction time; 1.5 of the molar ratio of ethyl acetoacetate to glycol; 0.5% of the mass fraction of catalyst in the reaction medium. The products were filtered to remove catalyst particles, followed by a GC analysis using a 30 m × 0.25 mm × 0.3 μm PEG-20M capillary column with FID as the detector. The column oven temperature started with an initial temperature of 100 °C for 6 min, followed by a temperature increase with a rate of 25 °C/min and a final temperature of 200 °C for 4 min. Both detector temperature and injector temperature were 260 °C. The conversion of ethyl acetoacetate was calculated based on a GC standard method. The products were qualitatively verified by GC–MS (Thermo Finnigan). For selected catalysts, the catalytic reusability was measured. After simply separating the used catalyst from the reaction medium by centrifuge, it was transferred and charged into the next reaction medium for a new reaction cycle without regeneration.

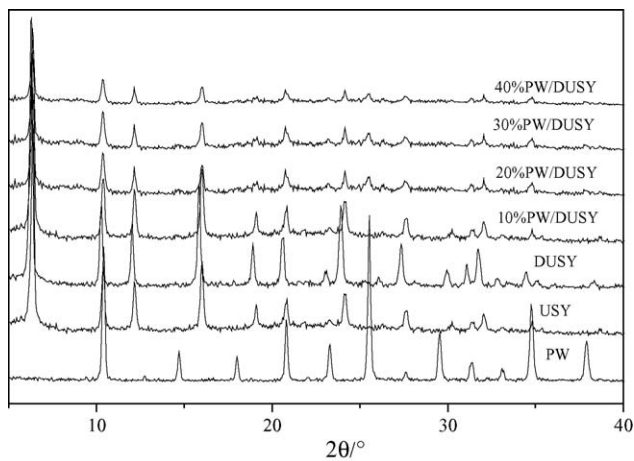


Fig. 1. XRD patterns of PW/DUSY catalysts with various PW loadings.

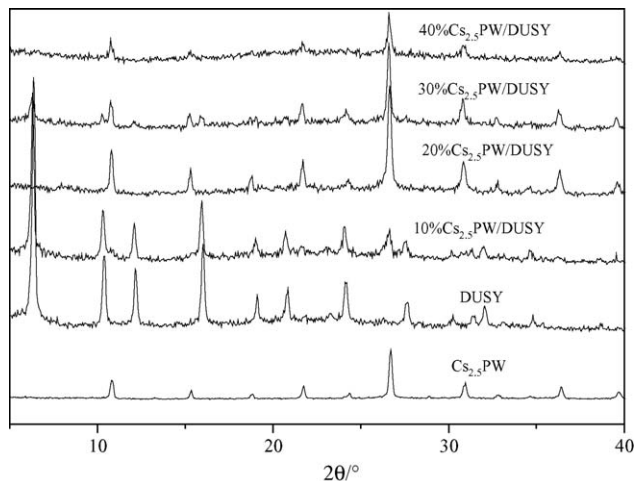


Fig. 2. XRD patterns of  $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  catalysts with various  $\text{Cs}_{2.5}\text{PW}$  loadings.

### 3. Results and discussion

#### 3.1. Characterization of catalysts

The powder XRD patterns of pure PW, USY, DUSY and PW/DUSY catalysts with various PW loadings are illustrated in Fig. 1. It can be seen that the XRD curve of DUSY is very similar to that of USY, indicating the high comparative crystallinity of DUSY in spite of the combined treatment by steaming and HCl acid leaching. When PW is impregnated onto DUSY, peaks assigned to Y zeolite are comparable to those for the parent support, and no characteristic peaks to PW crystal is clearly detected in PW/DUSY materials with the PW loading up to 40%, which implies the high dispersion of PW anions on the support with the microporosity of support unaltered. However, the intensities of the peaks ascribed to Y zeolite decrease gradually with increasing PW loadings. The XRD patterns of Cs salt and the DUSY supported Cs salt with various  $\text{Cs}_{2.5}\text{PW}$  loadings are displayed in Fig. 2. The location of XRD peaks of  $\text{Cs}_{2.5}\text{PW}$  are very similar to that of pure PW shown in Fig. 1, indicating the Cs salt has the same crystalline structure with that of PW. With the increase of  $\text{Cs}_{2.5}\text{PW}$  loadings on DUSY, the intensities of peaks assigned to Y zeolite decrease substantially. The peaks assigned to Y zeolite still could be retained with the  $\text{Cs}_{2.5}\text{PW}$  loadings up to 30%.

On the other hand, the diffraction peak corresponding to pure  $\text{Cs}_{2.5}\text{PW}$  crystal at around  $31^\circ$  is observed in  $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  when  $\text{Cs}_{2.5}\text{PW}$  loadings are above 20%, which indicates that a part of  $\text{Cs}_{2.5}\text{PW}$  inevitably deposit on the surface of DUSY support in form of crystal particle, the size of which is large enough to be detected by XRD.

