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**Hydrolysis and alcoholysis of polysaccharides with high efficiency catalyzed by  
(C<sub>16</sub>TA)<sub>x</sub>H<sub>6-x</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> nanoassembly**

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**Abstract**

Well-Dawson structure heteropolyacid (HPA) H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> was firstly used as a precursor to fabricate micellar assembly [C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sub>x</sub>H<sub>6-x</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> (abbreviated as (C<sub>16</sub>TA)<sub>x</sub>H<sub>6-x</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>). Hydrolysis and methanolysis of polysaccharides including cellobiose, starch, and cellulose was catalyzed by (C<sub>16</sub>TA)<sub>x</sub>H<sub>6-x</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>. (C<sub>16</sub>TA)<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> showed the highest activity, with hydrolysis rates of cellobiose, starch and cellulose of 0.74, 0.02, 0.0.8 min<sup>-1</sup> at 100 °C, 120 °C and 160 °C, respectively, much better than Keggin H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. Meanwhile, (C<sub>16</sub>TA)<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> performed 94.8 % conversion of cellulose into methyl levulinate (MLA) with 58.5 % yield in methanol. The high activity of catalyst was attributed to the synergistic effect of high concentration of acid, more substrates adsorbed, and oxidizing ability of (C<sub>16</sub>TA)<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>. The results demonstrated that it was an effective and reusable catalyst for the production of glucose and MLA from polysaccharides.

**Keywords:** Hydrolysis; alcoholysis; micellar heteropolyacid; Well-Dawson structure; heterogeneous catalysis

**1. Introduction**

Biomass is the only sustainable source for organic carbon on the earth, which is considered as one of the alternative ways for production of fuels and chemicals.<sup>1</sup> Therefore, efficient utilization of lignocelluloses biomass for the production of chemicals and fuels has attracted much attention in recent years.<sup>2-4</sup> For the efficient conversion of raw biomass to biofuel, essential processes has to be managed and optimized as (1) the separation of the diverse raw material fractions including cellulose, hemicellulose and lignin, (2) conversion of cellulose to glucose, and (3) conversion of glucose to the final products.<sup>5-7</sup> In addition, glucose is a versatile precursor to valuable chemicals

such as biodegradable plastics and ethanol. Therefore, hydrolysis of cellulose into glucose with high selectivity is recognized as a key technology.<sup>8</sup> Meanwhile, methanolysis instead of hydrolysis is also sufficient process to produce methyl - glucoside (MG) or further methyl levulinate, which are interesting platforms for further transformation.<sup>9</sup> For the above two processes, the important technology is the acid-catalyzed hydrolysis of cellulose to glucose, or acid-catalyzed alcoholysis of cellulose to sugar then alkylation to MG and MLA in a single pot.

Homogeneous catalysts such as mineral acids named  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  or cellulose enzymes produce glucose in high yields from cellulose,<sup>10,11</sup> but these processes suffer from the rigorous reaction conditions, the complicated separation of products from the solution, and high costs of enzymes. To fit with the “green chemistry”, recyclable solid catalysts are always desirable both in hydrolysis and in alcoholysis processes due to the concerning economy, simplicity, efficiency and environmental benign. Heterogeneous catalysts are expected to overcome these problems, as various types of catalysts with large pore size and strong acid strength can be designed and applied in a wide range of reaction conditions.<sup>12-15</sup> Several types of solid acids and their catalytic performance are summarized in Table S1. By now, the best yield of glucose had been obtained as about 77 % from cellulose catalyzed by  $\text{H}_5\text{BW}_{12}\text{O}_{40}$ , but long reaction time and high usage of catalyst were required to confirm the glucose yield. For alcoholysis of cellulose, the highest MG yield (90%) with the complete conversion of cellulose was achieved in methanol at 250 and 275 °C catalyzed by sulfonated bio-char after very short reaction times of 30 and 15 min, respectively.<sup>16</sup> Up to 40 % yield of MLA was achieved by acidic  $\text{TiO}_2$  nanoparticles at 175 °C for 20 h.<sup>17</sup>

Among the heterogeneous catalysts, heteropolyacids (HPAs) had been regarded as potential candidates for the conversion of biomass due to their fascinating architectures and excellent physicochemical properties such as strong Brønsted acidity, high proton mobility and good stability.<sup>18-21</sup> Among HPAs, Keggin structure  $\text{H}_n\text{XW}_{12}\text{O}_{40}$  ( $\text{X} = \text{P}, \text{Si}, \text{Ge}, \text{Al}, \text{Co}, \text{Ga}$  and  $\text{B}$ ) had been evaluated in hydrolysis of cellulose into glucose.<sup>22</sup>  $\text{H}_5\text{BW}_{12}\text{O}_{40}$  was found to be the most active species to give the highest yield of glucose due to its highly negatively charge. Despite the relative efficiency of these Keggin HPAs in cellulose hydrolysis, new HPAs are needed to be explored wherein the reaction can proceed even at relatively lower molar ratios, catalyst amounts and temperatures. Thus it is still a challenge to design a green and sustainable process for the same. Wells-Dawson structure  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  owns highly negatively charge and could provide six protons

much more than  $H_5BW_{12}O_{40}$  and  $H_3PW_{12}O_{40}$ , which might be more suitable for such desire. By now, there were so many affords had been paid for Keggin HPAs and their activity and little attention had been paid for Well-Dawson structure  $H_6P_2W_{18}O_{62}$ .

As is known, the hydrolysis or alcoholysis of cellulose is always restricted by the poor contact between a solid catalyst and cellulose in heterogeneous catalysis. Therefore, hydrolysis reactions always require higher catalyst/substrate mass ratios, higher temperature and longer reaction times to achieve maximum conversion. However, such harsh conditions always lead to a lower selectivity to glucose and more by-products. Many studies have focused on developing effective approaches or technologies for the conversion of cellulose. During our research, we found that micellar HPAs could provide a nano-reactor to concentrate cellulose molecules around catalytic sites to accelerate hydrolysis of cellulose<sup>[23]</sup>. Fabrication of micellar HPA catalysts is an essential way to improve the hydrolysis of cellulose. Therefore, we designed and synthesized micellar HPA catalysts  $[C_{16}H_{33}N(CH_3)_3]_nH_{6-n}P_2W_{18}O_{62}$  (abbreviated as  $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$ , while  $n = 1-6$ ), which is the first micellar assembly of Well-Dawson structure HPAs. The purpose of this work is to develop a new micellar HPA catalyst in hydrolysis of cellulose into glucose with higher efficiency. Another is to determine construction of Dawson type HPAs with surfactants, and whether such assembly is suitable for cellulose conversion or not. Third is to indicate the influence of oxidizing ability of  $H_6P_2W_{18}O_{64}$ <sup>24</sup> on accelerating the reaction rate of cellulose hydrolysis or alcoholysis (Table S3). To the best our knowledge, there is no report on the self-assembly of Well-Dawson HPAs and surfactants as building blocks. Meanwhile, there is either no report on hydrolysis and alcoholysis of cellulose catalyzed by micellar Dawson HPAs with high efficiency. More importantly, we firstly discussed the influence of oxidative on the cellulose hydrolysis.

