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Single step conversion of cellulose to levulinic acid using temperature-responsive dodeca-aluminotungstic acid catalysts

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Abstract

Conversion of cellulose into platform chemicals is essential for sustainable development of the chemical industry. With this aim, single step conversion of cellulose to industrially important levulinic acid (LA) using heteropolyacids (HPAs) as catalysts had been investigated. A new series of heteropolyacids (HPAs) $[(CH_3)_3NCH_2CH_2OH]_nH_{5-n}AlW_{12}O_{40}$ (abbreviated as $Ch_nH_{5-n}AlW_{12}O_{40}$, n = 0 ~ 5) had been synthesized by a precipitation/ion exchange method using choline chloride and $H_5AlW_{12}O_{40}$ as precursors. The resulted HPA nanohybirds exhibited a novel switchable property based on temperature variation due to the cooperation of choline cation, while it dissolved in the reactor mixture at higher temperature to form homogeneous catalytic system and then precipitated automatically from the mixture at room temperature. Three synergistic effects of temperature-stimulus, and combined with double Lewis and Brønsted acidity endowed $ChH_4AlW_{12}O_{40}$ to be more efficiency in catalyzing the conversion of cellulose into glucose in water with 75.9 % yield at 94.8 % conversion at 140 ºC for 3 h. Meanwhile, MIBK (methyl isobutyl ketone), a green co-solvent in a highly effective single phase conversion strategy, achieved LA of the highest reported production yield directly from cellulose with 74.8 % yield at 98.9 % conversion in one-pot, which is the best results comparable to previous reports so far. Moreover, the recycling of such HPA catalyst was easily detached with as lowing reaction temperature without structural change and loss of weight. In addition, the conversion of cellulose to glucose could be promoted by microwave assistance.

Keywords: Heteropolyacids; acidic catalysis; one-pot; biomass; temperature-responsive.

Introduction

The whole social concentrations on climate change and decrease of fossil fuel are driving us to search for the alternative and more sustainable energy sources derived from renewable feedstocks.[1-3] In this respect, chemicals from biomass as building blocks for petroleum refineries are highly desirable with academic and industrial value. [4] Among the promising building blocks, levulinic acid (LA) is identified by the US Department of Energy as one of the top 10 carbohydrate-derived target chemicals. [5] LA was derived from 5-hydroxymethylfurfural (HMF) and mainly produced by enzymatic or acid-catalyzed conversion of polymeric carbohydrates to hexoses, then one of hexose-glucose was firstly isomerized to fructose that was dehydrated to HMF, and in turn converted to LA. [6] By now, a various acid catalysts had been tested in LA production from cellulose. [7] Mineral acids like HCl and H_2SO_4 generally give high yields but drawbacks of recycling and ecofriendliness. Solid catalysts [8-17] are best candidates due to their easier recovery and tailorable properties. For pure Brønsted solid catalysts, the highest yield of LA was 65.5 % at 170 ºC for 10 h in water/γ-valerolactone biphases. [18] For double acidic center catalysts, the highest LA yield was obtained catalyzed by ZrO_2 as 53.9 mol % at 180 °C for 3 h in water. [19] Therefore, it can be concluded that the double acidic nature of catalysts is needed for efficient production of LA from cellulose[20, 21]. For requirement of LA production from cellulose, the strong Brønsted acid and properly Lewis acid are needed to be considered as designing solid acid catalysts.

In this respect, heteropolyacids are available for such design: strong Brønsted acidity and controllable Lewis acidity through changing their composition and structure. [22-25] Lewis acidic HPAs had been prepared by partial exchange of protons in $H_3PW_{12}O_{40}$ with Lewis metal cations including Sn, Al, Ti, Zn, Ag and Cr.[26-28] However, there is no report on LA production from cellulose catalyzed by reported HPAs due to their lower Brønsted acidity than others with high proton contents such as $H_5BW_{12}O_{40}$ or $H_5AlW_{12}O_{40}$.[29] In order to achieve the production of HMF or LA from cellulose in cascade reaction, to tailor acidic properties for HPAs is required including strong Brønsted acidity and certain amount of Lewis acidic strength. $H_5AlW_{12}O_{40}$ is much more beneficial than $H_5BW_{12}O_{40}$ is, because it contents as high content of protons as $H_5BW_{12}O_{40}$, and also exhibits some certain Lewis acidity in presence of Al^{3+}. By now, Al-exchanged HPAs only prepared by Al partial exchanging of protons in $H_3PW_{12}O_{40}$, [29] which Al ion was in the secondary structure of heteropolytungstate. There were some drawbacks compared to $H_5AlW_{12}O_{40}$, that aluminum ion in $AlPW_{12}O_{40}$ was prone to hydrolyze to $Al(OH)_3$ in aqueous conditions hindering the application in cellulose hydrolysis in water system. Therefore, $H_5AlW_{12}O_{40}$ is best candidate for hydrolysis of cellulose into glucose and isomerization of glucose to fructose further to LA. To the best of our knowledge, there is no report on organic transfer catalyzed by $H_5AlW_{12}O_{40}$ and either no report on the production of LA from cellulose catalyzed by HPA catalysts.

Meanwhile, solid acids often suffer low yields in long reaction time and at high temperature because of the poor solubility of cellulose in aqueous solution and weak affinity between cellulose and solid acids. Recently, the use of an amphiphatic solid-phase catalyst under a phase-transfer condition or an aqueous system is regarded as a potential strategy to form highly reactive catalytic systems. [7,30, 31]Nevertheless, the activity of amphiphatic HPA catalysts could not be competitive to that of homogeneous $H_3PW_{12}O_{40}$. For this reason, future practical applications of HPAs will require methods for “catalyst engineering” to link the gap between homogeneous and heterogeneous systems. Therefore, the thermoresponsive catalysts are needed for their potential benefits in controlling the exothermic reaction rate and the thermo-related catalyst recovering. [32] In our previous work,[33] we designed a temperature-responsive HPA catalyst $Ch_5PV_2Mo_{10}O_{40}$ (Ch represents $HOCH_2CH_2N(Me)_3^+$). Helping of ChCl, $Ch_5PV_2Mo_{10}O_{40}$ exhibited temperature controllable properties that its states changed as varying reaction temperature, whose temperature stimulus property was generated by incorporation of choline ion. Increasing the reaction temperature, it changed into solubility in water, while it changed into be insoluble and could be reused through decreasing the temperature. Therefore, the gap between heterogeneous and homogeneous system was linked, which resulted in high catalytic activity similar to homogenous HPAs.

Herein, we employed a series of aluminotungstic acid catalysts $Ch_nH_{5-n}AlW_{12}O_{40}$ (n = 1-5) containing different number of organic groups $HOCH_2CH_2N(Me)_3$. $Ch_nH_{5-n}AlW_{12}O_{40}$ exhibited strong Brønsted acidity, some certain Lewis acidic property, and the temperature - responsive property. In addition, the different number of organic group $HOCH_2CH_2N(Me)_3$ could control temperature-responsive properties and the molar ratio between Brønsted acidity and Lewis acidity as well. This is a good candidate for investigation the relationship between acidity and catalytic activity in LA production using HPA catalysts. And “hybrid approach” was used to confirm high yield of LA from cellulose in water/MIBK system (MIBK represents methyl isobutyl ketone), which helped to improve the selectivity of the unstable target product (LA) by its quick removal from the reaction mixture.[2]

Experimental

2.1 Materials

Microcrystalline cellulose (white, average particle size 50μm) was obtained from J＆K chemical Ltd (Beijing, China). $H_5AlW_{12}O_{40}$ was prepared according to the literature method.[34] All other reagents were of AR grade and used without further purification. 3, 5 - dinitrosalicylic acid (DNS) reagent was prepared according to Ref. 35.

FTIR spectra (4000 - 500 cm^{-1}) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. The elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. TEM micrographs were recorded on a Hitachi H-600 transmission electron microscope. The ^{27}Al nuclear magnetic resonance (NMR) spectra of the sample were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP/MAS probehead whose X channel was tuned to 100.62 MHz. The critical micellar concentration (CMC) of $ChH_4AlW_{12}O_{40}$ was determined by a plot of conductivity versus concentration using the conductometer model DDS-11A. The X-ray diffraction analysis was carried out on Japan Rigaku Dmax 2000 X-ray diffractometer with Cu Kα radiation (λ= 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. 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 HMF and LA were determined periodically on Shimazu GC-14C fitted with a HP-INNO Wax capillary column and flame ionization detector. The amount of LA was analyzed by gas chromatography (Agilent 6890) equipped with an Agilent 19091J-416 capillary column and flame ionization detector.