$^{29}\text{Si}$  MAS NMR spectra for selected catalysts were recorded in Fig. 3(a) in order to compare the chemical environment of silicon atoms in supports and HPAs-containing samples. In case of USY, two peaks appear clearly at  $-104$  and  $-99$  ppm, which are assigned to  $\text{Si}(\text{OSi})_3(\text{OH})$  and  $\text{Si}(\text{OSi})_2(\text{OH})_2$  units, respectively [26,27]. For DUSY, the intensity of the peak at  $-99$  ppm decreases remarkably compared with that for USY, indicating that less Si–OH groups were included in DUSY [26]. Comparing the  $^{29}\text{Si}$  MAS NMR spectra of DUSY with those for 30%PW/DUSY and 30% $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$ , no remarkable differences were observed. This suggests that the pore structure of Y zeolite is still retained for DUSY after impregnation with PW or Cs salt of PW, which are in accordance with the results in Figs. 1 and 2.

Fig. 3(b) shows the  $^{31}\text{P}$  MAS NMR spectra for pure PW, 30%PW/DUSY and 30% $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  catalysts. Pure PW

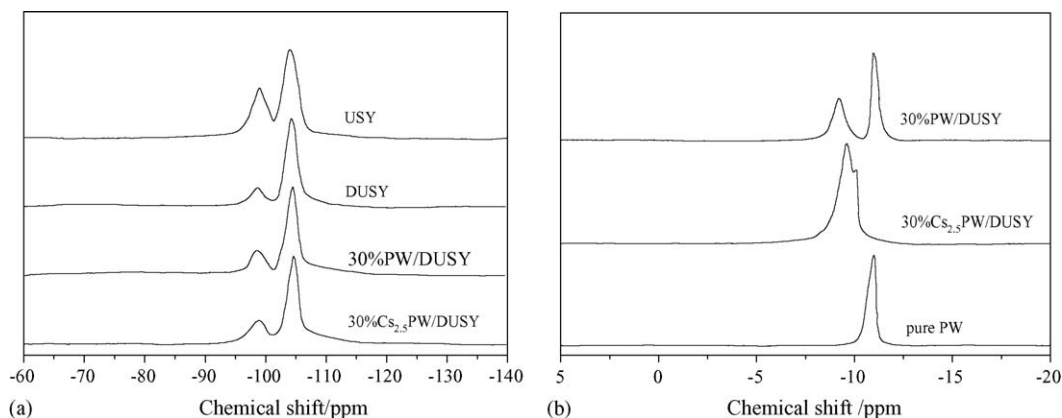


Fig. 3.  $^{29}\text{Si}$  and  $^{31}\text{P}$  MAS NMR for various catalysts: (a)  $^{29}\text{Si}$  and (b)  $^{31}\text{P}$ .

Table 1  
BET surface area and acid strength ( $H_0$ ) of various catalysts

Catalyst	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$H_0$
USY	645	$>-8.2$
DUSY	716	$>-8.2$
PW	6.0	-13.60
$\text{Cs}_{2.5}\text{PW}$	154	-13.60
30%PW/USY	280	-8.2
30% $\text{Cs}_{2.5}\text{PW}/\text{USY}$	272	-11.35
30%PW/DUSY	466	-12.70
30% $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$	496	-12.70
30% $\text{Cs}_1\text{PW}/\text{DUSY}$	530	-12.7
30% $\text{Cs}_{1.5}\text{PW}/\text{DUSY}$	527	-11.35
30% $\text{Cs}_2\text{PW}/\text{DUSY}$	512	-11.35
30% $\text{Cs}_3\text{PW}/\text{DUSY}$	411	-8.2
30%PW/ $\text{SiO}_2$	204	-12.7

gives only one peak, as expected, at  $-11.0$  ppm, which is in agreement with previous report for PW without water of crystallization [28]. However, for the supported samples, two separate peaks are observed at  $-11.0$  and  $-9.2$  ppm for 30%PW/DUSY, and at  $-10.1$  and  $-9.6$  ppm for 30% $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$ . For the supported PW sample, the peak at  $-11.0$  ppm corresponds to the Keggin units, interacting weakly with the support [29], and the other peak at  $-9.2$  ppm may correspond either to a chemically modified Keggin anion, for example, a species like  $\text{P}_2\text{W}_{18}$  or  $\text{P}_2\text{W}_{21}$ , or PW interacting strongly with hydroxyl groups in support [29]. Moreover, it is suggested for 30% $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  that the two peaks probably imply the weak and strong interaction between the Cs salt of polyanions and DUSY support.