## 2. Materials and Methods

### 2.1 Materials and Instrument

Microcrystalline cellulose (white, average particle size 50 $\mu$ m) was obtained from J & K chemical Ltd (Beijing, China). The X-ray diffraction analysis was carried out on Japan Rigaku Dmax 2000 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154178$  nm) to analyze the structure of cellulose, and the degree of cellulose crystallinity was about 0.6. The degree of polymerization was 300 measured by viscosity.  $H_6P_2W_{18}O_{62}$  was prepared according to the literature method<sup>[25]</sup>. All other reagents were of analytical reagent (AR) grade and used without further purification.

3,5-dinitrosalicylic acid (DNS) reagent was prepared according to Ref. [26].

FTIR spectra ( $4000\text{-}400\text{ cm}^{-1}$ ) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. X-ray diffraction (XRD) patterns of the sample were collected on a Japan Rigaku D/max-2000 X-ray diffractometer with Cu-K $\alpha$  radiation 40 kV/40 mA ( $\lambda = 0.154178\text{ nm}$ ). TEM micrographs were recorded on a Hitachi H-600 transmission electron microscope. The  $^{31}\text{P}$  NMR spectra was recorded on a Bruker AVANCE III 400 MB spectrometer equipped with a 4 mm standard bore CPMAS probe head whose X channel was tuned to 162 and 100.62 MHz, respectively. The critical micellar concentration (CMC) of  $(\text{C}_{16}\text{TA})\text{H}_5\text{P}_2\text{W}_{18}\text{O}_{62}$  was determined by a plot of conductivity versus concentration using the conductometer model DDS-11A. Centrifugation was performed on T4C Centrifuge (4000 rpm, 5 min, Beijing Yiyao). The leaching of  $(\text{C}_{16}\text{TA})\text{H}_5\text{P}_2\text{W}_{18}\text{O}_{62}$  during the reaction were also measured through analyzing the dissolved concentration of W in aqueous solution using a Leeman Plasma Spec (I) ICP-ES. The concentration of glucose was measured in the aqueous phase by High-performance liquid chromatography (HPLC), which conducted on a system equipped with a refractive index detector (Shimadzu LC-10A, HPX-87H column). The concentrations of monoester were determined periodically on Shimadzu GC-14C fitted with a HP-INNO Wax capillary column and flame ionization detector. The amount of MLA was analyzed by gas chromatography (Agilent 6890) equipped with an Agilent 19091J-416 capillary column and flame ionization detector.

## 2.2 Preparation of catalyst

A typical preparation of  $(\text{C}_{16}\text{TA})\text{H}_5\text{P}_2\text{W}_{18}\text{O}_{62}$  was as follows: 10 mL 40 mM of hexadecyltrimethylammonium bromide (CTAB) was added into 10 mL 40 mM of  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  solution with stirring. Immediately the pale yellow precipitate formed and collected by filtration then calcined at  $100\text{ }^\circ\text{C}$  for 3 h. The yield of  $(\text{C}_{16}\text{TA})\text{H}_5\text{P}_2\text{W}_{18}\text{O}_{62}$  was about 40 %. Anal. Calcd. for  $(\text{C}_{16}\text{TA})\text{H}_5\text{P}_2\text{W}_{18}\text{O}_{62}$ : W, 71.12; P, 1.33; C, 4.90; N, 0.30; H, 1.02 %. Found: W, 71.45; P, 1.21; C, 4.81; N, 0.29 %.

Other catalysts were synthesized in the same method except using different molar ratio of surfactant CTAB and  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ . The yields of  $(\text{C}_{16}\text{TA})_2\text{H}_4\text{P}_2\text{W}_{18}\text{O}_{62}$ ,  $(\text{C}_{16}\text{TA})_3\text{H}_3\text{P}_2\text{W}_{18}\text{O}_{62}$ ,  $(\text{C}_{16}\text{TA})_4\text{H}_2\text{P}_2\text{W}_{18}\text{O}_{62}$ ,  $(\text{C}_{16}\text{TA})_5\text{HP}_2\text{W}_{18}\text{O}_{62}$  and  $(\text{C}_{16}\text{TA})_6\text{P}_2\text{W}_{18}\text{O}_{62}$  were 44, 51, 58, 63 and 70%, respectively. The elementary results were given in Table S2.

### 2.3 Catalytic procedure

For hydrolysis of starch, a mixture of starch (0.1 g) and catalyst (0.08 mmol) in distilled water (5 mL) were heated at 120 °C in a steel autoclave lined with Teflon under air for 5 h with agitation (300 rpm). At the end of the reaction, the mixture was cooled to room temperature and was centrifuged to separate the catalyst and unreacted starch.

For hydrolysis of cellulose, a mixture of cellulose (0.1 g) and catalyst (0.08 mmol) was added into water (5 mL). Then it was heated at 160 °C in a steel autoclave lined with Teflon under air for 9 h with stirring (300 rpm). The reaction was stopped by rapidly cooling the reactor in an ice bath at 0 °C. At the end of the reaction, the mixture was centrifuged to separate the catalyst and unreacted cellulose.

For alcoholysis of cellulose, a mixture of cellulose (0.1 g) and catalyst (0.07 mmol) in methanol (8 mL) were heated at 160 °C in a steel autoclave lined with Teflon under air for 7 h with agitation (1200 rpm). At the end of the reaction, the mixture was centrifuged to separate the catalyst and unreacted cellulose.

