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Hydrolysis of Cellobiose to Monosaccharide Catalyzed by Functional Lanthanum (Ⅲ) Metallomicelle

Xiao Peng, Xiang-Guang Meng*, Chun Mi, Xiao-Hong Liao

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A novel surfactant 3-(dodecylimino)butan-2-one-oxime (DMBO) was synthesized. The metallomicelle $La(DMBO)_2$ was prepared and used as mimic β-glucosidase to catalyze the hydrolysis of cellobiose in weakly alkaline aqueous solution at relative low temperature (80-110ºC). This study indicated that the functional metallomicelle displayed effective catalytic activity for hydrolysis of cellobiose to monosaccharide (glucose, fructose and 1,6-anhydroglucose) and glucosyl-erythrose. The conversion of cellobiose and selectivity of monosaccharide could reach 38.5% and 71.1% for reaction 10h at pH9.0 and 95ºC, respectively. The possible reaction pathways of cellobiose hydrolysis were proposed and the catalysis reaction rate constant k_{cat} and Michaelis constant K_m for the cellobiose hydrolysis were calculated. The apparent activation energy (E_a=84.6kJ·mol^{-1}) of cellobiose to monosaccharide was evaluated.

1. Introduction

Cellulose, a linear macromolecule connected by β-1,4-glycosidic bond of D-glucose units, is the most abundant organic compound in nature.[1,2] Glucose is an important platform compound to produce biofuels and chemicals such as 5-(hydroxymethyl)furfural, lactic acid and 3-hydroxyacrylic acid.[3-6] Therefore hydrolysis of cellulose into glucose is one of bottlenecks and challenging problems in the field of utilization of biomass.[7,8] Although some researchers have reported the hydrolysis of cellulose into glucose through acid catalysts,[9-12] subcritical and supercritical water[13-16] and ionic liquid,[17-19] the problems of low activity and/or selectivity, severe reaction conditions and potential environment pollution have not been resolved. Cellulase catalyzed hydrolysis is an ideal process for cellulose degradation owing to the high selectivity of product of glucose and the benign environment.[20,21] However the high cost and unstability of enzyme limited its further application.[22] There are three kinds of cellulase for cellulose hydrolysis by synergistic action: β-1,4-endoglucanase (EC3.2.1.4), β-1,4-exoglucanase (EC3.2.1.91) and β-glucosidase (EC3.2.1.21).[23,24] β-glucosidase constitutes a major group of glycoside hydrolase and hydrolyzes cellobiose to glucose efficiently.[25,26] The catalysis mechanism of β-glucosidase was believed to encounter two reaction steps involving glycosylation and deglycosylation step.[27,28]

Functional micelles, a new kind of self-assembly supramolecular system, which could not only simulate the active centre but also the hydrophobic microenvironment of enzyme, attract extensive concern of biologists and chemists.[29-33] Micelle, especial for metallomicelle consisted of metal and long-chain surfactant micelle, are widely applied to catalyze reactions[34-36] and to prepare new materials.[37-39] In this paper, a novel metallomicelle $La(DMBO)_2$, as mimic β-glucosidase, was employed to catalyze the hydrolysis of cellobiose which is the basic structure unit and a good model of cellulose in weakly alkaline aqueous solution at relative low temperature (80-110□). This metallomicelle displayed excellent catalytic activity and selectivity of monosaccharide for cellobiose hydrolysis.

2. Experimental

2.1 Materials

β-D-(+)-Cellobiose was biological grade and purchased from *J&K* Corp Company. Diacetyl monoxime (Damx), dodecylamine, $La(NO_3)_3·6H_2O$ and methanol were analytical grade and purchased from Kelong Chemical Company and used with certain purification. Acetonitrile was chromatographic pure grade and purchased from Adamas Company. Whatman 42 filter paper was purchased from GE Healthcare companies.

