CSIRO PUBLISHING

Aust. J. Chem.
https://doi.org/10.1071/CH18138

Full Paper

Efficient Hydrolytic Breakage of β-1,4-Glycosidic Bond Catalyzed by a Difunctional Magnetic Nanocatalyst

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A novel difunctional magnetic nanocatalyst (DMNC) was prepared and used to catalyse the hydrolytic breakage of β-1,4-glycosidic bonds. The functional nanoparticle displayed excellent catalytic activity for hydrolysis of cellobiose to glucose under moderate conditions. The conversion of cellobiose and yield of glucose could reach 95.3 and 91.1 %, respectively, for a reaction time of 6 h at pH 4.0 and 130°C. DMNC was also an efficient catalyst for the hydrolysis of cellulose: 53.9 % microcrystalline cellulose was hydrolyzed, and 45.7 % reducing sugar was obtained at pH 4.0 and 130°C after 10 h. The magnetic catalyst could be recycled and reused five times without significant loss of catalytic activity.

Manuscript received: 5 April 2018.
Manuscript accepted: 5 July 2018.
Published online: 14 August 2018.

Introduction

Increasing energy demand and environmental problems have highlighted the importance of using renewable lignocellulosic biomass to produce chemicals to replace fossil fuels.[1–3] Cellulose, a linear macromolecule connected by β-1,4-glycosidic bonds of D-glucose units, is one of the most abundant renewable biomass on earth.[4] The realisation has been made that the hydrolysis of cellulose into glucose is crucial for its subsequent conversion into valuable chemicals. As an important platform compound, glucose can be converted into biofuel,[5] polymer materials,[6] and chemicals such as 5-hydroxymethlfurfural, ethanol, and lactic acid.[7–9] Therefore, hydrolysis of cellulose into glucose is still one of the significant and challenging problems in the field of biomass utilisation.[10,11]

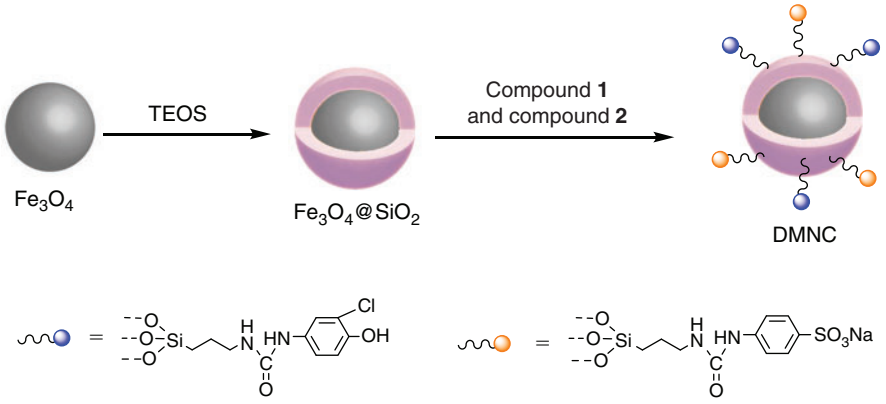
In recent years, some non-enzyme studies were reported for the hydrolysis of cellulose through acid catalysts,[12–14] ionic liquids,[15,16] and subcritical and supercritical water.[17,18] Among those, the problems of either low activity and selectivity, severe reaction conditions, or potential environmental pollution remain. The separation and recovery of the catalyst is also significant for industrial applications. Magnetic nanoparticles with loaded functional groups as a catalyst have attracted extensive attention.[19,20] Magnetic nanocatalysts can be easily separated and recycled by applying a simple external magnetic field. Recently, some magnetic catalysts loaded with sulfonic acid were reported to catalyse the degradation of cellulose. However, the lower catalytic activity or selectivity and relative acidic reaction conditions for the hydrolysis of cellulose need to be improved.[21–23] With the aim of developing sustainable chemistry, it would be much more preferable to use recyclable catalysts.

To develop an effective recyclable catalyst for the catalytic hydrolysis of β-1,4-glycosidic bonds, we designed a solid phase catalyst usingFe_3O_4@SiO_2 nanoparticles as supporters to which catalytic groups were grafted. A difunctional magnetic nanoparticle with *o*-chlorophenol and sodium benzene sulfonate groups was prepared and used to catalyse the hydrolysis of cellobiose and cellulose under relatively mild conditions. Cellobiose is connected by the same β-1,4-glycosidic bonds as in cellulose, and is considered as the simplest model molecule of cellulose. The recyclable magnetic nanocatalyst displayed excellent catalytic activity for the hydrolysis of cellobiose into glucose, and also good activity for the hydrolysis of microcrystalline cellulose and filter paper cellulose under relatively mild reaction conditions.