### 2.4 Total reducing sugars (TRS) analysis <sup>26</sup>

A mixture that contained 2 mL of DNS reagent and 1 ml of reaction sample was heated for 2 min in a boiling water bath, then cooled to room temperature by flowing water, and mixed with deionized water to 25 mL. The color intensity of the mixture was measured in a UV757CRT Model spectrophotometer at 540 nm. The concentration of total reducing sugars was calculated based on a standard curve obtained with glucose.

### 2.5 Critical micelle concentration (CMC) determination

The CMC of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  was determined by break points of two nearly straight-line portions of the specific conductivity versus concentration plot <sup>[27]</sup>.

### 2.6 Adsorption experiments

Adsorption experiments were carried out to determine the adsorption capacity of catalysts for polysaccharides. In the simultaneous adsorption experiments, 0.07 mmol of catalyst and 0.05 g of cellulose were mixed in a steel autoclave lined with Teflon for 12 h at room temperature in order to determine the adsorption effects by the IR spectroscopy.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. S1 gave the IR spectra of the  $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$ . Obviously, the characteristic bands of the Dawson structure were observed at 1098, 966, 901, and 790  $cm^{-1}$  corresponding to the stretching vibrations of the  $PO_4$  tetrahedron [25], W-O (terminal bonds), and W-O-W bridges, respectively. These results determined the as prepared HPAs kept the Well-Dawson structure after self-assembling with surfactant. C-H stretching vibrational peaks at 2927 and 2833  $cm^{-1}$ , and C-N at 1673  $cm^{-1}$  determined the existence of  $C_{16}TA$  in the catalysts.

The  $^{31}P$  MAS NMR spectra of  $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$  ( $n=1-6$ ) all gave one signal peak around  $\delta = -14.01 \sim -13.956$  (Fig. S2), corresponding to  $(C_{16}TA)H_5P_2W_{18}O_{62} \sim (C_{16}TA)_6P_2W_{18}O_{62}$ , respectively. The  $H_6P_2W_{18}O_{62}$  gave one peak at -12.9 ppm [28]. The shifts of  $^{31}P$  MAS NMR were attributed to the introduction of organic cations into  $H_6P_2W_{18}O_{62}$ . This could confirm the formation of one assembly of HPAs and  $C_{16}TA$  and there was no the physical mixture of  $C_{16}TA$  and  $P_2W_{18}O_{62}^{6-}$ . The different shifts of these HPAs were attributed to the different number of organic group.

Powder X-ray diffraction patterns were used to confirm the structure of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ . Compared with the diffraction peaks of  $H_6P_2W_{18}O_{62}$ ,  $(C_{16}TA)H_5P_2W_{18}O_{62}$  gave the similar diffraction peaks (Fig. S3b). This result indicated the original structure of  $H_6P_2W_{18}O_{62}$  being attained after forming the micelles.

The CMC of  $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$  ( $n=1, 2, 3, 4, 5, 6$ ) were given in Fig. S4, which showed that the CMC of  $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$  ( $n=1, 2, 3, 4, 5, 6$ ) were 0.92 mM. This also confirmed the formation of micelle in aqueous solution. [27]

The cryo-TEM image of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  also showed that it could form relatively uniform micellar nanorod. The length of the nanorod was 200 nm.(Fig. S5) EDX measurement results suggested the molar ratio of C: P: W= 19: 2: 18. The elementary results also determined the formula of  $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$ .

The acid amount of the catalyst was also measured by titration. The acidity content of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  was 3.2 mmol/g, which was lower than  $H_6P_2W_{18}O_{62}$  (3.8 mmol/g) because of the exchange of one proton by  $C_{16}TA$  cation.

### 3.2 Effect of catalysts

It was known that hydrolysis of polysaccharides could be catalyzed by Brønsted acid, while the strength of Brønsted acid played an important role on the hydrolysis reaction. Therefore,

the different micellar HPAs with various amount of protons had been used in hydrolysis of cellulose to determine the catalytic activity under the reaction conditions as 100 mg of cellulose, 0.08 mmol of catalyst, 5 mL H<sub>2</sub>O at 160 °C in 9 h. It can be seen from Table 1, the cellulose conversion and turnover frequency (TOF) followed the order of (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>2</sub>H<sub>4</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>3</sub>H<sub>3</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>4</sub>H<sub>2</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>5</sub>HP<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, which was corresponding to the order of acid contents. This indicated that the Brønsted acidity of such HPA catalysts influenced the conversion of cellulose and the yield of glucose as well. H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> performed 93.5 % conversion of cellulose better than (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> due to its homogeneous form and one more proton. Among micellar HPAs, the best conversion of cellulose was obtained as 87.2 % by (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>. As for glucose yields, the order was (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>2</sub>H<sub>4</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>3</sub>H<sub>3</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>4</sub>H<sub>2</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>5</sub>HP<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>. For homogeneous HPAs, the yield of glucose was lower than those of micellar HPAs, determining that the glucose yield was enhanced by using micellar HPA catalysts. The high acidic sites on H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> would result in higher conversion (TOF 12.9×10<sup>-2</sup> g/mmol · h ) but lower yield of glucose. The selectivity of glucose for micellar HPAs were in range of (C<sub>16</sub>TA)<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>5</sub>HP<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>4</sub>H<sub>2</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>3</sub>H<sub>3</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)<sub>2</sub>H<sub>4</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> > (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>. It could be seen that the selectivity to glucose was consistent with the order of their Brønsted acidity. Among the micellar HPA catalyst, (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> gave cellulose conversion lower than H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> with 6.3 % form 93.5 % to 87.2 % , but selectivity increased from 48.8 to 79.2 %. The high conversion of (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> was contributed to the formation of micellar assembly, which could accumulate cellulose molecules around H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub><sup>-</sup> sites. For the HPA micelles containing the same organic group, the activity of (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> was higher than that of (C<sub>16</sub>TA)H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>, which could be attributed to the amount of cellulose molecules adsorbed by different HPA micelles. And this difference was also contributed to the different morphology of micellar assembly, which (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> was nanorod with 200 nm length and (C<sub>16</sub>TA)H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub> was nanosphere with 10 nm. The adsorption test for (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> and (C<sub>16</sub>TA)H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub> determined this hypothesis (Fig. S6). The IR spectrum (Fig. S6a) of (C<sub>16</sub>TA)H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> adsorbed cellulose gave four characteristic peaks