Table 1 lists the BET surface areas of various catalysts with the loading of PW or its Cs salt being 30% by weight on supports. It can be seen that pure PW exhibits a very low surface areas of  $6 \text{ m}^2 \text{ g}^{-1}$  whereas  $\text{Cs}_{2.5}\text{PW}$  gives a considerable value of  $154 \text{ m}^2 \text{ g}^{-1}$ , which is in good agreement with the previous report [9]. The surface areas of supported catalysts decrease remarkably compared with their parent supports, however, it is still much higher than the pure PW or its Cs salt. Generally speaking, all the supported samples possess rather high surface areas due to the dispersion effect of the porous carriers. For USY, DUSY, 30%PW/DUSY and 30% $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  samples, the external surface area (pore size above 2.0 nm) and mesopore size distribution are measured. USY gives an external surface area of  $72.5 \text{ m}^2 \text{ g}^{-1}$ , and DUSY gives  $100.0 \text{ m}^2 \text{ g}^{-1}$ , due to the creation of more secondary mesopores during dealumination. For 30%PW/DUSY and 30% $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$ , the external surface areas drop to 74.3 and  $71.0 \text{ m}^2 \text{ g}^{-1}$ , respectively, indicating the incorporation of PW and  $\text{Cs}_{2.5}\text{PW}$  into the mesopores of DUSY. This result is conformed by the variation of secondary mesopore size distribution of the four samples, as shown in Fig. 4. Although the most probable distribution point is almost the same (ca. 3.89 nm) for the four samples, the pore volumes of 30%PW/DUSY and 30% $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  are substantially lowered than that of DUSY.

The acid strength ( $H_0$ ) for typical catalysts is also displayed in Table 1. As expected, pure PW and the Cs salt show superacidity with  $H_0$  being  $-13.6$ , which is lower than  $-11.93$  for 100%

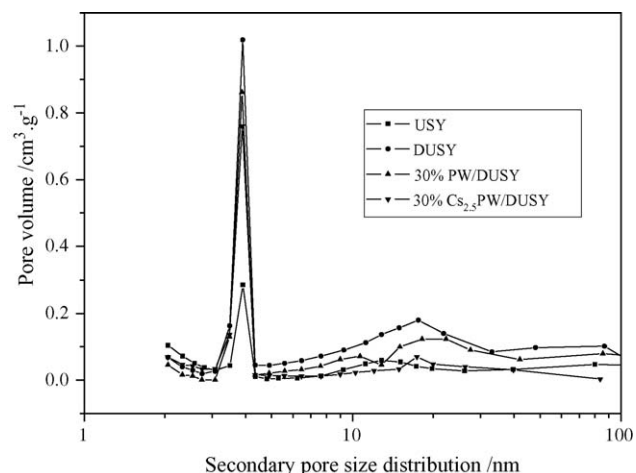


Fig. 4. Secondary pore size distribution for selected samples.

$\text{H}_2\text{SO}_4$ . USY and DUSY only show comparatively weak acidity with  $H_0$  above  $-8.2$ . When PW is introduced on USY, a much weaker acid strength of  $-8.2$  is observed compared with pure PW. As known, when  $\text{NH}_4^+\text{Y}$  is subjected to hydrothermal treatment to produce USY, secondary mesopores are created with the removed Al species filling the insides of secondary pores. These retained Al species may be basicity, and accelerate the partial decomposition of PW on USY [18], which may accounts for the weak acidity of 30%PW/USY. Further steaming and acid leaching for USY could not only create more secondary mesopores but also remove the extra-framework Al species from the zeolite crystal [30], as a result of which, 30%PW/DUSY and 30% $\text{Cs}_x\text{PW}/\text{DUSY}$  exhibit superacidity or near superacidity, as shown in Table 1. On the other hand, it is suggested that the mesopores of DUSY would be favorable to the dispersion of PW or its Cs salts on the support [17]. In all, the acidity is not as strong as that of pure heteropoly compounds for all supported catalysts, which may ascribe to the interaction between heteropoly anions and the hydroxyl groups in the support [29]. As a control sample, 30%PW/ $\text{SiO}_2$  also possesses superacidity with a  $H_0$  value of  $-12.7$ .

SEM images of DUSY and  $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  catalysts with various  $\text{Cs}_{2.5}\text{PW}$  loadings are illustrated in Fig. 5. It can be seen that the crystal particle size of DUSY is approximately  $0.4\text{--}0.8 \mu\text{m}$  and a smaller value of about  $0.2 \mu\text{m}$  corresponds to pure  $\text{Cs}_{2.5}\text{PW}$ . When  $\text{Cs}_{2.5}\text{PW}$  is supported onto DUSY, the edge of the carrier particle becomes obscure and a few of Cs salt particles are observed on the surface of DUSY crystal. In addition, it can be found that the comparatively small  $\text{Cs}_{2.5}\text{PW}$  particles disperse uniformly on the surface of DUSY, and observed that  $\text{Cs}_{2.5}\text{PW}$  particle numbers in the SEM images increase gradually with the increase of  $\text{Cs}_{2.5}\text{PW}$  loadings.