2.2 Preparation of the catalysts

Typical preparation procedure of $ChH_4AlW_{12}O_{40}$ was as following: 10 mL 40 mM of $H_5AlW_{12}O_{40}$ solution added drop wise into the 10 mL 40 mM of ChCl solution, a faint yellow precipitate was formed immediately. Then the solid was removed by filtration and washed with diluted water until no free of HPAs and chloride ($AgNO_3$ test) were found. The final product was dried in air under ambient conditions giving 30 % yield. Anal. Calcd (Found) for $ChH_4AlW_{12}O_{40}$: C, 2.08 (2.01); H, 1.1 (0.61); N, 0.32 (0.47); W, 76.45 (74.02); and Al, 1.81 (0.91) %, respectively. IR (KBr pellet): 972, 899, 795 (broad), 747 (broad), 538, and 477 cm^{-1}. Other catalysts were synthesized in the same method except using different molar ratio of surfactant ChCl and $H_5AlW_{12}O_{40}$.

2.4 Catalytic procedure

For hydrolysis of cellulose in water, a mixture of cellulose (0.1 g) and catalyst (0.08 mmol) was added into water (7 mL). Then it was heated at 140 °C in a steel autoclave lined with Teflon under air for 3 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. Cellulose conversions (wt%) were determined by the change of cellulose weight before and after the reaction. HMF and LA were determined by HPLC (High Performance Liquid Chromatography).

Conversion of cellulose in water/MIBK system was done in the similar way as described in water system except using water/MIBK mixture solvent and reaction temperature of 120 °C. The reaction was stopped by rapidly cooling the reactor in an ice bath at 0 °C. The reaction mixture was separated into three layers: the upper is the organic solvent containing small organic products such as HMF or LA; the middle is water containing glucose and TRS, the lower is unreacted cellulose, by-product humin and catalyst. Cellulose conversions (wt%) were determined by the change of cellulose weight before and after the reaction. HMF and LA were determined by GC (Gas Chromatograph).

For the first six recycles the catalyst did not separated from the mixture of unreacted cellulose, by-product of humin and catalyst due to the almost conversion of cellulose and litter amount of humin. Therefore, the recycle experiment was done only adding some fresh cellulose. After six recycles, the separated powder of unreacted cellulose, humin and catalyst was washed with hot water with 80°C for three times. The temperature-responsive $ChH_4AlW_{12}O_{40}$ was washed to water phase to be separated. Then distillation of water at 50 °C gave solid catalyst for reuse.

2.5 Total reducing sugars (TRS) analysis [35]

A mixture that contained 2 mL of DNS regent 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.

2.6 Hammett acidity (H_0) analysis [36]

A sample of the catalyst (100 mg) and Hammett indicator (p-nitroaniline, pK(I)aq = 0.99) were dissolved in 20 mL secondary distilled water. The mixture was stirred for 12 h in the sealed reactor at room temperature, and then the solid was separated by filtration. The color intensity of the mixture was measured in a Cary 500 UV/Vis/NIR spectrophotometer at 380 nm.

Surface acidity was investigated using the irreversible adsorption of pyridine on the solid surfaces according to Ref. 37.

Titration was used to evaluate the total acid content of the solids. 0.05 g of solid suspended in 45 mL of acetonitrile and stirred for 3 h. The density of acid sites in the catalysts was then measured by titration with a solution of n-butylamine in acetonitrile (0.05 M) using the indicator anthraquinone (pKa = -8.2).

2.7 Critical micelle concentration (CMC) determination

The CMC of $Ch_nH_{5-n}AlW_{12}O_{40}$ was determined by break points of two nearly straight-line portions of the specific conductivity versus concentration plot. [38]

2.8 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 with 7 mL water in a steal autoclave lined with Teflon for 1 h at 150 ºC in order to determine the adsorption effects by the IR spectroscopy.

3. Results and discussion

3.1 Characterization of catalysts

The elemental analyses of $Ch_nH_{5-n}AlW_{12}O_{40}$ were given in Table S1. These results gave the molar ratio of Al: W = 1: 12, showing that heteropolyacid anions kept 1:12 Keggin structure. The C and H contents were well corresponding to the calculated results.

The FTIR spectra of $Ch_nH_{5-n}AlW_{12}O_{40}$ were presented in Fig. S1. Fig. S1a gave the four characteristic peaks for $ChH_4AlW_{12}O_{40}$ at 960, 884, 820, and 762 cm^{-1}, respectively. Its parent

$H_5AlW_{12}O_{40}$ exhibited four characteristic peaks [35] of Al-O stretching vibration (752 cm^{-1}), W-O_{ter} stretching (972 cm^{-1}), W-O_c-W stretching of inter bridges between corner-sharing WO_6 octahedra (893 cm^{-1}), and W-O_e-W stretching of intra bridges between edge-sharing WO_6 octahedra (812 and 792 cm^{-1}). Four characteristic peaks of Keggin structure were intact for $ChH_4AlW_{12}O_{40}$, indicating no structural change during the reaction with ChCl. And IR spectra of other dodecatungstoaliminates also gave the same results. In addition, the peaks at 3409, 3032 and 1476 cm^{-1} were attributed to C-H and C-N, respectively, showing that quaternary ammonium existed in $Ch_nH_{5-n}AlW_{12}O_{40}$.

Powder X-ray diffraction patterns were used to confirm the structure of $Ch_nH_{5-n}AlW_{12}O_{40}$. Compared to the diffraction peaks of $H_5AlW_{12}O_{40}$, $Ch_nH_{5-n}AlW_{12}O_{40}$ gave the similar diffraction peaks (Fig. S2). This result indicated the original structure of $H_5AlW_{12}O_{40}$ was attained after forming HPA hybrids.

The ^{27}Al MAS NMR spectra (Fig. S3) of $ChH_4AlW_{12}O_{40}$ and $Ch_5AlW_{12}O_{40}$all gave one signal peak around δ = 72.06 and 71.93 ppm, respectively. The $H_5AlW_{12}O_{40}$ gave one peak at 72.10 ppm. [35] The shifts of ^{27}Al MAS NMR for $ChH_4AlW_{12}O_{40}$ and $Ch_5AlW_{12}O_{40}$ were attributed to the introduction of organic cations into $H_5AlW_{12}O_{40}$. This could confirm the formation of one assembly of HPA anion and $HOCH_2CH_2N(Me)_3$ cation, and it was not the physical mixture between Ch^- and $AlW_{12}O_{40}^{5-}$. The different shifts of these HPAs were attributed to the different number of organic group.

The TEM image of $ChH_4AlW_{12}O_{40}$ showed that it could form relatively uniform micellar particle about 10 nm (Fig. S4a, Scheme S1). And the CMC of $Ch_nH_{5-n}AlW_{12}O_{40}$ (n=1, 2, 3, 4, 5) were given in Fig. S5, which showed that the CMC of $Ch_nH_{5-n}AlW_{12}O_{40}$ (n=1, 2, 3, 4, 5) were 0.80 mM. This also confirmed the formation of micelle in aqueous solution. [39]

The Brønsted acidity of different catalysts can be measured by using a UV-indicator. [36] Table 1 gave the H_0 values of different dodecatungstoaliminates. In general, the lower H_0 of an acid is, the stronger the acidity of the catalysts is. It can be seen that the H_0 value would increase as increasing ratio of ChCl to $H_5AlW_{12}O_{40}$. The acid strength was in range of $H_5AlW_{12}O_{40} > ChH_4AlW_{12}O_{40} > Ch_2H_3AlW_{12}O_{40} > Ch_3H_2AlW_{12}O_{40} > Ch_4HAlW_{12}O_{40} > Ch_5AlW_{12}O_{40}$.