corresponding to polyoxoanion  $P_2W_{18}O_{62}^{6-}$ , showing no structural change of the catalyst during the reaction. Compared to that of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , some vibration bands shifted, indicating that some interaction occurs between the O atom from cellulose and the terminal oxygen atom from the HPA molecules. Compared to the peak of the original cellulose at  $1164\text{ cm}^{-1}$ , the C-O-C stretching bands shifted to  $1170\text{ cm}^{-1}$  for  $(C_{16}TA)H_5P_2W_{18}O_{62}$  but  $1163\text{ cm}^{-1}$  for  $(C_{16}TA)H_2PW_{12}O_{40}$  due to the interaction between C-O-C and HPAs. Higher shift was attributed to the more cellulose molecules being absorbed by Well-Daswon  $(C_{16}TA)H_5P_2W_{18}O_{62}$  than by Keggin  $(C_{16}TA)H_2PW_{12}O_{40}$ . This might be resulted by the bigger size of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  than  $(C_{16}TA)H_2PW_{12}O_{40}$ , which could provide bigger rooms for cellulose molecules. This was the another reason that Well-Daswon HPAs were selected in cellulose conversion. Therefore, cellulose was accumulated compared to the surrounding water phase through interactions with the micelle surface or through insertion into the micelle itself, which overcame the insolubility of cellulose in water. Hereby, two synergistic effects enabled superior results, which were the adsorption of cellulose on micellar HPA catalysts, and the conversion of cellulose into glucose by Brønsted acid.

**Table 1**

For cellulose hydrolysis, the usages of Brønsted acid catalyst might affect the conversion. Therefore, the influence of catalyst amounts on the hydrolysis of cellulose was investigated by varying the amount of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ . From the Fig. 1, it can be seen increasing the catalyst usage from 0.05 mmol to 0.08 mmol, the conversions of cellulose increased from 39.5 % to 87.2 % and the glucose selectivity also increased. A continuing increased the catalyst usage to 0.09 mmol, the conversion increased to 92.6 %, while the selectivity decreased to 76.5 %. The maximum selectivity and glucose yield of 79.2 % and 69.1 % were obtained by using 0.08 mmol catalyst.

**Fig. 1**

Water was a necessary reactant in the hydrolysis of cellulose, but excess volume of water would affect the hydrolysis of cellulose. It could be seen from Fig. 2 that conversion, TRS and glucose yield increased with added the amount of water from 4 to 5 mL and reached a maximum at 5 mL of water. Further addition of water into the reaction system caused the efficiency of hydrolysis decreased sharply, which might be attributed to the decrease of acidic sites.

**Fig. 2**

Reaction time and temperature were key parameters to determine the products of cellulose hydrolysis. Therefore, the formation of glucose was done in different reaction times (5 to 10 h) and temperatures (130 - 160 °C) (Fig. 3). It could be seen that increasing the reaction time could increase the conversion of cellulose. The reaction time for maximum yields of TRS and glucose was different based on the different reaction temperature. It could be seen that the trend of glucose yield was increasing first then decreasing. The yield of glucose reached highest values of 69.1 % at 9 h. This result demonstrated that the conversion of cellulose to glucose could be obtained by acid-catalyst for a long reaction time.

In the low temperature at 130 °C, the conversion, yield of glucose increased, the conversion of cellulose and the yield of glucose reached 35.9% and 30.7% at 9 h, respectively. In the high temperature at 150 °C and 160 °C, although both the conversion and the yield of glucose were increasing with longer time, the selectivity of glucose was first increasing then decreasing.

**Fig. 3**

The hydrolysis of cellobiose and starch were also done catalyzed by  $(C_{16}TA)H_5P_2W_{18}O_{62}$ . It could be seen that the micellar  $(C_{16}TA)H_5P_2W_{18}O_{62}$  catalyst (0.08 mmol) could catalyze the hydrolysis of starch (0.1 g) at 120 °C for 2 h with 99.1% conversion and 94.2% yield of glucose. (Fig. 4a) Besides that, the hydrolysis of cellobiose (0.1 g) at 100 °C for 1 h with 100 % conversion and 92.4% yield of glucose. (Fig. 4b) Compared to the conversion of cellulose, the reaction condition for cellobiose and starch was not harsh.

**Fig. 4**

The alcoholysis of cellulose by this micellar HPA catalyst  $(C_{16}TA)H_5P_2W_{18}O_{62}$  was done in order to evaluate its catalytic activity. It could be seen that the micellar  $(C_{16}TA)H_5P_2W_{18}O_{62}$  catalyst (0.07 mmol) could catalyze the alcoholysis of cellulose (0.1 g) at 160 °C for 7 h with the methyl levulinate yield of 58.5% (Fig. 5). Further increasing of time did not increase the yield of methyl levulinate due to the side-reaction.

**Fig. 5**

We also discussed the effect on alcoholysis of cellulose with different structure of HPAs between Keggin and Dawson (Table 2). From the table, we could know Dawson HPAs were more

activity than Keggin HPAs. The conversion and yield were increased by Dawson HPAs in the same reaction conditions. The reason might be higher acidic contents.

**Table 2**

### 3.3 Reusability of the catalyst

The life span of a catalyst was a more important parameter for its evaluation. The regeneration of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  from the starch system was only done by washing with hot water to separate unreacted starch from the catalyst. And then the catalyst was dried for reuse. The leaching of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  into the mixture was only 18 ppm for one time.

The way to assay life span of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  in cellulose system was explored in the following way: after the first run of the reaction finished, the residues of unreacted cellulose and the catalyst were separated by centrifuge and dried on air. After dry, we refilled a certain amount of fresh cellulose into the sample for the next reaction and maintained the amount of cellulose as 100 mg (Fig. 6). It could see that the catalyst was still active in each recycle run with slight decrease for conversion and yield. The stability of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  during the reaction was determined by IR spectroscopy (Fig. S7). There was no change for IR spectrum compared to that of fresh one, showing that reused catalyst kept the Dawson structure during the reaction. After five reaction cycles,  $^{31}P$  MAS NMR spectra of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  (Fig. S2 d) did not change indicating the stability during the reactions.