2.2 Synthesis of 3-(dodecylimino)butan-2-one-oxime (DMBO)

Diacetyl monoxime (Damx) (2.525g) was dissolved in 20ml absolute methanol, and then the solution was added dropwise into 30ml methanol solution of dodecylamine (3.70g), then 0.4g NaOH was added. The mixture was heated to 70□ and refluxed for 20h, then cooled to room temperature. The mixture solution was treated by silica gel column chromatography (v/v 2:3, ethyl acetate-chloroform) and yellowish crystalline was obtained. Yield: the 3-(dodecylimino)butan-2-one-oxime (3.49g, 65%). The contents of C, H, N and O elements of DMBO were determined using an elemental analyzer (MOD 1106, Carlo Erba Company of Italy). Found: C, 71.62; H, 11.98; N, 10.39; O, 5.93%. Calc. for $C_{16}H_{32}N_2O$: C, 71.64; H, 11.94; N, 10.45; O, 5.97%. ^{1}H NMR (AM-400, Bruker of Switzerland): δ (400MHz, $CDCl_3$): 11.8 (1 H, s,-OH), 1.21-1.52: (22 H, m, 11-CH_2); 3.15 (3 H, s, -CH_3CNOH), 2.04 (3 H, s, -CH_3CN-$C_{12}H_{25}$); 0.84 (3 H, m, -$CH_3C_{11}H_{22}$).

2.3 Methods

The initial reaction solution, containing 0.02 mol·L^{-1} cellobiose and 0.002 mol·L^{-1} catalyst, was heated and kept at desired temperature. Before heating, the gas N_2 was passed into the solution for 30min for the cases of reaction at temperature below 100ºC. For the case of reaction at above 100 ºC, the N_2 was passed into reaction solution until reaction completed. The sample was extracted from the reactor periodically and cellobiose and products in reaction solution were analyzed and their concentrations were determined by HPLC equipped with a RI detector (Shodex 201R, Japan) and a Sugar-D chromatographic column. The pH of solution was adjusted by H_2SO_4 or NaOH. For the hydrolysis of cellulose (Whatman 42 filter paper), the N_2 gas was passed into the flask continuously until reaction completed, and the total reducing sugar was detected by DNS method[40,41] through UV-5300 spectrophotometer (Yuanxi Company, China). On a carbon basis, the conversion of cellobiose X was calculated as $X=(C_0-C_t)/C_0$), yield of monosaccharide Y was calculated as $Y=C_{1t}/2C_0$ and the selectivity of monosaccharide S was calculated as $S=Y/X$. Where C_0, C_t are the concentrations of cellobiose at reaction time t=0 and t=t, respectively, C_{1t} is the total concentration of monosaccharide (glucose, fructose and 1,6-anhydroglucose) at time t.

3. Results and discussion

3.1 cmc of surfactant and Job plots

Surfactant molecule could aggregate to form micelle above critical micelle concentration (cmc). Both the characteristic and the self-assembly supramolecular structure of micelle are far different from its monomer.[42] In this work cmc of surfactant DMBO was measured with electric conductivity method using a conductivity meter (DDS-307, China). According to plots of electric conductivity *vs*. concentrations of DMBO (Fig.S1 in the ESI), cmc of DMBO, which was corresponding to the cross point of two straight lines, was evaluated about 1.63×10^{-4} mol·L^{-1}.

In order to determining the chelating stoichiometry of the reactive metal complex, the kinetic version of Job-plots were utilized, as shown in Fig.S2 in the ESI, in which the conversion of cellobiose or yield of monosaccharide was plotted as a function of the mole fraction (r) of ligand or La^{3+} keeping their total concentration constant.[30,43] From Fig.S2 in the ESI it can be seen that the r-values corresponding to the maximum conversion of cellobiose and yield of monosaccharide were all at about 0.67, which suggesting that the 1:2 complex (metal: ligand) should be the active species at pH9.0.

3.2 Comparison of catalytic activity

Cellobiose is stable and difficult to hydrolyze at near neutral aqueous solution. However it can be rapidly degraded under strong acid (pH<2) or alkali (pH>10) conditions (Fig.S3 in the ESI). The results of cellobiose hydrolysis catalyzed by different catalytic systems at pH9.0, 90°C and 10h were listed in table 1, from which we can see that in the absence of any catalyst cellobiose could degrade only 3.7% for reaction 10h at pH9.0 and 90°C. Damx containing N-OH functional group in relatively low concentration displayed certain catalytic activity for the cellobiose hydrolysis. Metal complex $La(Damx)_2$ enhanced the reaction rate obviously. Interestingly, when long hydrocarbon chain was grafted to Damx, the micelle formed and showed excellent catalytic activity probably owing to the microenvironmental effects of enzyme-like.[30,31] Further it was also found that the metallomicelle $La(DMBO)_2$ showed best catalytic activity under the same conditions. To understand the effect of structure of metal complex on reaction activity, several metal complexes (Fig.S4 in the ESI) were employed as catalysts to catalyze cellobiose hydrolysis under the same condition. It can be found that these catalysts showed far lower catalytic activity than that of $La(Damx)_2$ (Table S1 in the ESI), this indicated that the strong nucleophilic functional group N-O$^-$ may play important role in the catalysis process under weakly alkaline condition.