Results and Discussion

Characterization of the DMNC

The synthetic strategy for the preparation of the difunctional magnetic nanocatalyst (DMNC) is outlined in Scheme 1. Compounds **1** and **2** represent 1-(3-chloro-4-hydroxyphenyl)-3-(3-(triethoxysilyl)propyl)urea and sodium 4-(3-(3-(triethoxysilyl) propyl)ureido)benzenesulfonate, respectively. The detailed synthesis methods are described in the *Experimental*. The active groups *o*-chlorophenol and benzenesulfonate, were loaded on the surface of Fe_3O_4@SiO_2. Fe_3O_4 nanoparticles and the surface modified Fe_3O_4@SiO_2 particles were prepared as described in the Supplementary Material. In this work, the DMNC was successfully prepared by grafting the two functional groups onto Fe_3O_4@SiO_2. Transmission electron microscopy (TEM) images of Fe_3O_4 and Fe_3O_4@SiO_2 are shown in Fig. S1 in the Supplementary Material. As seen in Fig. S1b, the dark Fe_3O_4 core was surrounded by a light amorphous silica shell ~2–4 nm thick. TEM images of the DMNC are shown in Fig. 1a. From Fig. 1a, it can be seen that the nanoparticles are uniform and the size was ~20–30 nm in diameter. The TEM images showed no significant difference between Fe_3O_4@SiO_2 and DMNC.



Scheme 1. Preparation of DMNC.

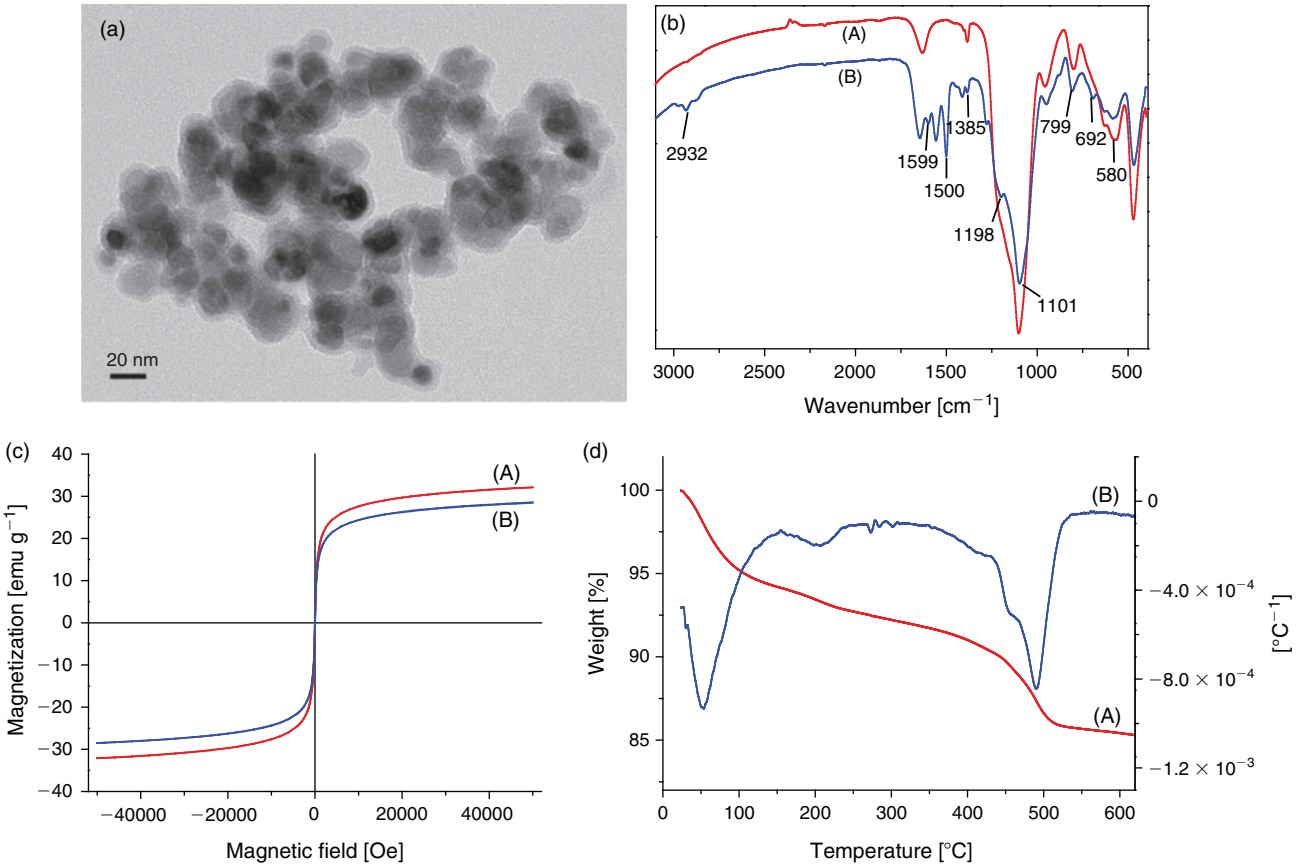
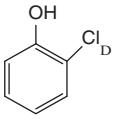
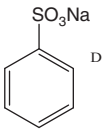