Table 1

The total acid amount of the catalyst was also measured by titration with *n*-butylamine (Table

1). The HPAs with a different amount of $HOCH_2CH_2N(Me)_3$ gave different acid amounts with the range of $ChH_4AlW_{12}O_{40}$ > $Ch_2H_3AlW_{12}O_{40}$ > $Ch_3H_2AlW_{12}O_{40}$ > $Ch_4HAlW_{12}O_{40}$ > $Ch_5AlW_{12}O_{40}$. The different surface acidic sites of $Ch_nH_{5-n}AlW_{12}O_{40}$ was determined by pyridine adsorption infrared spectroscopy (Fig. S6). As shown in Fig. S6, the Brønsted acid sites can be observed at band 1545 cm^{-1}, while the band at 1450 cm^{-1} referred to the Lewis acid sites. In addition, a band at 1490 cm^{-1} was correlated to both Brønsted and Lewis acid sites [34]. Therefore, $Ch_nH_{5-n}AlW_{12}O_{40}$ exhibited double acidic sites including Brønsted acid and Lewis acid sites as well. Based on the peak tenses, it could be seen that Brønsted acid sites decreased in the following order: $ChH_4AlW_{12}O_{40}$ > $Ch_2H_3AlW_{12}O_{40}$ > $Ch_3H_2AlW_{12}O_{40}$ > $Ch_4HAlW_{12}O_{40}$ > $Ch_5AlW_{12}O_{40}$, which the intensity was correlated mainly to the number of Ch^+ similar to the results of H_0. And based on the strength ratio between Brønsted and Lewis acid sites in adsorbed pyridine IR spectra, molar ratios between the Brønsted and Lewis acidic contents were 2.67, 2.18, 0.95, 0.58, and 0.16 corresponding to $ChH_4AlW_{12}O_{40}$, $Ch_2H_3AlW_{12}O_{40}$, $Ch_3H_2AlW_{12}O_{40}$, $Ch_4HAlW_{12}O_{40}$, and $Ch_5AlW_{12}O_{40}$, respectively. It can be concluded that tailing the number of organic group could control the molar ratio between Brønsted and Lewis acidic contents for $Ch_nH_{5-n}AlW_{12}O_{40}$.

3.2 Catalytic activity

Hydrolysis of cellulose in water

Firstly of all, the catalytic activity of $Ch_nH_{5-n}AlW_{12}O_{40}$ was evaluated in cellulose hydrolysis to glucose (Fig. 1). It can be seen that the conversion of cellulose was only 5 % when catalyzed by ChCl due to its weak acid sites. HCl, $H_3PW_{12}O_{40}$ and $H_5BW_{12}O_{40}$ are pure Brønsted acids giving 27.1, 6.0, and 49.7 % conversions, respectively, while $AlCl_3$ is a Lewis acid only giving 15.0 % conversion under the reaction conditions. $H_5AlW_{12}O_{40}$ is a homogeneous acid catalyst with strong Brønsted acidity and total acid amount, which is favorable for the hydrolysis of cellulose with 96.4 % conversion and 71.2 % glucose yield at 140 ºC for 3 h. This result indicated that HPAs with double acidity was much more active compared to the single Brønsted acids HCl, $H_3PW_{12}O_{40}$, $H_5BW_{12}O_{40}$ and single Lewis acid $AlCl_3$. The conversion order of 12-tungstoaluminates was in range of $ChH_4AlW_{12}O_{40}$ (93.8 %) > $Ch_2H_3AlW_{12}O_{40}$ (80.5%) > $Ch_3H_2AlW_{12}O_{40}$ (46.0 %) > $Ch_4HAlW_{12}O_{40}$ (27.0 %) > $Ch_5AlW_{12}O_{40}$ (19.3 %). Such conversions were also coherent with the total acidic contents and Brønsted acidity of $Ch_nH_{5-n}AlW_{12}O_{40}$ (Table 1), showing that strong total acidic contents and Brønsted acidity are essential for hydrolysis of cellulose to glucose.

Fig. 1

For the yield of glucose, the different catalysts showed the different performance as the range of $ChH_4AlW_{12}O_{40}$ > $H_5AlW_{12}O_{40}$ > $Ch_2H_3AlW_{12}O_{40}$ > $H_5BW_{12}O_{40}$ > $Ch_3H_2AlW_{12}O_{40}$ > HCl > $Ch_4HAlW_{12}O_{40}$ > $Ch_5AlW_{12}O_{40}$ > $AlCl_3$ > $H_3PW_{12}O_{40}$. $H_5AlW_{12}O_{40}$ gave highest cellulose conversion but low glucose yield (71.2 %) compared to $Ch_nH_{5-n}AlW_{12}O_{40}$, indicating that acid catalysts with highest H_0 favored for further degradation of glucose into small organic molecules, such as HMF and LA. The conversion of cellulose and the yield of glucose were 94.6 % and 75.9 %, respectively, catalyzed by $ChH_4AlW_{12}O_{40}$ for reactions of 3 h at 140 ºC. The catalytic activity of $ChH_4AlW_{12}O_{40}$ was comparable to homogeneous $H_5AlW_{12}O_{40}$, which might be attributed to its temperature-responsive properties (Fig. 2). It can be seen that $ChH_4AlW_{12}O_{40}$ could no dissolve in water before reaction (Fig. 2a). As increasing the temperature up to 120 º C, $ChH_4AlW_{12}O_{40}$ changed into homogeneous form and uniformly dispersed around the reactor (Fig. 2b). The morphology of $ChH_4AlW_{12}O_{40}$ in this phase was tested by TEM (Fig. S4a), showing that $ChH_4AlW_{12}O_{40}$ assembled as micellar spheres with sizes around nanometers. Therefore, this nanoassembly provided nanoreactor for cellulose into glucose with higher conversion comparable to $H_5AlW_{12}O_{40}$. From the visible spectra of $ChH_4AlW_{12}O_{40}$ at different temperature (Fig. S8), it can be seen that increasing temperature could promote the dissolution of $ChH_4AlW_{12}O_{40}$ into water. Therefore, phase changing was controlled by temperature confirming the catalytic behavior of $ChH_4AlW_{12}O_{40}$ like homogeneous one.

Fig. 2

In order to confirm the effect of choline ion on catalytic activity of $ChH_4AlW_{12}O_{40}$, other micellar HPA catalyst $(CTA)H_4AlW_{12}O_{40}$ was prepared to determine using different surfactant cation $C_{16}H_{33}N(CH_3)_3$ (abbreviated as CTA). $(CTA)H_4AlW_{12}O_{40}$ was a micellar HPAs acting as a heterogeneous catalyst in cellulose hydrolysis giving 36.0 % cellulose conversion and 24.2 % yield of glucose under the same reaction conditions much lower than $ChH_4AlW_{12}O_{40}$. The main difference for $(CTA)H_4AlW_{12}O_{40}$ and $Ch_4HAlW_{12}O_{40}$ was the different organic group in heteropolyainon. $(CH_3)_3NCH_2CH_2OH$ group could help $Ch_4HAlW_{12}O_{40}$ to behavior like thermoregulated nanoreactor. $(CTA)H_4AlW_{12}O_{40}$ was only micellar type catalyst without any temperature-responsibility.

During the reaction, $ChH_4AlW_{12}O_{40}$ could form disperse micellar spheres, which could adsorb some cellulose molecules determined through IR spectroscopy. The adsorption test had been processed with stirring $ChH_4AlW_{12}O_{40}$ and cellulose together for some time at 140 ºC. Under such conditions, cellulose hydrolyzed a little and some was adsorbed by catalyst. From the IR spectrum (Fig. S7a), the peak at 1162.9 cm^{-1} could be attribute to C-O-C of cellulose, suggesting that certain amount of cellulose was gathered closely to this catalyst. Compared to the peak of the original cellulose at 1167.0 cm^{-1}, C-O-C stretching shifted to 1162.9 cm^{-1} due to the interaction between C-O-C and HPAs. The IR spectrum of $ChH_4AlW_{12}O_{40}$ adsorbed cellulose gave four characteristic peaks at 972, 882, 811, and 741 cm^{-1}, showing no structural change during the adsorption. But some vibration bands shifted changed, indicating that some interaction occurs between the O atom from cellulose and the terminal oxygen atom from the HPA molecules. Compared to the adsorption IR by $(CTA)H_4AlW_{12}O_{40}$, there was litter change for the $(CTA)H_4AlW_{12}O_{40}$ in the Fig S7b. Therefore, the existence of $(CH_3)_3NCH_2CH_2OH$ in $ChH_4AlW_{12}O_{40}$ contributed to the more adsorption of cellulose. It had been reported that choline chloride could form deep eutectic solvent for helping cellulose to well disperse in water through hydrogen bonds.[40] Therefore, $Ch_4HAlW_{12}O_{40}$ could adsorb much more cellulose than $(CTA)H_4AlW_{12}O_{40}$ did resulting in higher conversion of cellulose.