Table 1 Comparison of catalytic activity for various systems*

Systems	Conversion of cellobiose /%	Yield of monosaccharide/ %	Selectivity of monosaccharide/%
Bulk solution	3.7	1.9	48.6
Damx	8.9	4.6	51.7
DMBO	11.1	5.8	52.2
$La(Damx)_2$	17.7	9.7	54.8
$La(DMBO)_2$	29. 5	17.8	60.3

*$[Cellobiose]_0$=0.02mol·L^{-1}, [Catalyst]=0.002mol·L^{-1},pH9.0, 90°C, 10h

3.3 Effect of pH

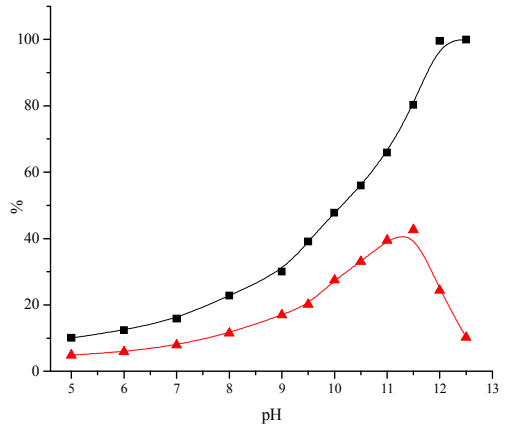


Fig.1 Plots of conversion of cellobiose(■) and yield of monosaccharide(▲) versus pH under condition of 90°C, 10h

From Fig.1 it can be found that for the metallomicelle $La(DMBO)_2$ catalyzed system, pH has great influence on conversion of cellobiose and yield of monosaccharide. The conversion of cellobiose increased with increasing pH and arrived about 100% for reaction 10h at pH12 and 90°C. However the yield of monosaccharide was complex. Initially the yield of monosaccharide increased with increasing pH and reached the maximum at pH11.5. From table 2 it can be found that the main component is glucose. According to our experimental data, glucose and fructose can be rapidly degraded to smaller molecule substances including 5-(hydroxymethyl)furfural, laevulinic acid and methanoic acid under strong alkali conditions (pH>11.5).

3.4 Effect of temperature

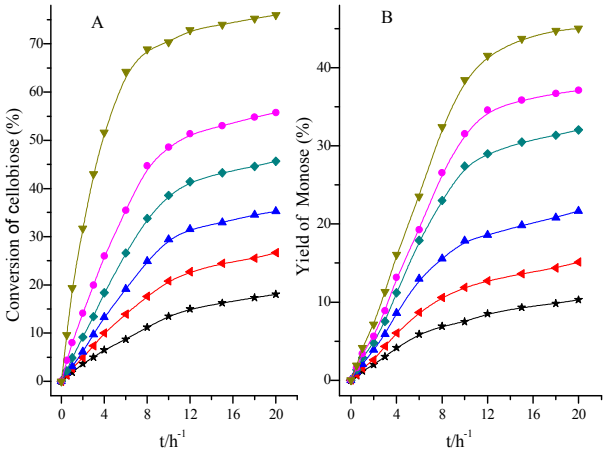


Fig.2 Conversion of cellobiose (A) and yield of monosaccharide (B) catalyzed by $La(DMBO)_2$ with time at different temperature at pH9.0
(★)80 °C, (◂)85°C , (▲)90°C, (◆) 95°C, (●)100°C, (▼)110□

Cellulose is stable and difficult to hydrolyze under mild condition owing to the large activation energy of its hydrolysis reaction, so the hydrolysis reaction was usually carried out under high temperature. However glucose could be easily decomposed to smaller molecule substances, therefore the selectivity of monosaccharide was generally very low under high temperature.[15,44] In this work cellobiose hydrolysis reaction was carried out at relatively low temperature (80-110°C). Fig.2 showed the effect of temperature on both conversion of cellobiose and yield of monosaccharide. Apparently, higher temperature accelerated the reaction rate of cellobiose hydrolysis. However it can be further found that the selectivity of monosaccharide increased gradually with increasing temperature from 80 to 95°C, and then decreased from 95 to 110°C.