### 3.2. Acetalization of ethyl acetoacetate with ethylene glycol

#### 3.2.1. Effect of $\text{Cs}^+$ content in the 30% $\text{Cs}_x\text{PW}/\text{DUSY}$ catalyst on the conversion of ethyl acetoacetate

Under the employed reaction conditions, the selectivity for fructose in products over all catalysts is above 97%. 3-

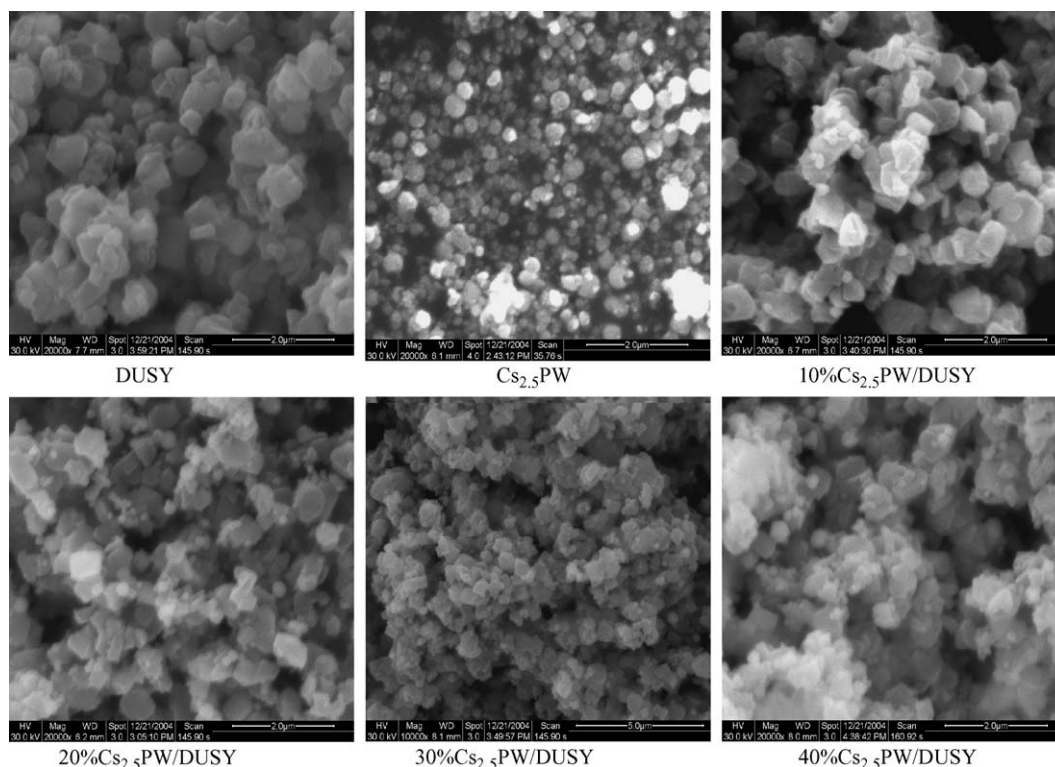


Fig. 5. SEM images of  $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  catalysts with various  $\text{Cs}_{2.5}\text{PW}$  loadings.

Oxobutyric acid, 2-hydroxyethylester is found to predominate in the by-products, and only a negligible amount of 3,3-ethylenedioxy-butanoic acid is detected, which suggests that the hydrolysis of the formed fructose is undetectable. Effect of substitute number of  $\text{Cs}^+$  in the  $30\%\text{Cs}_x\text{PW}/\text{DUSY}$  catalyst on the conversion of ethyl acetoacetate is shown in Fig. 6. It can be seen that, for  $30\%\text{Cs}_{2.5}\text{PW}/\text{DUSY}$ , i.e.,  $x = 2.5$ , a maximum conversion of 71.6% is observed. Previous results [9] indicated that the acidity and surface areas of pure Cs salt of heteropoly acid were influenced largely by the substitute number of  $\text{Cs}^+$ , and the maximum catalytic activity of the pure  $\text{Cs}_{2.5}\text{PW}$  was ascribed