Main parameters affecting the hydrolysis reaction including temperature, reaction time, catalyst dosage and H_2O amount was investigated as following (Fig. 3). It can be seen that without any catalyst, the cellulose could not be hydrolyzed into water-soluble saccharides under such reaction conditions, and the hydrolysis of cellulose can be promoted by using acid catalysts (Fig. 3a). With enhancement of catalyst usages from 0.05 to 0.08 mmol, the yields of TRS and glucose increased from 50.2 and 44.5 % to 86.5 and 75.9 %, respectively. This increase can be attributed to an increase in the availability of the number of catalytically active sites. [39] The amount of water could influence the conversion of cellulose because altering of water content led to the change of catalyst' concentration. [40] It can be seen from Fig. 3b that the cellulose conversion, TRS and glucose yields increased with an increase in the amount of water from 5 to 7 mL, and reached a maximum at 7 mL of water. Further addition of water into the reaction system caused the efficiency of hydrolysis decrease sharply, which might be attributed to the decrease of acidic sites. Reaction temperature is a key parameter to determine the products of cellulose hydrolysis. It showed that under $ChH_4AlW_{12}O_{40}$ catalyzing, the yields of TRS and glucose reached maximum values of 86.5 % and 75.9 % in 3 h at the higher temperature of 140 °C, respectively (Fig. 3c). The reaction time also influenced the yield of glucose (Fig. 3c), showing that increasing the reaction time gave decreasing trend for glucose yield for three reaction temperature. This might be attributed to the decomposition of glucose during long time reaction. Therefore, the final optimum conditions were 140 ^{o}C for 3 h with final 94.6 % conversion and 75.9 % glucose yield. To the best of our knowledge, heterogeneous catalysts (Table S2) gave the maximum yield of glucose as 77 % catalyzed by $H_5BW_{12}O_{40}$ by now. [29] Our results were comparable to the best results.

Fig. 3

It is known that the microwave irradiation might be absorbed deeply into the folding layers of the cellulose to destroy the crystal structures and improve the effective contraction between the HPAs and the solid substrate, which accelerated the hydrolysis process. [40] Fig. 4 gave the results of catalytic activity for the hydrolysis of cellulose under microwave irradiation. Evidently, compared with the conventional heating method, the microwave irradiation significantly accelerated the hydrolysis reaction. The yield of glucose under microwave irradiation was 70.5 % at 140 ºC for 80 min, which was very fast than under conventional process. Further increasing reaction time only promoted the conversion of cellulose and had opposite effect on glucose yield.

Fig. 4

Besides cellulose, $ChH_4AlW_{12}O_{40}$ was also used in conversion of other polysaccharides including sucrose, cellobiose, and starch. The conversion of feedstocks and the yield of glucose were given in Fig. 5. It can be seen that almost all polysaccharides were converted and as high as 97.9, 92.6, and 95.5 % yields of glucose were obtained from sucrose, cellobiose, and starch, respectively. Compared to previous reports, temperature-responsive HPA catalyst $ChH_4AlW_{12}O_{40}$ was most active in transformation of polysaccahrides into water-soluble products in water so far.

Fig. 5

An interesting finding is that our $ChH_4AlW_{12}O_{40}$ temperature-responsive catalyst is available for the conversion of lignocellulosic biomass in water solution. Efficient production of fuels or chemicals from crude biomass often requires pretreatment processes. Using our method, HMF can be produced directly and readily from untreated lignocellulosic biomasses such as corn stover. At 140 °C for 10 h, 58 % of dry weight of corn stover was transformed into 10.3 % glucose, 18.9 %

HMF and 5.6 % LA, respectively. Even more important, the furfural is formed from these biomasses under our reaction conditions in yields of 11.1 %. Further deep study was on going.

Hydrolysis cellulose in double solvent

During our research work, we found that distribution of products varied under different reaction temperature and time (Table 2) in cellulose hydrolysis reaction in water. It can be seen that at lower temperature of 120 ºC, the main product was glucose and the yield increased as prolonging the reaction time. At high temperature above 130 ºC, the yield of glucose increased first then decreased, while HMF and LA increased as longing the reaction time. The maximum values of HMF and LA could yield 38.9 % and 19.2 % at 150 ºC for 5 h, respectively. It is well known that HMF is a product of the dehydration of glucose, and levulinic acid is a further product from the subsequent rehydration of HMF. Therefore, for the different require, controlling the reaction time and temperature is essential to obtain the target products. In order to confirm the highest yield of glucose, the reaction conditions were low temperature and short time. If HMF or LA was wanted, some new reaction conditions would be evaluated.

Table 2

First of all, we assayed the nature of $Ch_nH_{5-n}AlW_{12}O_{40}$ on the distribution of the products in cellulose conversion. From Scheme 1, large amount of Brønsted acid sites is essential in the entire reaction path ways involved including hydrolysis, isomerization and dehydration/rehydration for LA production. Meanwhile, the isomerization of glucose to fructose requires Lewis acid sites, whereas the combination of Brønsted and Lewis acid sites favors for the dehydration or rehydration. $Ch_nH_{5-n}AlW_{12}O_{40}$ exhibited varied molar ratio between Brønsted and Lewis acid sites as changing the amount of organic groups, which gave the different activity and selectivity to LA. As summarized in Table 1, the different contents of Ch^+ and H^+ influcenced the total acidic contents and molar ratio between Brønsted and Lewis acidity as well, which $M_{Brønsted}$: M_{Lewis} decreased in the order as $ChH_4AlW_{12}O_{40} > Ch_2H_3AlW_{12}O_{40} > Ch_3H_2AlW_{12}O_{40} > Ch_4HAlW_{12}O_{40} > Ch_5AlW_{12}O_{40}$. It was found that the trend of LA yield from cellulose was consistent with the acid sites per unit surface area. Therefore, the stronger the acidity of $Ch_nH_{5-n}AlW_{12}O_{40}$, the higher conversion of cellulose and higher yield of LA were obtained, indicating the essential role of the acidity in the catalytic cleavage of cellulose, possibly through protonation of glycosidic oxygen. [42] It was also observed that the LA production was lower for 19.5 % $Ch_4HAlW_{12}O_{40}$ and 2.2 %

$Ch_5AlW_{12}O_{40}$. For 12-tungstoaluminates, the Lewis acidity was litter different due to the almost the same amount of Al center. The difference of LA yield was due to the relative stronger Lewis acidity for $Ch_4HAlW_{12}O_{40}$ and $Ch_5AlW_{12}O_{40}$ in the same amount of catalysts compared to the other three HPA catalysts resulting to the formation of other byproduct lactic acid, which had been detected but not quantified in all reaction products. This was also observed by N.A.S. Amin in glucose to LA catalyzed by Fe/HY zeolite catalysts due to the presence of Lewis acid sites.[43] Therefore, the increase in Lewis acid sites could decrease the LA production by catalyzing the decomposition of glucose to lactic acid and formation of humins between glucose and furfural.[20] The effect of Lewis center mainly effected the isomerization of glucose to fructose.[44] Catalyzing by $H_3PW_{12}O_{40}$ and $H_5BW_{12}O_{40}$ under the same reaction conditions, the LA yields were 14.2 and 42.7% at 35.6 and 64.3% conversions, respectively. It can be seen that pure Bronsted acid also catalyzed cellulose convert to LA with weak activity. Therefore, Lewis centers are needed for production of LA from cellulose.

In addition, Brønsted acid is valuable for glucose dehydration initiated by the protonation of hydroxyl groups leading to form furfuryl alcohol (FAL). In acid solution, FAL is very reactive and could form LA through rehydration. Glucose was direct dehydration without HMF formation is also plausible for both glucose and fructose in acidic solutions. This implies that cellulose conversion to LA not only proceeded glucose isomerizaion to fructose than to HMF catalyzed by functional Brønsted and Lewis acid sites, and also underwent the direct conversion to LA catalyzed by Brønsted sites as well.[45] Therefore, $ChH_4AlW_{12}O_{40}$ gave the highest LA yield among all HPA catalysts due to its strong Bronsted acidity and some certain Lewis acidity.

Scheme 1

Finally, the experimental results revealed that $ChH_4AlW_{12}O_{40}$ gave the highest catalytic performance with nearly 100 % cellulose conversion and 74.8 % LA yield at 120 ºC in 10 h reaction time.