3.5 Products analysis and possible reaction pathway

In order to analyze the reaction products, HPLC and Pulsed Amperometric Detection and Mass Spectrometry (PAD-MS) (LCMS-IT-TOF, Shimadzu of Japan) were employed. These studies indicated that there were four products: glucose, fructose, 1,6-anhydroglucose and glucosyl-erythrose (GE) in the reaction solution, which was illustrated in Fig.3. For the monosaccharide (glucose, fructose and 1,6-anhydroglucose), their content in reaction solution were determined by HPLC with external standard method. An unknown substance, whose mass spectrometry 283.1 ($[GE+H]^+$) and 304.3 ($[GE+Na]^+$) by PAD-MS(E+) were showed in Fig.S5 in the ESI, was believed as glucosyl-erythrose (GE), which has been widely reported as one of main products of cellobiose decomposition,[13,15] although it cannot be accurately identified. The conversion of cellobiose and distribution of products at various temperatures for reaction 10h at pH9.0 were listed in table 2. Based on these studies, possible reaction pathways of cellobiose hydrolysis were suggested as illustrated in scheme 1.

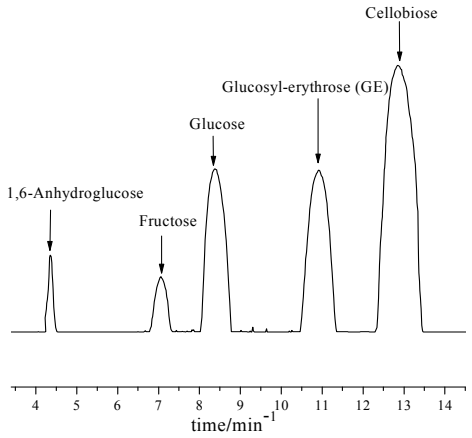
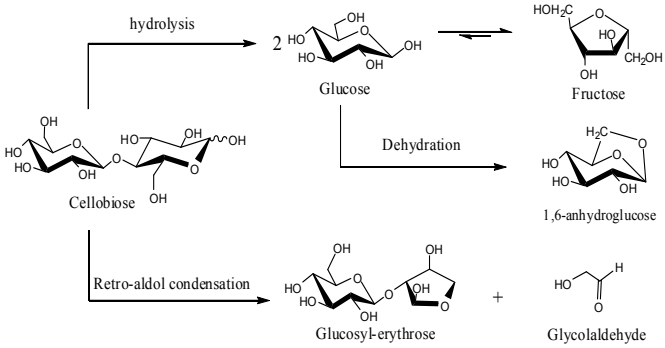


Fig.3 HPLC chromatograph of reaction solution of cellobiose hydrolysis



Scheme 1 Possible reaction pathways of cellobiose hydrolysis

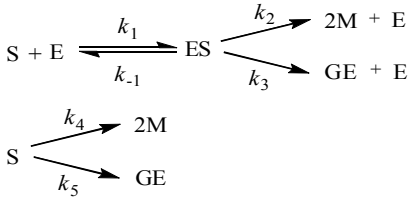
Table 2 Conversion of cellobiose, distribution of products and selectivity of monosaccharide at pH9.0, 10h

T/°C	Conversion of cellobiose /%	Yield of monosaccharide			Yield of monosaccharide/ %	Yield of GE/%	Selectivity of monosaccharide/ %
		glucose /%	Fructose/ %	1,6-anhydroglucose/%			
80	13.5	5.2	1.1	1.2	7.5	5.7	55.6
85	20.8	7.7	1.6	2.6	11.9	7.8	57.2
90	29.5	11.4	2.5	3.9	17.8	10.5	60.3
95	38.5	18.5	3.4	5.5	27.4	10.1	71.1
100	48.6	21.5	3.9	6.1	31.5	15.3	64.8
110	70.4	26.0	4.7	7.7	38.4	30.3	54.5