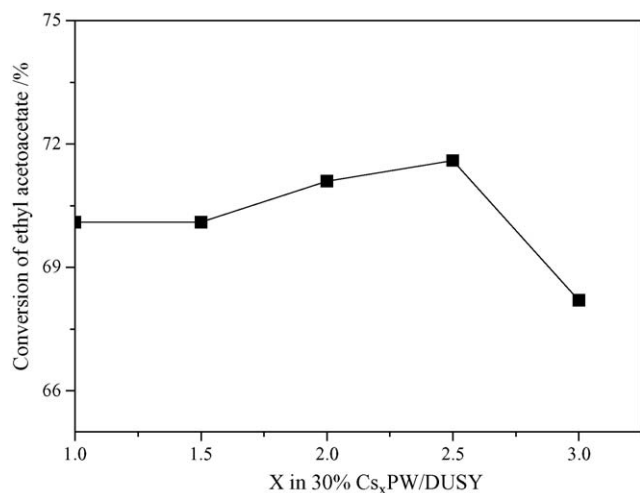


Fig. 6. Effect of substitute number of  $\text{Cs}^+$  in the catalyst of  $30\%\text{Cs}_x\text{PW}/\text{DUSY}$  catalysts with various  $x$  value in the synthesis of fructose.

to its high surface area. As known, acetalization is a typical acid catalyzed reaction, and the acid strength of catalyst would exert a great influence to the catalytic activity. The maximum conversion of ethyl acetoacetate over  $30\%\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  may thus be due to its comparative high acid strength as well as the considerable surface area of  $\text{Cs}_{2.5}\text{PW}$ , which could facilitate its high dispersion on the support of DUSY.

### 3.2.2. Effect of PW and $\text{Cs}_{2.5}\text{PW}$ loadings on the conversion of ethyl acetoacetate over $\text{PW}/\text{DUSY}$ and the $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$ catalysts

Effect of PW and Cs salts loading on the conversion of ethyl acetoacetate over  $\text{PW}/\text{DUSY}$  and  $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  catalysts are compared in Fig. 7. It is shown that DUSY gives a low conversion of 36.6%. When PW is impregnated onto DUSY, the catalytic conversion is enhanced substantially with the increase of PW loading. However, the conversion reaches the plateau when the PW loading is as high as 30%, with the ethyl acetoacetate conversion of about 74%. Along with the further increase of PW loading, the conversion remains nearly constant. The pure PW also gives a considerable high conversion of 73.7% because of its high solubility in polar reaction system and the reaction actually takes place in a completely homogeneous condition. In comparison, pure  $\text{Cs}_{2.5}\text{PW}$  only exhibits a very low conversion of 8.2% because of its highly water-insoluble and the heterogeneity of reaction system. On the other hand, When  $\text{Cs}_{2.5}\text{PW}$  is supported on DUSY, a remarkable promotion effect is observed on  $\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  catalysts. A conversion above 70% is found over  $30\%\text{Cs}_{2.5}\text{PW}/\text{DUSY}$  catalyst, and it is much higher than that over pure  $\text{Cs}_{2.5}\text{PW}$  or DUSY. However, just like the sup-

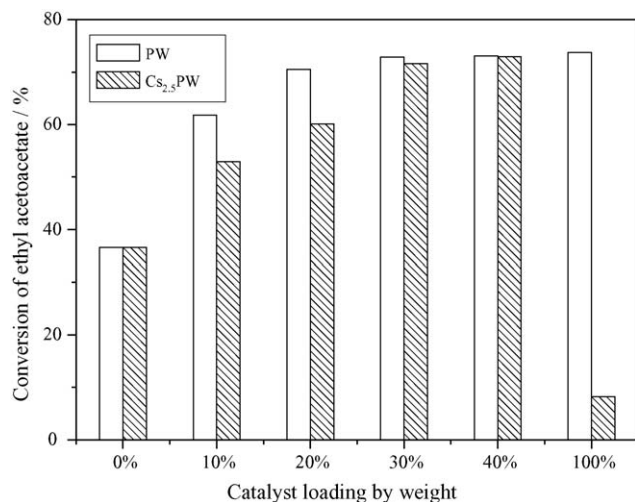


Fig. 7. Effect of PW and Cs salt loading on the conversion of ethyl acetoacetate over the PW/DUSY and the Cs<sub>2.5</sub>PW/DUSY catalysts.

ported PW catalyst, when Cs<sub>2.5</sub>PW loading exceeded 30%, no obvious enhancement of conversion is observed on the supported catalysts. It can be proposed that the high activity of supported heteropoly compounds is associated with their high surface area, as well as the superacidity.

### 3.2.3. Optimal reaction conditions for synthesis of fructose over 30%Cs<sub>2.5</sub>PW/DUSY catalyst

At the above we have investigated the catalytic behavior of the supported catalysts in acetalization of ethyl acetoacetate with ethylene glycol at the typical reaction conditions. In the following we optimize the reaction parameters over 30%Cs<sub>2.5</sub>PW/DUSY catalyst with the use of cyclohexane as the water removal agent in order to maximize the yield of fructose.