**Fig. 6**

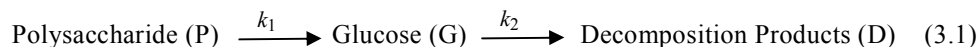
In order to determine the leaching of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , the UV-vis spectroscopy of the sample in methanol was done at 160 °C. The two characteristic bands at 236 nm and 297 nm could be seen corresponding to the charge transfer of oxygen to tungsten, indicating that  $(C_{16}TA)H_5P_2W_{18}O_{62}$  dissolved in  $H_2O$  with Well-Dawson structure. It could be concluded that the leaching of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  was attributed to the dissolution in solvent during the reaction. The total leaching of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  into the mixture for five times was 64 ppm, showing a little leaching of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  into mixture and  $(C_{16}TA)H_5P_2W_{18}O_{62}$  performing as heterogeneous catalysts for hydrolysis of cellulose.

The nanorod micellar catalyst could adsorbed more cellulose. It was benefited for oligomers derived from the partial hydrolysis of cellulose; further degradation is considered an indirect method of transforming cellulose. The high Brønsted acid concentration could be promoted the

oligomers conversion to glucose. (Scheme 1)

### Scheme 1

In order to demonstrate the determine step of polysaccharide to glucose, a study on kinetic behavior for polysaccharide hydrolysis to glucose was carried out over  $(C_{16}TA)H_5P_2W_{18}O_{62}$  in water. In this work a simplified reaction model according to the pattern of a single consecutive reaction described by (3.1) was used:



Rogalinski reported<sup>[29]</sup> that the mathematical models based on pseudo-first-order kinetics had been applied in the cellulose hydrolysis. When  $t = 0$ , the reaction rate equation was:

$$-\frac{dC_c}{dt} = kC_0 \quad (3.2)$$

Where  $C_c$  is the concentration of the polysaccharide (mg/mL),  $C_0$  is the initial concentration of the polysaccharide (mg/mL), and  $k$  is the reaction rate constant ( $\text{min}^{-1}$ ).

Integral (3.2) and divide  $C_0$ , the equation was:

$$\frac{C_c}{C_0} = e^{-kt} \quad (3.3)$$

Because of the cellulose was the pseudo-first-order kinetics and  $C_c/C_0 = 1 - X_c$ , the result was:

$$-\ln(1-X_c) = kt \quad (3.4)$$

Using equation (3.4) was carried out on the microcrystalline cellulose conversion linear fitting. (Fig. 7) The reaction rate constant ( $k$ ) for cellulose to glucose at 160 °C was found to be  $0.004 \text{ min}^{-1}$ . In the same, we also discussed the starch and cellobiose hydrolysis to glucose at 120 and 100 °C, respectively. The rate constant ( $k$ ) was 0.017 and  $0.17 \text{ min}^{-1}$  for starch and cellobiose, respectively.

**Fig. 7**

## 4. Conclusions

Micellar HPAs with Well-Dawson structure were the first assembled by surfactants and  $H_6P_2W_{18}O_{62}$ . The hydrolysis of polysaccharides such as cellobiose, starch, and cellulose had been achieved by the catalysts. Meanwhile,  $(C_{16}TA)H_5P_2W_{18}O_{62}$  was active in alcoholysis of cellulose into ester with 58.5 % yield. The good performance of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  was attributed to the micellar structure and highly acidic contents to provide more chance for substrates accessing to catalytic sites. High Brønsted contents overcame the difficulty in mass transport for solid - solid

reaction. In addition, this micellar HPA catalyst acted as heterogeneous one to be recycled by simple centrifuge for reuse.

### Acknowledgements

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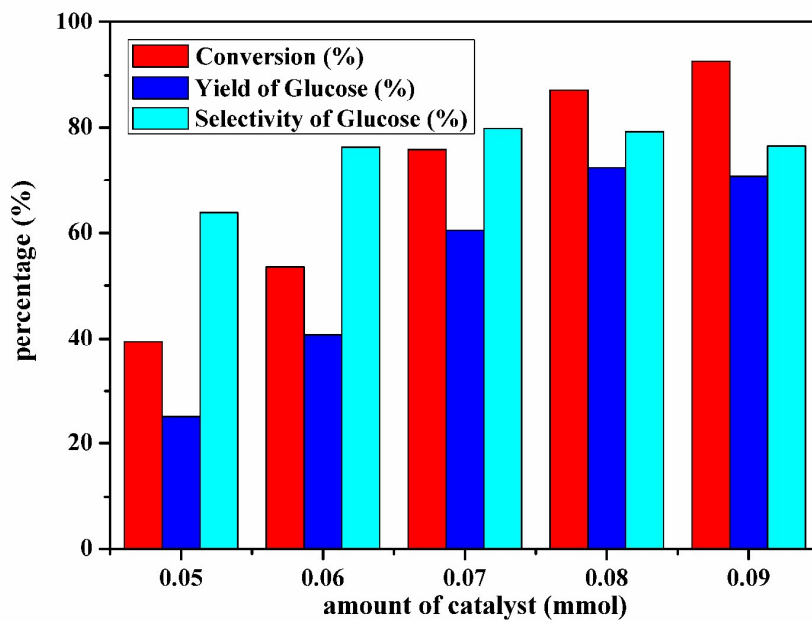
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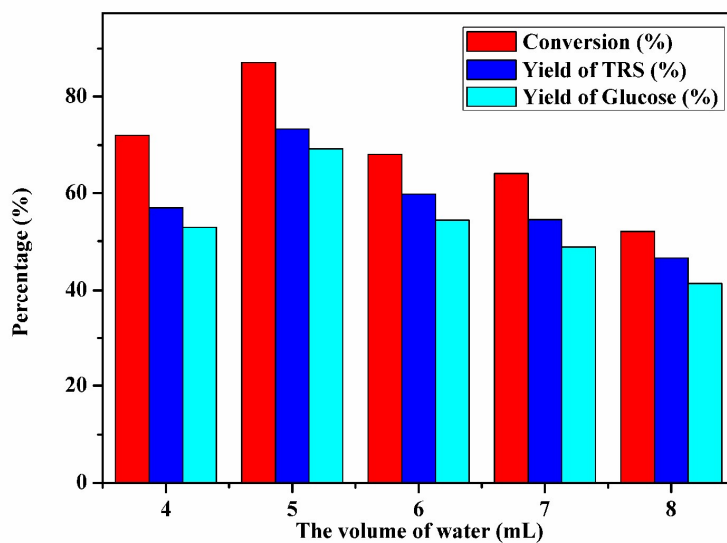
### Figure caption