Secondly, different solvents had been selected to determine their effect on distribution of products. It is known that double solvent system is essential for production of biomass-derived molecules from cellulose.[2] Therefore, dimethyl sulfoxide (DMSO), methyl isobutyl ketone (MIBK), tetrahydrofuran (THF), and methylbenzene were selected to determine the influence of solvent on distribution of products catalyzed by $ChH_4AlW_{12}O_{40}$ (Table 3 Entry 1-5). Except methylbenzene, all polar solvents gave almost the same conversion of cellulose. For polar solvents, the yield of LA varied. Based on the general knowledge of solvent effect, the strong polar solvents such as DMSO was beneficial to stabilize HMF.[46] And also THF favored for the production of HMF with minimal levulinic acid formation. [47] Thus, high LA yield was obtained when the hydrolysis of cellulose catalyzed by $ChH_4AlW_{12}O_{40}$ was carried out in MIBK. Hence we selected MIBK as a reaction solvent, which could act as extractive phase available for the organic molecules LA hence to enhance the conversion of cellulose. [48]

Table 3

Thirdly, the MIBK-water ratio was varied from 8: 1 to 11: 1 (by volume) to determine the extent of improved LA yields (Table 3 Entry 6-8). It can be seen that at MIBK/water ratio lower than 9:1, the LA yield was lower than 60 %. Increasing amount of MIBK could enhance LA production, showing that MIBK could suppress polymerization. The LA yield reached maximum value of 74.8 % at MIBK/water ratio of 10:1. This result demonstrated that water has a positive effect for stabilizing glucose as reported. [49] Further increase amount of MIBK did not give positive effect due to the other unidentified compounds, such as humins was generated.

The product distribution varied according to the increase of reaction time and reaction temperature (Table 4). From table 4, we can see the HMF yield increased firstly then decreased with longing the time, while LA yield increased gradually. The highest yield of LA reached nearly 74.8 % at 120 °C for 10 h. Further increasing of reaction time did not give the positive effect on LA production, but some polymer formed instead. It can be seen that the yield trends of HMF increased first then decreasing as enhancement of reaction temperature. The yields of HMF reached highest value at 6 h. On the contrary, the yields of LA increased as prolonging the reaction time, and reached 74.8 % at 120 °C for 10 h.

Table 4

In order to determine the determine step of fructose to LA, a study on kinetic behavior for fructose dehydration to LA and 5-HMF rehydration to LA was carried out over $(Ch)H_4AlW_{12}O_{40}$ in double solution. The graph of ln c_0/c vs. t was plotted (Table 5) was determined from the plot. The rate constant (k) for fructose to LA and 5-HMF to LA at 120 ºC were found to be 2.9×10^{-2} min^{-1} and 2.7×10^{-2} min^{-1}, respectively. It can be seen that 5-HMF rehydration to LA was fast reaction, which fructose dehydration to HMF was determine step for cellulose into LA. HMF was a swift reaction. So we can obtain high yield of LA.

Table 5

3.3 Recycling of the catalyst

Reusability of catalyst is very important for practical applications. As mentioned above, this thermoregulated catalyst $ChH_4AlW_{12}O_{40}$ can be readily recovered by decreasing the temperature with slightly loss (Fig. 6b). Also, its catalytic activity on cellulose hydrolysis remained high-efficiency after six times repeated experiments (Fig. 6a). Moreover, the total amount of $ChH_4AlW_{12}O_{40}$ leaching over six runs of reaction was only 6.4 % that of the initial amount. The IR spectrum of the catalyst after the reaction also indicated its stability during the reaction (Fig. S9b). We also tested the IR spectrum of the mixture solvent after the reaction. It was found that there were no characteristic peaks for $ChH_4AlW_{12}O_{40}$ at 960, 884, 820, and 762 cm^{-1} (Fig. S10), respectively, showing that there was no catalyst existence in mixture solvent. Therefore, the above test revealed that $ChH_4AlW_{12}O_{40}$ has excellent stability and could be reused about six times as a rapid heterogeneous catalyst by a simple treatment.

Fig. 6

Conclusions

The temperature-responsive of HPA catalysts $[(CH_3)_3NCH_2CH_2OH]_nH_{5-n}AlW_{12}O_{40}$ (n = 0 ~ 5) had been synthesized by a precipitation/ion exchange method using choline chloride and $H_5AlW_{12}O_{40}$ as precursors. Helping by choline cation, such HPA nanohybirds exhibited a novel switchable property based on temperature variation linking the gap between homogeneous and heterogeneous systems. Also introduction of Al and choline groups resulted to various Lewis and Brønsted acidity for $Ch_nH_{5-n}AlW_{12}O_{40}$. Three synergistic effects of temperature-stimulus, and double acidic property endowed $ChH_4AlW_{12}O_{40}$ to be more efficiency in catalyzing the conversion of cellulose into glucose in water with 75.9 % yield at 94.6 % conversion, which is comparable to the best result using solid acid catalysts. MIBK, a green co-solvent in a highly effective single phase conversion strategy, achieved LA of the highest reported production yield directly from cellulose with 74.8 % yield at 98.9 % conversion in one-pot. Moreover, the recycling of such temperature- responsive HPA catalyst was easily as changing reaction temperature without structural change and loss of weight. In addition, the conversion of cellulose to LA could be promoted by microwave assistance. It was also a promising approach for converting renewable feedstock (polysaccharides, lignocellulosic materials) into valuable chemicals. Further deep study was on going.

Acknowledgments

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References

1 L. Wang and F. S. Xiao, *Green Chem*., 2015, **17**, 24 - 39.

2 I. Delidovich, K. Leonhardb and R. Palkovits, *Energy Environ. Sci.*, 2014, **7**, 2803 - 2830.

3 Y. B. Huang and Y. Fu, *Green Chem*., 2013, **15**, 1095 - 1111.

4 J. Julis and W. Leitner, *Angew. Chem., Int. Ed*., 2012, **51**, 8615 - 8619.

5 a) H. Lin, J. Strull, Y. Liu, Z. Karmiol, K. Plank, G. Miller, Z. Guo and L. Yang, *Energy Environ. Sci.*, 2012, **5**, 9773 - 9777; b) L. Peng, L. Lin, J. Zhang, J. Zhuang, B. Zhang and Y. Gong, *Molecules*., 2010, **15**, 5258 - 5272.

6 D.W. Rackemann and W.O.S. Doherty, *Biofuels Bioprod. Bioref.*, 2011, **5**, 198-214.

7 A. Mukherjee, M. J. Dumout, and V. Raghavan, *Biomass Bioeng*., 2015, **72**, 143-183.

8 S. Van de Vyver, J. Geboers, P. A. Jacobs and B. F. Sels, *ChemCatChem*., 2011, **3**, 82 - 94.

9 J. A. Geboers, S. Van de Vyver, R. Ooms, B. Op de Beeck, P. A. Jacobs and B. F. Sels, *Catal. Sci. Technol.*, 2011, **1**, 714 - 726.

10 H. Kobayashi, H. Ohta and A. Fukuoka, *Catal. Sci. Technol.*, 2012, **2**, 869 - 883.

11 D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem. Soc. Rev.*, 2012, **41**, 8075 - 8098.

12 H.Z. Chen ,B. Yu and S. Y. Jin, *Bioresource. Technol.*, 2011, **102**, 3568 - 3570.

13 P. Wang, S. Zhan and H. Yu, *Adv. Mater. Res.* 2010, **96**, 183 - 187.

14 D.M. Lai, L. Deng, Q. X. Guo and Y. Fu, 2011, **4**, 3552 - 3557.

15 S. Van de Vyver, J. Thomas, J. Geboers, S. Keyzer, M. Smet, W. Dehaen, P. A. Jacobs and B. F. Sels, *Energy Environ. Sci*., 2011, **4**, 3601- 3610.

16 D. Q. Ding, J. J. Wang, J. X. Xi, X. H. Liu, G. Z. Lu and Y. Q. Wang, *Green Chem*., 2014, **16**, 3846 - 3853.

17 R. Weingarten, W. C. Conner, Jr and G. W. Huber, *Energy Environ. Sci*., 2012 **5**, 7559 - 7574.

18 Y. Zuo, Y. Zhang and Y. Fu, *ChemCatChem.*, 2014, **6**, 753 - 757.

19 S. S. Joshi , A. D. Zodge, K. V. Pandare and B. D. Kulkarni, *Ind. Eng. Chem. Res.*, 2014, **53**, 18796 - 18805.

20 R. Weigarten, G. A. Tompsett, W. C. Conner Jr and G. W. Huber, J. *Catal.*, 2011, **279**, 174 - 182.

21 I. A. Telleria, J. Gandarias and P. L. Arias, *Catal. Today.*, 2014, **234**, 42 - 58.

22 S. Q. Hu, Z. F. Zhang, J. L. Song, Y. X. Zhou and B. X. Han, *Green Chem.*, 2009, **11**, 1746 - 1749.

23 W. Shi, J. Zhao, X. Yuan, S. T. Wang, X. H. Wang and M. X. Huo, *Chem. Eng. Technol.* 2012, **35**, 347 - 352.

24 H. W. Zheng, Z. Sun, X. H. Yi, S. T. Wang, J. X. Li, X. H. Wang and Z. J. Jiang, *RSC Adv.*, 2013, **3**, 23051 - 23056.