Effect of mass fraction of 30%Cs<sub>2.5</sub>PW/DUSY in reaction medium on the conversion of ethyl acetoacetate is measured. As shown in Fig. 8, the conversion of ethyl acetoacetate increases with the increase of mass fraction of 30%Cs<sub>2.5</sub>PW/DUSY, and reaches the plateau value of 98.7% when the mass fraction of catalyst is 0.6%. The further increase usage of the catalyst leads to no obvious enhancement of conversion. This indicates that the optimal mass fraction of catalyst in the reactants is 0.6%.

Effect of molar ratio of ethyl acetoacetate with ethylene glycol on the conversion of ethyl acetoacetate is revealed in Fig. 9. It can be found that the conversion of ethyl acetoacetate is influenced by the molar ratio of reactants. A maximum conversion of ethyl acetoacetate about 99% was achieved when the molar ratio of ethyl acetoacetate to ethylene glycol is 1:1.5.

The purpose of using water removal agent is to separate the water from reaction medium as quickly as possible during the acetalization reaction, so as to promote the reaction equilibrium. Effect of the concentration of water removal agent on the conversion of ethyl acetoacetate is examined. As shown in Fig. 10, the conversion of ethyl acetoacetate reaches the maximum when the concentration of water removal agent is 40% in the reaction

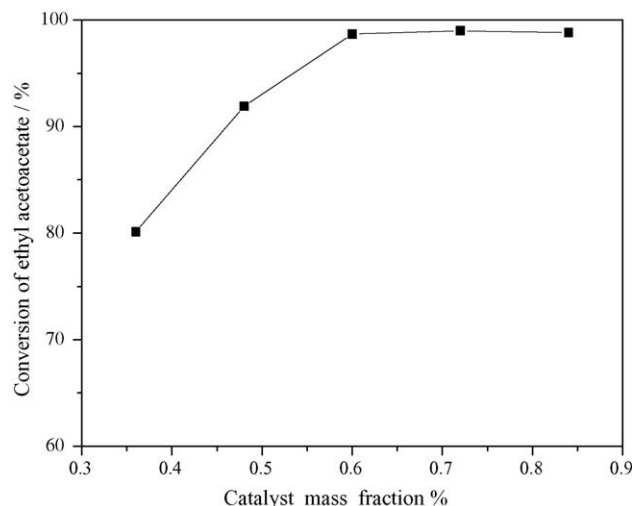


Fig. 8. Effect of catalyst mass fraction in the reaction medium on the conversion of ethyl acetoacetate. Reaction conditions: molar ratio of ethyl acetoacetate to ethylene glycol being 1:1.5, concentration of water removal agent being 40% in the reaction medium, reaction temperature being 90 °C, and reaction time being 90 min.

medium. More usage of cyclohexane leads to the decrease of conversion of ethyl acetoacetate probably due to decreasing the concentration of reactants.

Effect of reaction time on the conversion of ethyl acetoacetate is inspected at the reaction temperature of 70 and 90 °C, respectively, as presented in Fig. 11. It can be seen that the conversion of ethyl acetoacetate increases remarkably with the prolonging of reaction time regardless of the reaction temperature, and a high conversion of about 99% and a low conversion of 73% are obtained after 90 min of reaction time at the reaction temperature of 90 and 70 °C, respectively. It is noteworthy of that the con-

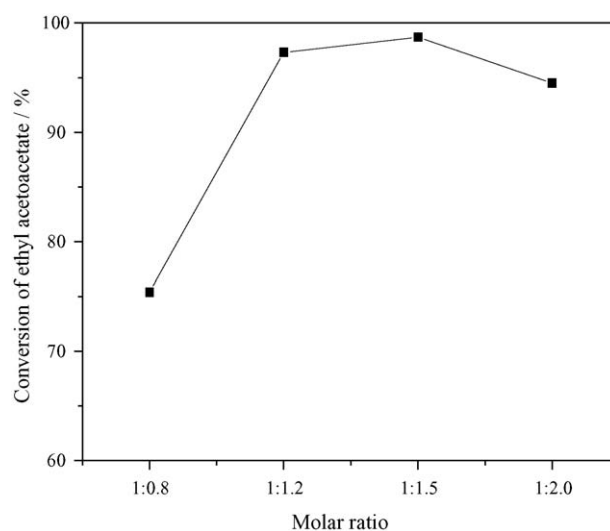


Fig. 9. Effect of molar ratio of ethyl acetoacetate with ethylene glycol on the conversion of ethyl acetoacetate. Reaction conditions: the mass fraction of catalyst being 0.6% in the reactants, concentration of water removal agent being 40% in the reaction medium, reaction temperature being 90 °C, reaction time being 90 min.