- Fig. 1** The effect of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  dosages on cellulose hydrolysis. Reaction conditions: 100 mg of cellulose, 5 mL water at 160 °C in 9 h.
- Fig. 2** The effect of water addition on cellulose hydrolysis. Reaction conditions: 100 mg of cellulose, 0.08 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , at 160 °C in 9 h.
- Fig. 3** The effect of reaction temperature and time on cellulose hydrolysis. Reaction conditions: 100 mg of cellulose, 0.08 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , 5 mL  $H_2O$ .
- Fig.4** The influence of reaction time and temperature on starch (a) and cellobiose (b) dehydration. Reaction conditions: 0.1g of substrates, 0.08 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , 5 ml of water at 120 °C for starch and 0.03 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , 100 °C for cellobiose, respectively
- Fig. 5** The effect of reaction time on alcoholysis of cellulose. Reaction conditions: 100 mg of cellulose, 0.07 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , 8 mL methanol at 160 °C.
- Fig. 6** The catalytic activity of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  in five reaction cycles. Reaction conditions: 100 mg of cellulose, 0.08 mmol of catalyst, 5 ml of water at 160 °C for 9 h.
- Fig.7** Kinetic behavior for polysaccharide to glucose over  $(C_{16}TA)H_5P_2W_{18}O_{62}$ .
- Table 1** The compared results obtained by  $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$  (n = 1~6)
- Table 2** The effect on alcoholysis of cellulose with different kind of catalyst
- Scheme 1** The mechanism of the cellulose conversion by the catalyst.

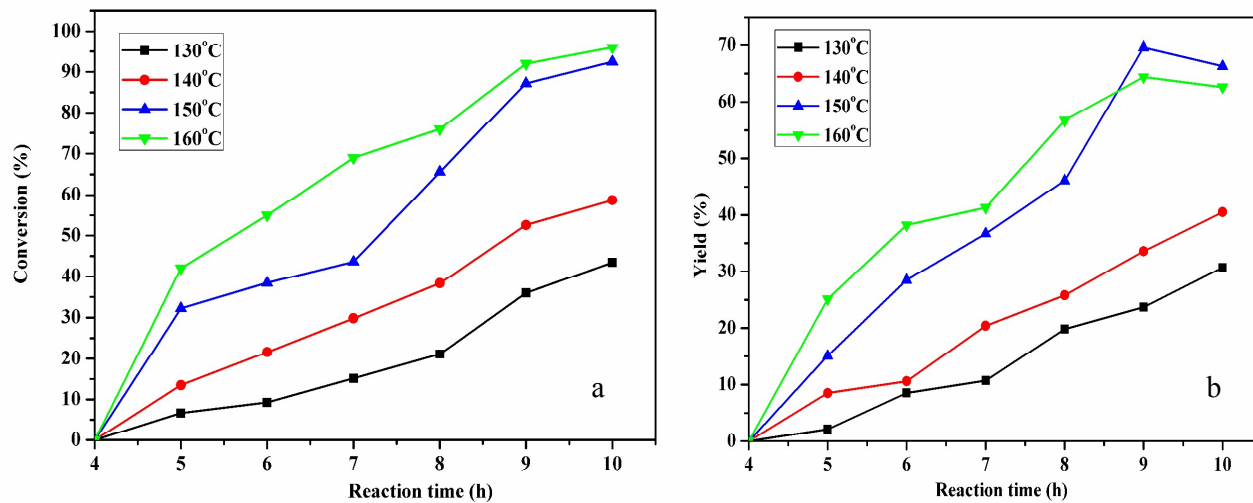


**Fig. 1** The effect of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  dosages on cellulose hydrolysis. Reaction conditions: 100 mg of cellulose, 5 mL water at 160 °C in 9 h.



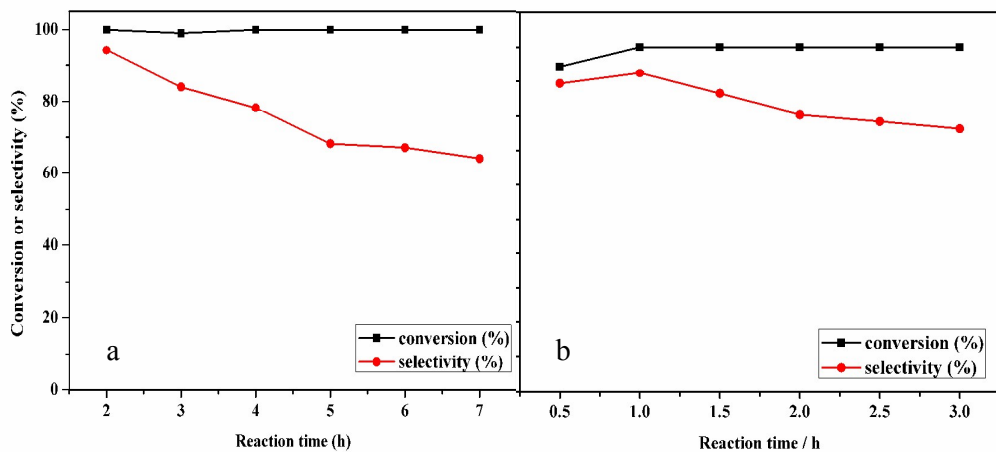


**Fig. 2** The effect of water addition on cellulose hydrolysis. Reaction conditions: 100 mg of cellulose, 0.08 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , at 160 °C in 9 h.