25 X. H. Yi, I. Delidovich, Z. Sun, S. T. Wang, X. H. Wang and R. Palkovits, *Catal. Sci. Technol.*, 2015, **5**, 2496 - 2502.

26 S. H. Zhu, X. Q. Gao, F. Dong, Y. L. Zhu, H. X. Zheng and Y. W. Li, *J. Catal*., 2013, **306**, 155-163.

27 K. Jagadeeswaraiah, C. R. Kumar, Prasad, Lingaiah and P. S. S.N. *Catal Sci Technol*., 2014, **4**, 2969-2977.

28 S. Zhao, M. X. Cheng, J. Z. Li, J. Tian and X. H. Wang, *Chem. Commun.*, 2011, **47**, 2176 - 2178

29 Y. Ogasawara, S. Itagaki, K. Yamaguchi and N. Mizuno, *ChemSusChem* 2011, **4**, 519 - 525.

30 M. X. Cheng, T, Shi, H. Y. Guan, S. T. Wang, X. H. Wang and Z. J. Jiang, *Appl. Catal. B: Environ*., 2011, **107**, 104 - 109.

31 Z. Sun, M. X. Cheng, H. C. Li, T. Shi, M. J. Yuan, X. H. Wang and Z. J. Jiang, *RSC Adv.*, 2012, **2**, 9058 - 9065.

32 X. W. Wu, Y. F. Hu, X. H. Wang and L. Chen, *Catal. Commun.*, 2015, **58**, 164-168.

33 X. L. Chen, B. Souvanhthong, H. Wang, H. W. Zheng, X. H. Wang and M. X. Huo, *Appl. Catal. B: Environ.*, 2013, **138 - 139**, 161 - 166.

34 I. A. Weinstock, J. J. Cowan, E. M. G. Barbuzzi, H. D. Zeng and C. L. Hill, *J. Am. Chem. Soc.*, 1999, **121**, 4608 - 4617.

35 J. J. Cowan, A. J. Bailey, R. A. Heintz, B. T. Do, K. I. Hardcastle, C. L. Hill and I A. Weinstock, *Inorg. Chem.*, 2001, **40**, 6666-6675.

36 D. Fang, J. M. Yang, C. M. Jiao, *ACS Catal*., 2011, **1**, 42 - 47

37 E. P. Parry, *J. Catal.*, 1963, **2**, 371 - 379.

38 P. Mukherjee and K.J. Mysels, NSRDS-NBS, 1971, 36.

39 K. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya and A. Satsuma, *Green Chem.*, 2009, **11**, 1627 - 1632.

40 J. A. Sirviö, M. Visankob and H. Liimatainen, Green Chem., 2015, **17**, 3401-3406.

41 Y. Wu, Z. Fu, D. Yin, Q. Xu, F. Liu, C. Lu and L. Mao, Green Chem., 2010, **12**, 696 - 700.

42 H. F. Ren, B. Girisuta, Y. G. Zhou and L. Liu, Carbohyd Polym., 2015, **117**, 569 - 576.

43 N.A.S. Ramli and N.A.S. Amin, Appl. Catal. B: Environ., 2015, **163**, 487-498.

44 R. Gounder and M. E. Davis, J. Catal., 2013, **308**, 176 -188.

45 L. Yang, G. Tsilomelekis, S. Caratzoulas and D. G. Vlachos, ChemSusChem., 2015, **8**, 1334-1341.

46 L. Hu, G. Zhao, X. Tang, Z. Wu, J. X. Xu, L. Lin and S. J. Liu, Bioresource. Technol., 2013, **148**, 501-507.

47 C. M. Charles, N. Nagane, K. Rajeev and W. E.Charles, Green Chem., 2014, **16**, 3819-3829.

48 R. Weingarten, G. A. Tompsett, W. C. Conner Jr., and G.W. Huber, J. Catal., 2011, **279**, 174 - 182.

49 J. B. Binder and R. T. Raines, *Proc. Natl. Acad. Sci.,* U.S.A. 2010, **107**, 4516-4521.

Figure caption

Fig. 1 Activity comparsion between different catalysts for cellulose hydrolysis

Fig. 2 The states of $ChH_4AlW_{12}O_{40}$ as changing temperatures. (a) At room temperature, (b) heating to 120 ºC, and (c) cooling to room temperature.

Fig. 3 The effect of $ChH_4AlW_{12}O_{40}$ at different reaction conditions. (a) amount of catalyst, (b) the volume of water, and (c) the reaction temperture and reaction time.

Fig. 4 The effect of reaction time on cellulose hydrolysis under microwave.

Fig. 5 The effect on different kinds of polysaccharose hydrolysis.

Fig. 6 The reusability of catalyst with six times repeated experiments. (a) conversion; (b) the loss of $ChH_4AlW_{12}O_{40}$.

Table 1 Determination of acidic properties for $Ch_nH_{5-n}AlW_{12}O_{40}$ and yield to LA

Table 2 The distribution of products in cellulose hydrolysis in water under different reaction time and temperature.

Table 3 Effect of the solvents on the hydrolysis of cellulose into LA in different of volume ratio

Table 4 The effect on cellulose hydrolysis in different temperature and reaction time.

Table 5 Kinetic behavior for different reactions over $(Ch)H_4AlW_{12}O_{40}$.

Scheme 1. Conversion pathways of cellulose into levulinic acid.

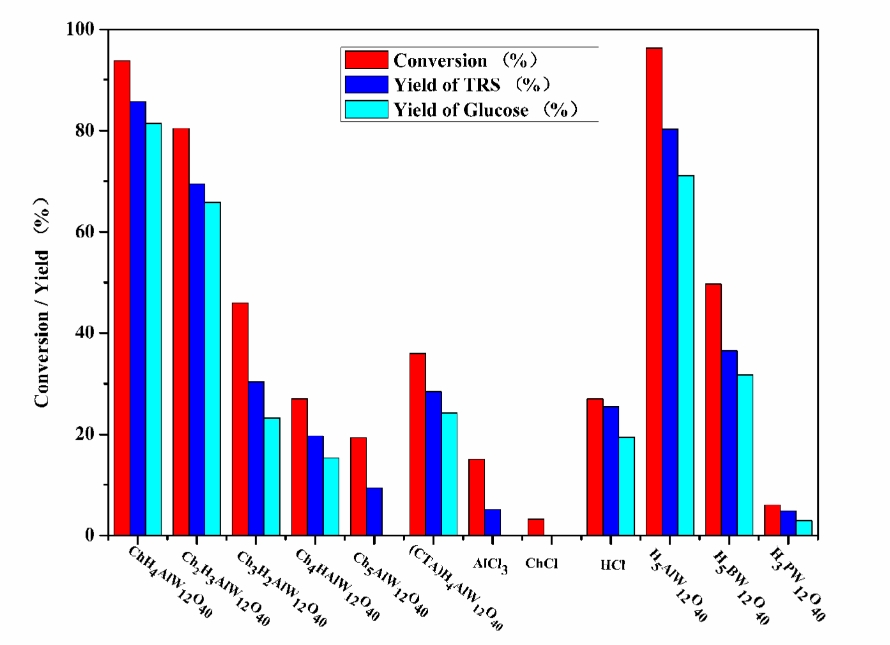


Fig. 1 Activity comparsion between different catalysts for cellulose hydrolysis. Reaction conditions: 0.1g of cellulose, 0.08 mmol of catalyst, 7 mL of water at 140 °C in 3 h.