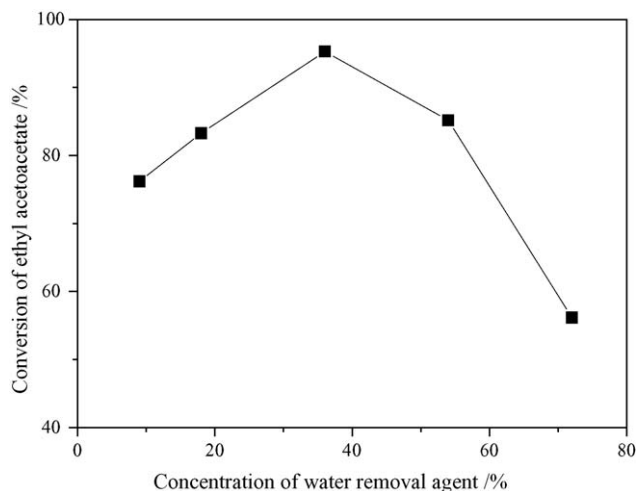


Fig. 10. Effect of the concentration of water removal agent on the conversion of ethyl acetoacetate. *Reaction conditions:* molar ratio of ethyl acetoacetate to ethylene glycol being 1:1.5, the mass fraction of catalyst being 0.6% in the reactants, reaction temperature being 90 °C, and reaction time being 90 min.

version reaches the plateau value after 90 min of reaction time at the different reaction temperatures. At this moment, no more produced water could be separated from water knockout vessel and no clearly enhancement of ethyl acetoacetate conversion can be observed. This indicates that the reaction reaches its steady state after 90 min. In addition to the reaction temperature, the heating temperature could exert considerable impact upon the reaction rate. When the heating temperature is beyond 90 °C, an enhancement of conversion at similar reaction time could be obtained, which should be due to the acceleration of refluxing and the more quickly removal of produced water. However, the reaction solution is still kept at 90 °C, which indicates that an azeotropic temperature has already been reached.

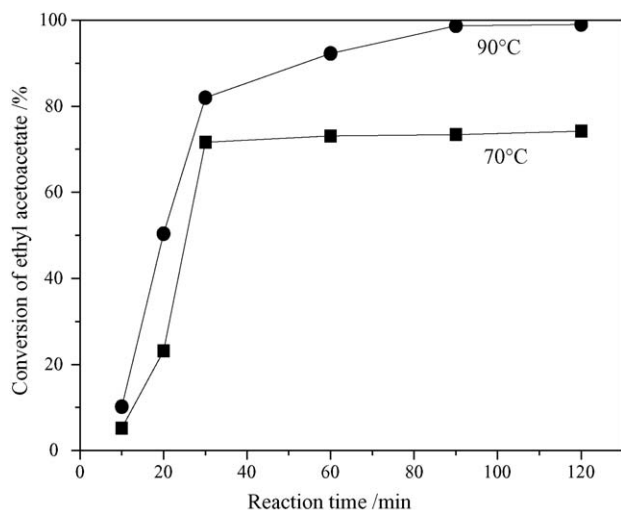


Fig. 11. Effect of reaction time on the conversion of ethyl acetoacetate at the reaction temperature of 70 and 90 °C. *Reaction conditions:* molar ratio of ethyl acetoacetate to ethylene glycol being 1:1.5, the mass fraction of catalyst being 0.6% in the reactants, concentration of water removal agent being 40% in the reaction medium.

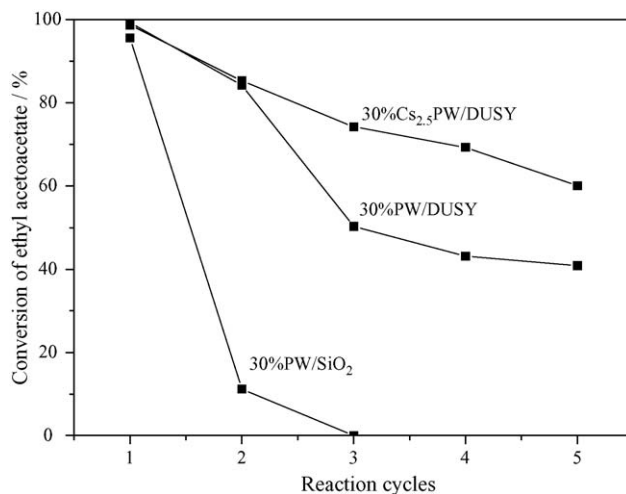


Fig. 12. Comparison of the catalytic stability of 30%PW/SiO<sub>2</sub>, 30%PW/DUSY and 30%Cs<sub>2.5</sub>PW/DUSY catalysts. *Reaction conditions:* molar ratio of ethyl acetoacetate to ethylene glycol being 1:1.5, the mass fraction of catalyst being 0.6% in the reactants, concentration of water removal agent being 40% in the reaction medium, reaction temperature being 90 °C, reaction time being 90 min.