3.6 Reaction kinetics

In many previously reports, kinetic behavior of cellulose and cellobiose degradation were generally described as pseudo-first-order reaction.[1,10,13] However when the association of catalyst (or enzyme) with substrate before further reacting can't be ignored, the catalysis reaction would involve in more complex kinetic process rather than simple first-order kinetics. In this work we found the hydrolysis of cellobiose showed complex kinetic characteristics. It seemed that two apparent first-order kinetic process appeared, as illustrated in Fig.S6 in the ESI, there were two straight lines of -ln(1-

c_t/c_0)-t. It was possible that the reaction product would inhibit the reaction, and which resulted in much slower reaction rate in the later stage than in the early stage of hydrolysis reaction. Thus according to our experimental results a more detailed reaction pathway for cellobiose hydrolysis was proposed as shown in scheme 2: firstly cellobiose S combined with surfactant E to form an intermediate compound ES, and then ES further reacted to monosaccharide M and glucosyl-erythrose GE. In the first step, the surfactant E combined with substrate S reversibly with rate constants k_1 and k_{-1}, then followed the rate-determining steps with rate constants k_2 and k_3. k_4 and k_5 are the rate constants of cellobiose hydrolysis to M and GE in bulk solution, respectively. Based on reaction kinetic theory, kinetic equation (1) and equation (2) were deduced and the detailed deduce process can be found in Electronic Supplementary Information.



Scheme 2 The reaction pathway proposed for catalysis reaction

$$K_m k_0 \ln\frac{c_t}{c_0} + k_{cat}E_T \ln\frac{k_{cat}E_T + K_m k_0 + k_0 c_t}{k_{cat}E_T + K_m k_0 + k_0 c_0} = -(k_{cat}E_T + K_m k_0) * k_0 t \quad (1)$$

$$[M] = \frac{k_2 E_T + k_4 K_m}{k_0} \ln\frac{k_{cat}E_T + K_m k_0 + k_0 c_0}{k_{cat}E_T + K_m k_0 + k_0 [S]} + \frac{k_4}{k_0}(c_0 - [S]) - \frac{k_4(k_{cat}E_T + K_m k_0)}{k_0 * k_0} \ln\frac{k_{cat}E_T + K_m k_0 + k_0 c_0}{k_{cat}E_T + K_m k_0 + k_0 [S]} \quad (2)$$

Where $K_m = \frac{k_2 + k_3 + k_{-1}}{k_1}$, is the Michaelis constant, $k_{cat}=k_2+k_3$, $k_0=k_4+k_5$, E_T is the total concentration of surfactant. To avoid the interference of reaction products to reaction rate, the data of initial reaction time of 10h was used to calculate the k_{cat}, K_m and k_2 in this work. K_m and k_{cat} were obtained by nonlinear fitting according to equation S(9) in the ESI. k_2 was calculated according to the equation S(16) in the ESI. The calculated results were listed in table 3. From Figs.S7 and S8 in the ESI it can be seen that the experimental data were in good agreement with the theoretical curves, and both the nonlinear correlation coefficients of equation S(9) and the linear correlation coefficients of equation S(16) were all above 0.97. This indicated that the reaction pathways (Scheme.2, equation (1) and equation (2)) were reasonable.

Table 3 K_m, k_{cat} and k_2 of cellobiose hydrolysis catalyzed by La(DMBO)$_2$ at pH9.0

T/°C	80	85	90	95	100	110
10^2K_m/mol·L^{-1}	2.48	2.55	2.89	3.03	3.47	3.53
10^4k_{cat}/s^{-1}	0.879	1.29	1.94	2.90	4.53	11.5
10^4k_2/s^{-1}	0.57	0.77	1.21	2.04	2.89	4.91

From table 3 it can be seen that values of K_m were all relatively small, which indicated the association of catalyst with cellobiose was obvious in kinetic reaction process. Although the reaction rate constants k_{cat} and k_2 were 100-300 folds smaller than those catalyzed by natural β-glucosidases,[20,45] the metallomicelle La(DMBO)$_2$ displayed considerable catalytic activity under this conditions. The hydrolysis mechanism for β-glucosidase was believed as a two-step displacement process involving glycosylation and deglycosylation steps. In catalytic active domain, two carboxylic acid groups –COOH and COO$^-$ of glutamate residues play essential role for the catalysis reaction.[27,28] In previous reports organic acid catalysts, such as oxalic acid, fumaric and maleic acid showed good catalytic activity only for the pretreatment of cellulose.[46-48] In our recent studies, we found that micelle containing carboxylic acid group -COOH showed certain catalytic activity for hydrolysis of Methyl-β-D-cellobioside, however the micelle displayed catalytic activity only for the glycosylation step rather than for the deglycosylation step.[49] In this work it can be found that metallomicelle containing oximido group N-OH displayed excellent catalytic activity for both hydrolysis of cellobiose and selectivity of monosaccharide, although functional group oximido doesn't appear in the catalytic active domain of nature cellulase.