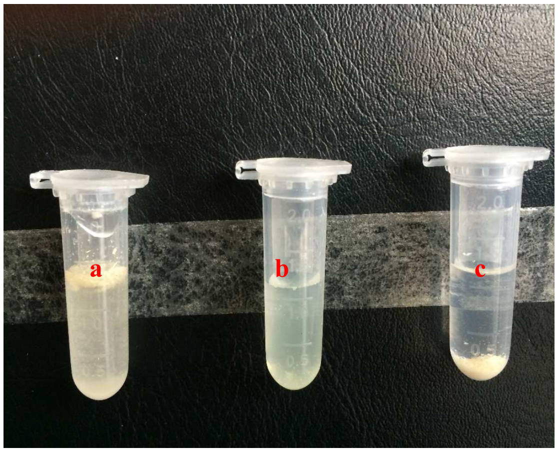


Fig. 2 The states of $ChH_4AlW_{12}O_{40}$ as changing temperatures. (a) At room temperature, (b) heating to 120 ºC, and (c) cooling to room temperature.

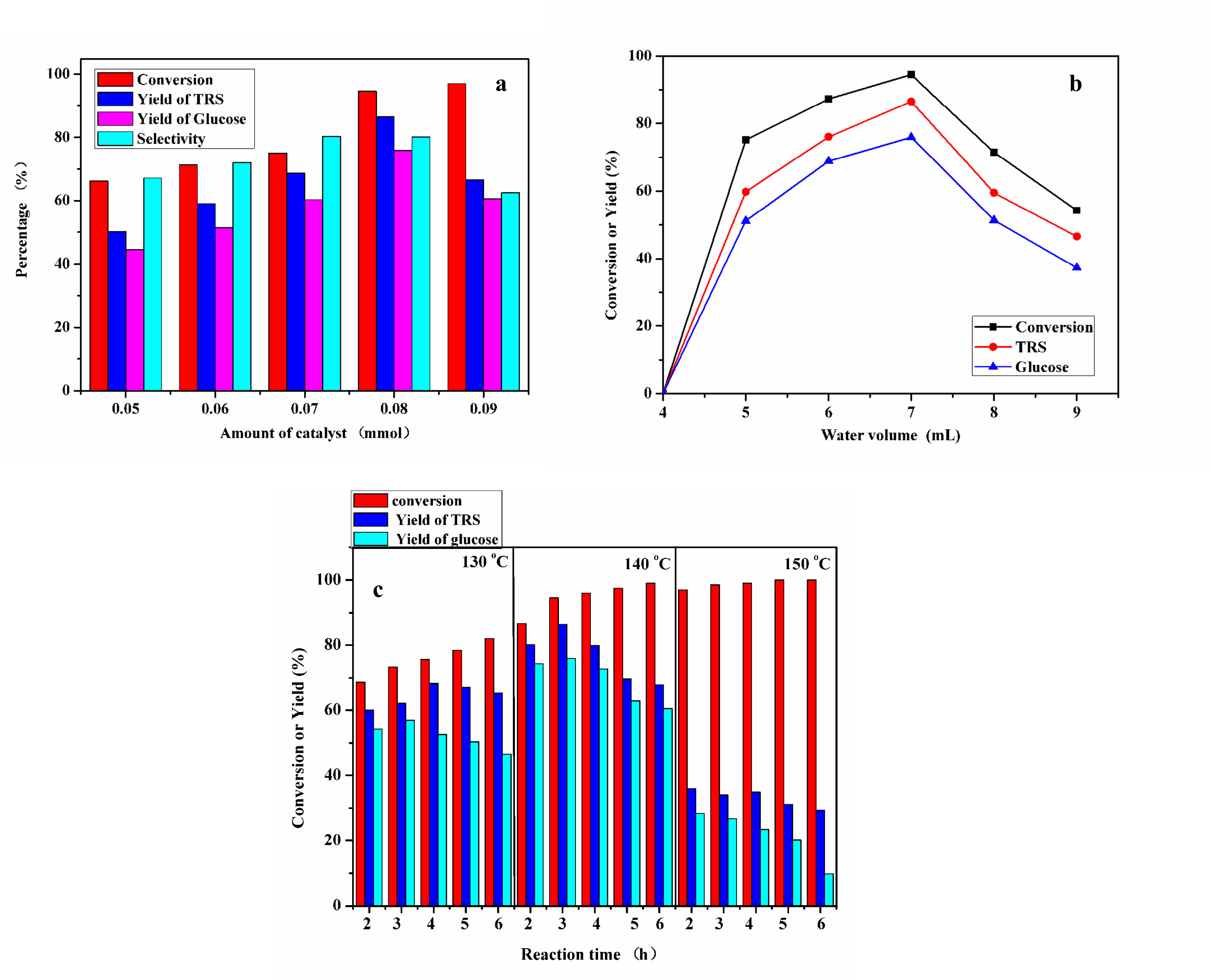


Fig. 3 The effect of $ChH_4AlW_{12}O_{40}$ at different reaction conditions. (a) amount of catalyst, (b) the volume of water, and (c) the reaction temperture and reaction time.

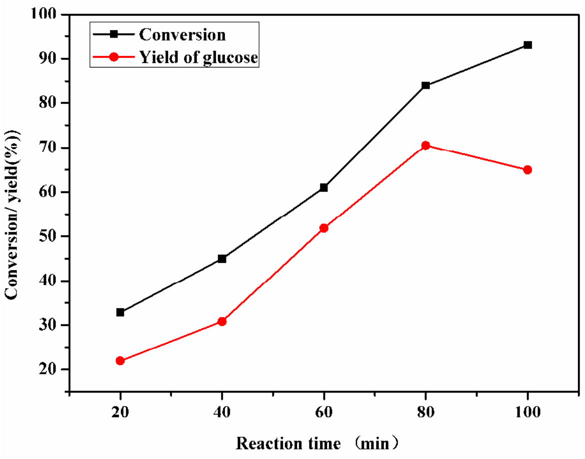


Fig. 4 The effect of reaction time on cellulose hydrolysis under microwave. Reaction conditions: 0.1g of cellulose with 0.08 mmol of catalyst, 7 mL water at 140 ºC.

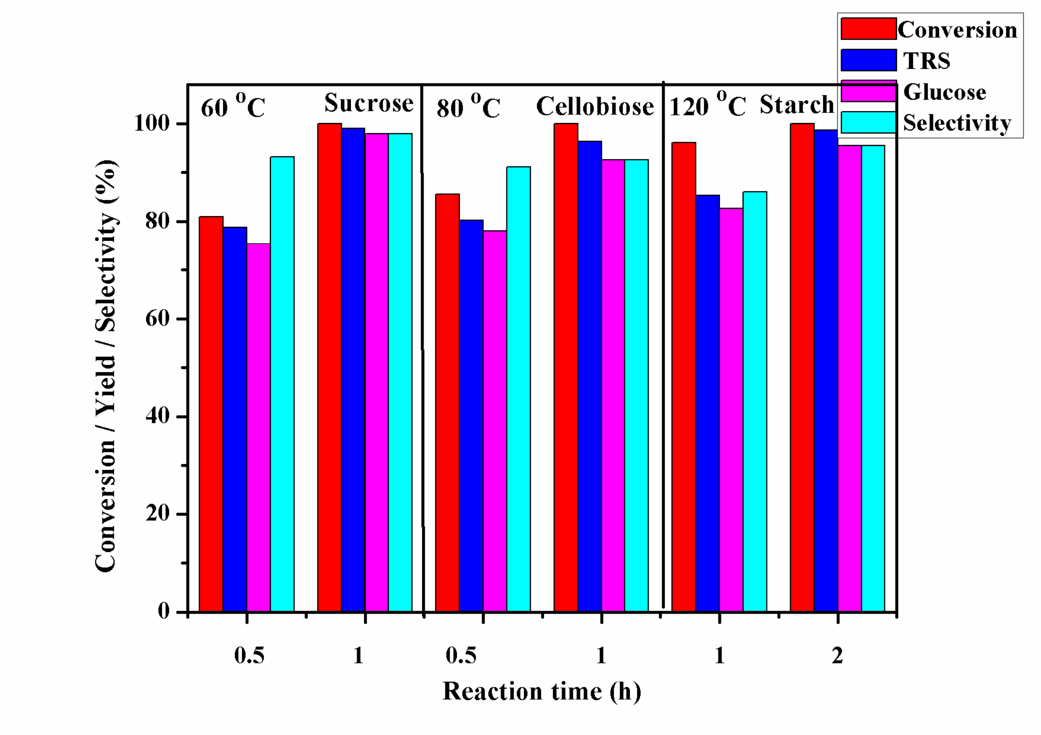


Fig. 5 The effect on different kinds of polysaccharose hydrolysis. Reaction conditions: 1.0 g of socrose, 0.02 mmol catalyst, 7 mL water at 60 °C; 0.15 g of cellobose, 0.02 mmol catalyst, 7 mL water at 80 °C; 0.15 g of strach, 0.02 mmol catalyst, 7 mL water at 120 °C.