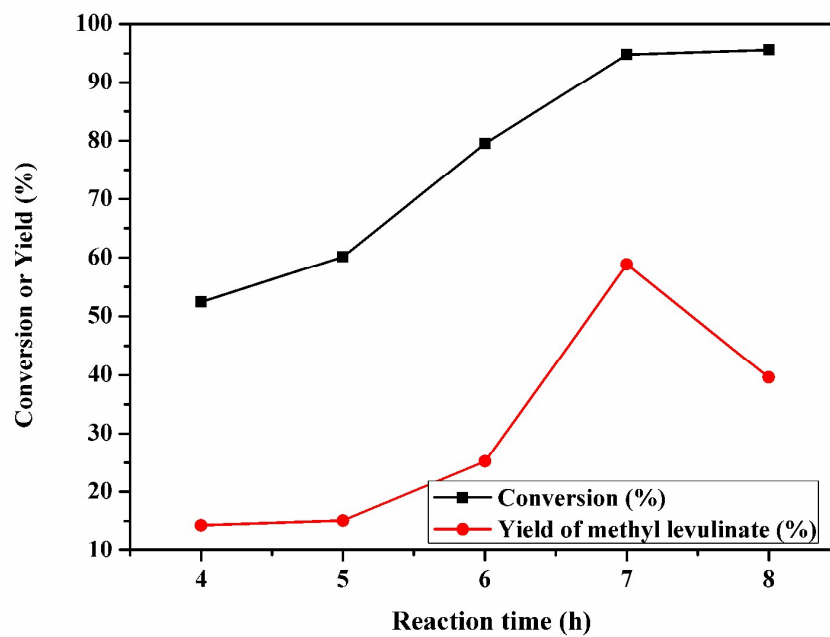


**Fig. 3** The effect of reaction temperature and time on cellulose hydrolysis. Reaction conditions:

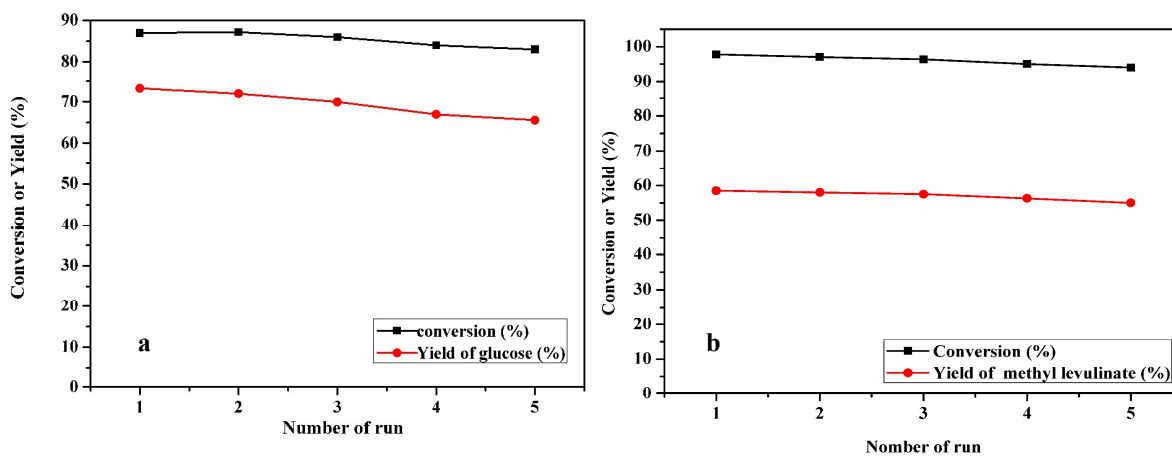
100 mg of cellulose, 0.08 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , 5 mL  $H_2O$ .



**Fig. 4** The influence of reaction time and temperature on starch (a) and cellobiose (b) dehydration. Reaction conditions: 0.1g of substrates, 0.08 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , 5 ml of water at 120 °C for starch and 0.03 mmol of  $(C_{16}TA)H_5P_2W_{18}O_{62}$ , 100 °C for cellobiose, respectively



**Fig. 5** The effect of reaction time on alcoholysis of cellulose. Reaction conditions: 100 mg of cellulose, 0.07 mmol of  $(C_{16}TA)H_3P_2W_{18}O_{62}$ , 8 mL methanol at 160 °C.



**Fig. 6** The catalytic activity of  $(C_{16}TA)H_5P_2W_{18}O_{62}$  in five reaction cycles. (a) cellulose hydrolysis (b) cellulose alcoholysis Reaction conditions: (a) 100 mg of cellulose, 0.08 mmol of catalyst, 5 ml of water at 160 °C for 9 h; (b) 100 mg of cellulose, 0.07 mmol of catalyst, 8 ml methanol of at 160 °C for 7 h;