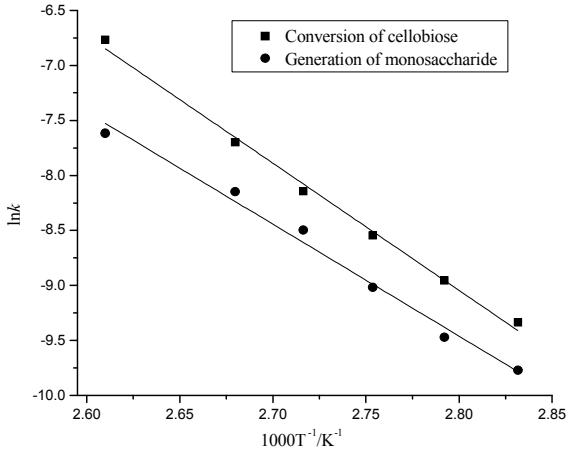


Fig.4 Plots of lnk_{cat} *vs.* 1/T for the cellobiose hydrolysis and lnk_2 *vs.* 1/T for the generation of monosaccharide

The activation energy and pre-exponential factor of the reactions were determined by the Arrhenius plots of lnk_{cat} *vs.* 1/T and lnk_2 *vs.* 1/T, as shown in Fig.4. The activation energy E_{a1} and pre-exponential factor A_1 of cellobiose conversion were evaluated as 96.13kJ·mol^{-1} and 1.36×10^{10}s^{-1} respectively. The activation energy E_{a2} and pre-exponential factor A_2 of generation of monosaccharide were evaluated as 84.6kJ·mol^{-1} and 1.88×10^{8}s^{-1} respectively, which were obtained easily through slope and intercept of the liner respectively and the correlation coefficient of linear were above 0.98. It was reported that the activation energy E_a of cellobiose hydrolysis catalyzed by enzyme were about 3-50kJ·mol^{-1},[20,50,51] and the activation energy of cellobiose hydrolysis catalyzed by non-enzyme were in the range of 110-200kJ·mol^{-1}, [1,13,52-55] and the activation energy of generation of monosaccharide ranged 100-130kJ·mol^{-1}.[52,53] The activation energy for the hydrolysis of cellobiose and the generation of monosaccharide in this work

are all relative smaller, which indicated that the metallomicelle system displayed good catalytic efficiency on the breakage of β-glycoside bond under mild conditions.

Further, the metallomicelle $La(DMBO)_2$ was also used to catalyze the hydrolysis of cellulose(Whatman 42 filter paper). The experimental results showed that for reaction 20h at pH9.0 and 95°C, the residual mass of insoluble filter paper was about 91.7%, and the yield and selectivity of total reducing sugar were 5.7% and 70%, respectively. This indicated that the metallomicelle $La(DMBO)_2$ could catalyze the hydrolytic breakage of β-1,4-glucoside bond inside the cellulose molecule as like β-glucosidase do.

4. Conclusions

This work investigated the catalysis hydrolysis of cellobiose to monosaccharide under mild conditions. The novel metallomicelle $La(DMBO)_2$ displayed excellent catalytic activity for both the conversion of cellobiose and yield of monosaccharide (glucose, fructose and 1,6-anhydroglucose) in weakly alkaline aqueous solutions at relative low temperature (80-110ºC). This catalytic activity could be attributed to the special enzyme-alike micelle microenvironment and the strong nucleophilicity of functional group N-OH. The relatively low activation energy E_{a1}=96.13kJ·mol^{-1} for the conversion of cellobiose and E_{a2}=84.6 kJ·mol^{-1} for generation of monosaccharide was calculated. This work may provide a new technology and method for hydrolysis of cellulose to monosaccharide under mild conditions.

Acknowledgments

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Notes and references

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, China. Fax: +86-28-85412291; Tel: +86-28-85462979; Email: mengxgchem@163.com.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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