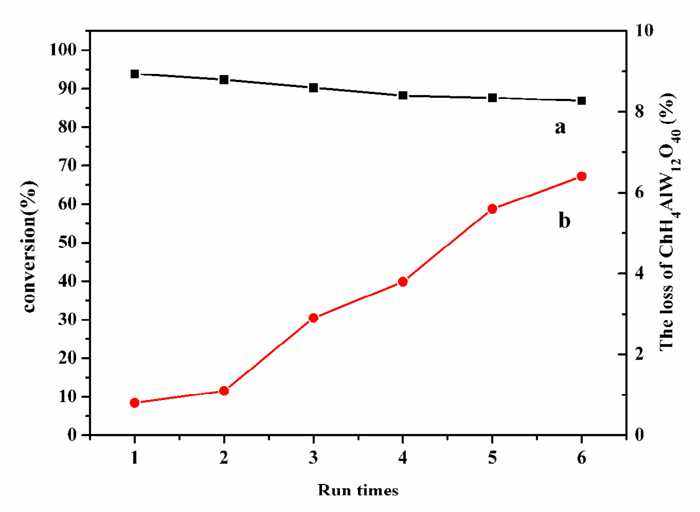


Fig. 6 The reusability of catalyst with six times repeated experiments. (a) conversion; (b) the loss of $ChH_4AlW_{12}O_{40}$. Reaction conditions: 0.1g of cellulose with 0.08 mmol of $ChH_4AlW_{12}O_{40}$ and 7 mL of water at 140 °C for 3 h.

Table 1 Determination of acidic properties for $Ch_nH_{5-n}AlW_{12}O_{40}$ and yield to LA[c]

Catalysts	Total Acid content[a] [mol/mol]	Brønsted acid content [mol/mol]	Lewis acid content [mol/mol]	Ratio of Brønsted to Lewis acidity	H_0[b]	Yield of LA [%]	TOF [$g \cdot mmol^{-1} \cdot h^{-1}$]
$H_5AlW_{12}O_{40}$	8.82	6.57	2.25	2.92	0.41	72.1	2.5×10^{-2}
$ChH_4AlW_{12}O_{40}$	8.04	5.85	2.19	2.67	0.49	74.8	3.1×10^{-2}
$Ch_2H_3AlW_{12}O_{40}$	7.09	4.86	2.23	2.18	0.52	65.3	3.2×10^{-2}
$Ch_3H_2AlW_{12}O_{40}$	6.06	2.95	3.11	0.95	0.55	33.1	3.1×10^{-2}
$Ch_4HAlW_{12}O_{40}$	4.28	1.57	2.71	0.58	0.59	19.5	3.0×10^{-2}
$Ch_5AlW_{12}O_{40}$	2.38	0.33	2.05	0.16	0.63	2.2	-

[a] 0.05 g of solid suspended in 45 mL of acetonitrile and stirred for 3 h. Measured by titration with a solution of n-butylamine in acetonitrile (0.05 M) using the indicator anthraquinone (pKa = -8.2).

[b] A sample of the catalyst (100 mg) and Hammett indicator (p-nitroaniline, pK(I)aq = 0.99) were dissolved in 20 mL of secondary distilled water for 12 h. Hammett acidity functions by using UV-visible spectroscopy at 380 nm.

[c] Reaction conditions: 0.1 g of cellulose, 0.08 mmol of catalyst, volume ratio of MIBK/H_2O = 10:1 at 120 °C for 10 h.

[d] TOF = Conversion of cellulose/molar of Brønsted acid contents × time (g/mol·h)

Table 2 The distribution of products in cellulose hydrolysis in water under different reaction time and temperature.*

Entey	Reaction temperature (° C)	Reaction time (h)	Yield (%)		
			Glucose	HMF	LA
1	120	2	32.6	1.2	-
2		3	35.3	2.3	-
3		4	38.4	3.5	-
4		5	43.8	4.0	-
5		6	48.6	4.9	-
6	130	2	54.3	6.8	1.4
7		3	56.9	9.6	4.5
8		4	52.6	10.3	7.5
9		5	50.4	13.8	10.3
10		6	46.6	19.7	13.6
11	140	2	64.3	8.8	4.4
12		3	79.1	12.6	8.5
13		4	62.7	16.3	10.5
14		5	52.8	18.8	13.3
15		6	40.5	25.7	16.6
16	150	2	28.4	29.8	13.6
17		3	26.8	32.6	14.6
18		4	23.5	34.5	15.8
19		5	20.1	38.9	17.7
20		6	9.8	36.1	19.2

*Reaction conditions: 0.1 g of cellulose with 0.08 mmol of $ChH_4AlW_{12}O_{40}$ and 7 mL of water.

Table 3 Effect of the solvents on the hydrolysis of cellulose into LA in different of volume ratio*

Entry	Solvent	Volume ratio	Yield of LA (%)
1	MIBK/H_2O	10:1	74.8
2	DMSO/H_2O	10:1	61.2
3	THF/H_2O	10:1	42.6
4	Methylbenzene/H_2O	10:1	30.6
5	H_2O	1	6.4
6	MIBK/H_2O	8:1	42.6
7	MIBK/H_2O	9:1	59.2
8	MIBK/H_2O	11:1	70.2

* Reaction condition: 0.1 g of cellulose, 0.08 mmol of $ChH_4AlW_{12}O_{40}$ in 7 mL solvent at 120 °C for 10 h.

Table 4 The effect on cellulose hydrolysis in different temperature and reaction time.[*]

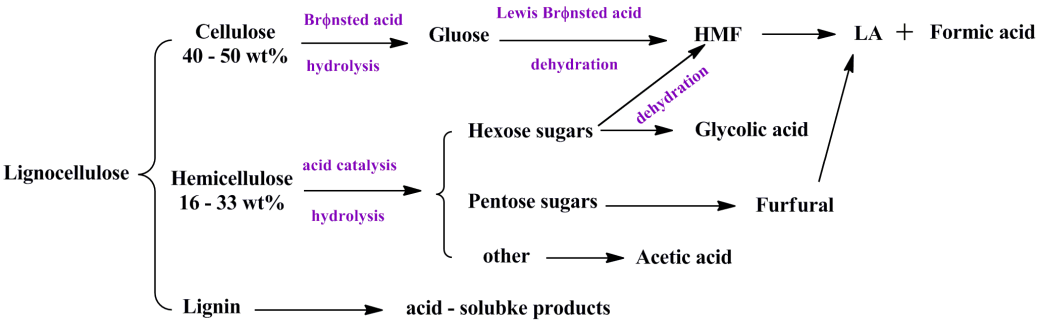
Entry	Cellulose (g)	Temperature (ºC)	Reaction time (h)	Yield of HMF (%)	Yield of LA (%)
1	0.1	120	8	20.4	9.8
2	0.1	120	8.5	26.7	12.3
3	0.1	120	9	47.5	27.7
4	0.1	120	9.5	27.1	41.9
5	0.1	120	10	5.2	74.8
6	0.1	120	11	-	61.2
7	0.1	130	5	34.4	36.7
8	0.1	130	6	35.1	63.4
9	0.1	130	7	33.7	66.2
10	0.1	140	3	19.3	10.1
11	0.1	140	4	31.8	27.5
12	0.1	140	5	22.1	28.7
13	0.1	140	6	18.9	55.3

[*] Reaction condition: 0.08 mmol of $ChH_4AlW_{12}O_{40}$, volume ratio of $MIBK/H_2O$ = 10:1

Table 5 Kinetic behavior for different reactions over $(Ch)H_4AlW_{12}O_{40}$.*

Entry	substance	Reaction time (min)	Conversion (%)	$\ln c_0/c$	*k*
1	Fructose	20	90.2	2.3	2.9×10^{-2}
2		40	93.4	2.7	
3		60	96.1	3.2	
4		80	97.9	3.9	
5		100	99.0	4.6	
6	HMF	10	73.9	1.3	2.7×10^{-2}
7		20	82.1	1.7	
8		30	87.8	2.1	
9		40	89.4	2.2	
10		50	91.1	2.4	

[*] Reaction condition: 0.1 g substance and 0.08 mmol of catalyst in 7 mL solvent, the volume ratio of MIBK/H_2O = 10:1 at 120 °C.



Scheme 1. Conversion pathways of cellulose into levulinic acid.