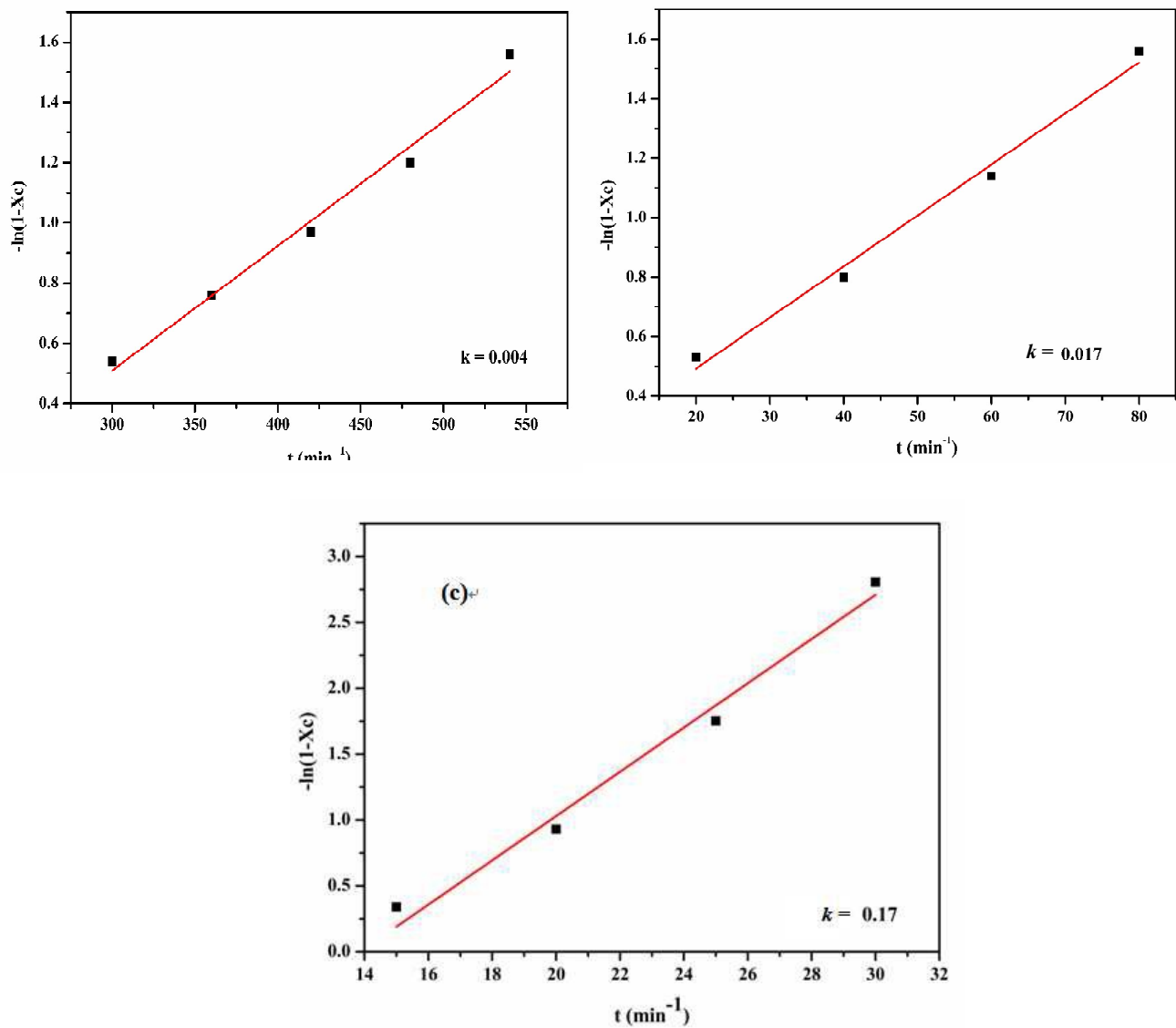
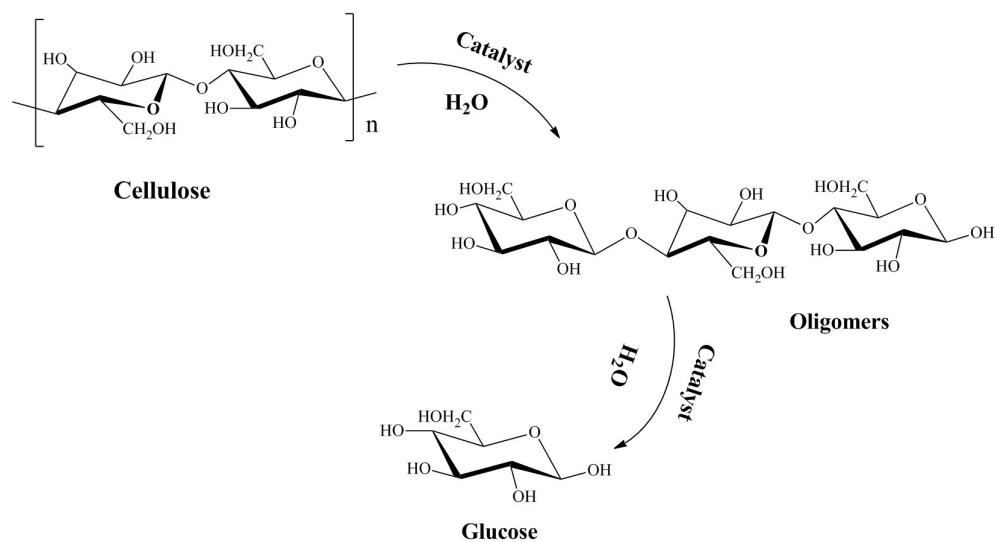


Fig.7 Kinetic behavior for polysaccharide to glucose over  $(C_{16}TA)H_5P_2W_{18}O_{62}$ . (a) cellulose; (b) starch; and (c) cellobiose.



**Scheme 1** The mechanism of the cellulose conversion by the catalyst.

**Table 1** The compared results obtained by (C<sub>16</sub>TA)<sub>n</sub>H<sub>6-n</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> (n = 1~6)

Catalyst <sup>a</sup>	Conversion (%)	Yield of TRS (%)	Yield of Glu. (%)	Selectivity (%)	Acid content [mol·kg <sup>-1</sup> ]	TOF <sup>b</sup> [g·mmol <sup>-1</sup> ·h <sup>-1</sup> ]
H <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	93.5	52.6	45.6	48.8	3.6	12.9×10 <sup>-2</sup>
(C <sub>16</sub> TA)H <sub>5</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	87.2	72.4	69.1	79.2	3.2	12.1×10 <sup>-2</sup>
(C <sub>16</sub> TA) <sub>2</sub> H <sub>4</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	75.5	64.4	61.7	81.7	2.8	10.5×10 <sup>-2</sup>
(C <sub>16</sub> TA) <sub>3</sub> H <sub>3</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	63.8	58.7	53.4	83.7	2.1	8.9×10 <sup>-2</sup>
(C <sub>16</sub> TA) <sub>4</sub> H <sub>2</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	58.3	53.0	49.4	84.7	1.5	8.1×10 <sup>-2</sup>
(C <sub>16</sub> TA) <sub>5</sub> HP <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	43.5	40.3	37.8	86.9	1.1	6.0×10 <sup>-2</sup>
(C <sub>16</sub> TA) <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	30.6	28.5	25.7	83.9	0.6	4.3×10 <sup>-2</sup>
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	81.6	75.3	63.3	77.6	2.4	11.3×10 <sup>-2</sup>
(C <sub>16</sub> TA)H <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	55.7	46.3	44.2	79.4	1.8	7.7×10 <sup>-2</sup>

<sup>a</sup> Reaction condition: 100 mg of cellulose, 0.08 mmol of catalyst, 5 mL H<sub>2</sub>O at 160 °C in 9 h.

$$^b \text{ TOF} = \frac{0.1 \text{ (g)} \times \text{Conversion}(\%)}{\text{Catalyst (mmol)} \times \text{Reaction time (h)}}$$



**Table 2** The effect on alcoholysis of cellulose with different kind of catalyst.

Catalyst	Reaction time (h)	Conversion (%)	Yield of methyl levulinate (%)
$H_6P_2W_{18}O_{62}$	5	96.6	52
$H_3PW_{12}O_{40}$	5	92.3	42.4
$(C_{16}TA)H_5P_2W_{18}O_{62}$	7	97.8	58.5
$(C_{16}TA)H_2PW_{12}O_{40}$	7	92.3	47.5

Reaction conditions: 100 mg of cellulose, 0.07 mmol of catalyst, 8 mL methanol at 160 °C.

## Graphic Abstract