### 3.2.4. Comparison of the catalytic stability

The catalytic stability of 30%PW/DUSY, 30%Cs<sub>2.5</sub>PW/DUSY and 30%PW/SiO<sub>2</sub> in acetalization of ethyl acetoacetate with ethylene glycol into fructose is compared under the optimal reaction conditions, as shown in Fig. 12. It is revealed that the 30%PW/SiO<sub>2</sub> catalyst exhibits an initial activity with conversion of ethyl acetoacetate being 95.6% and selectivity of fructose above 97%, which is comparable with those over DUSY supported samples. However, 30%PW/SiO<sub>2</sub> loses its catalytic activity completely after three reaction cycles, which indicates a very quick deactivation. The 30%PW/DUSY also deactivates quickly, and a low conversion of 40.9% remains at the fifth reaction cycle. In contrast, for 30%Cs<sub>2.5</sub>PW/DUSY, a rather high conversion of 66.2% still could be achieved after five times of reaction. It should be noted that the decrease of conversion in Fig. 12 arising from the catalyst lost during the separation and transfer of the catalyst for the next reaction recycle cannot be excluded.

### 3.2.5. Leakage of heteropoly species during water treatment

The solubility of heteropoly compounds in 30%PW/DUSY, 30%Cs<sub>2.5</sub>PW/DUSY and 30%PW/SiO<sub>2</sub> catalysts during the water treatment is compared in Table 2, where the concentration of heteropoly species in the water solution stands for the leaching amount. It can be seen that the HPAs in 30%PW/SiO<sub>2</sub> and 30%PW/DUSY are much easier to be released into water than 30%Cs<sub>2.5</sub>PW/DUSY. As shown in Table 2, during the first water treatment, a large amount of PW from the former two catalysts is leached into water with a very high concentration of heteropoly species in the filtrate (3.46 mol L<sup>-1</sup> for 30%PW/SiO<sub>2</sub> and 1.62 mol L<sup>-1</sup> for 30%PW/DUSY), both of which are more than 10 times higher than that for 30%Cs<sub>2.5</sub>PW/DUSY (0.145 mol L<sup>-1</sup>). Totally, after five times of water treatment, the leaching amount of PW is more than six times higher than that of the corresponding cesium salt.

Table 2

Concentration of heteropoly compound after water treatment for 30%PW/DUSY, 30%PW/SiO<sub>2</sub> and 30%Cs<sub>2.5</sub>PW/DUSY catalysts

	Water treatment times					Total
	1	2	3	4	5	
Concentration for 30%PW/DUSY (mol L <sup>-1</sup> )	1.62	0.161	0.0200	0.0201	0.0128	1.82
Concentration for 30%Cs <sub>2.5</sub> PW/DUSY (mol L <sup>-1</sup> )	0.145	0.0645	0.0323	0.0274	0.0173	0.287
Concentration for 30%PW/SiO <sub>2</sub> (mol L <sup>-1</sup> )	3.46	0.112	0.0139	0.00694	0.0022	3.61

This observation well verifies that the low catalytic stability of 30%PW/SiO<sub>2</sub> and 30%PW/DUSY in the acetalization reaction are mainly originated from their high leaching properties in polar medium, and the high reusability of 30%Cs<sub>2.5</sub>PW/DUSY comes from its low leaching amount. It could be suggested that, the low leaching amount of heteropoly species for 30%Cs<sub>2.5</sub>PW/DUSY is probably because of the existence of trace amount of free acid phases in the solid heteropoly acid salt [31].

#### 4. Conclusions

PW and DUSY supported PW catalysts exhibit high catalytic activities in the liquid-phase acetalization of ethyl acetoacetate with ethylene glycol for synthesizing fructose. However, continuous leaching of HPAs into the reaction medium leads to a poor catalytic stability. A very high catalytic activity and stability is found on Cs<sub>2.5</sub>PW/DUSY catalyst, which could ascribe to their superacidity, high surface area and water-tolerance. The reaction conditions to synthesize fructose are optimized as follows: molar ratio of ethyl acetoacetate to ethylene glycol being 1:1.5, the mass fraction of catalyst in reactants being 0.6%, concentration of water removal agent in reaction medium being 40%, reaction temperature being 90 °C, and reaction time being 90 min. In this case, an ethyl acetoacetate conversion of 98.7% with the fructose selectivity of above 97% is achieved, accompanying the high water-tolerance of catalyst and catalytic reusability without regeneration.

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