Fig. 1. (a) TEM images of DMNC; (b) FT-IR spectra of Fe_3O_4@SiO_2 (A) and DMNC (B); (c) magnetic hysteresis loop of DMNC at 300 K (A) and 400 K (B); (d) TGA (A) and differential thermal gravimetric (DTG) analysis (B) curves of DMNC.

The FT-IR spectra of Fe_3O_4@SiO_2 and DMNC are shown in Fig. 1b. The two particles both showed bands at ~1100 and 800 cm^{-1}, which can be assigned to the stretching vibration of Si–O bonds.[24] The band at 580 cm^{-1} can be assigned to the stretching vibration of Fe–O bonds.[25] The peaks at ~1385 and 1198 cm^{-1} are ascribed to the stretching vibration of S–O bonds in $–SO_3Na$ groups, which indicates that the DMNC was functionalized with $–SO_3Na$.[26] A signal for a C–Cl stretching vibration[27] appears at ~692 cm^{-1}, implying that *o*-chlorophenol was successfully introduced. The peaks at ~1599 and 1500 cm^{-1} are indicative of C=C stretching in the benzene ring.[28] The FT-IR spectra allows us to conclude that the desired chemical groups chlorophenol and benzene sulfonate were modified on the surface of the magnetic nanoparticles.

Magnetization profiles of the DMNC were examined using a vibrating sample magnetometer (*VSM*) at 300 and 400 K, as presented in Fig. 1c. The sample curve showed a non-linear and reversible behaviour with negligible coercivity and remanence, which confirms its superparamagnetism.[29] The saturation magnetization (Ms) for the DMNC is 32.10 and 28.43 emu g^{-1} at 300 and 400 K, respectively. When the temperature is 400 K, the Ms value of DMNC is slightly lower. The net magnetism is sufficient for efficient separation from solution

Table 1. Conversion of cellobiose in various systems[A]

System	Conversion of cellobiose [%]	Yield of glucose [%]	Yield of sucrose [%]	Selectivity of glucose [%]
Bulk solution	16.0	12.3	—[B]	77.3
$Fe_3O_4@SiO_2$[C]	12.4	4.4	5.5	35.7
 [D]	39.2	37.9	—	96.7
 [D]	63.3	54.9	—	86.7
DMNC[C]	95.3	91.1	—	95.5

[A]Reaction conditions: pH 4.0, 130°C, 6 h, 0.02 mol L^{-1} cellobiose.
[B]— represents no product.
[C]$Fe_3O_4@SiO_2$ and DMNC were 3.49 g L^{-1}.
[D]*o*-chlorophenol and sodium benzene sulfonate were 0.002 mol L^{-1}.

through use of a simple external magnetic force, as seen in Fig. S2 (Supplementary Material).

The thermostability of DMNC was evaluated by thermogravimetric analysis (TGA), as presented in Fig. 1d. From Fig. 1d, it can be seen that only 7 % weight loss occurred in the range of 30–400°C. The ~5 % weight loss below 100°C is caused by the evaporation of adsorbed water.[30] The trace amount (~2 %) of weight loss maybe due to the slow loss of combined H_2O in the silica shell in the temperature range of 100–400°C. A significant weight loss of 8 % was observed in the range of 400–500°C, which is attributed to the loss of organics grafted on the surface of the $Fe_3O_4@SiO_2$ particles. The results showed that the prepared DMNCs could be stable when it was used below 350°C.

Catalytic Performance

The hydrolysis of cellobiose catalyzed by various catalysts was carried out at pH 4 and 130°C. The results are listed in Table 1. As seen in Table 1, only 16.0 % of cellobiose conversion is observed in the absence of catalyst and some small molecule by-products appeared, such as hydroxymethylfurfural (*HMF*) and organic acids. The selectivity of glucose is 77.3 %. When the $Fe_3O_4@SiO_2$ nanoparticle was used, only 12.4 % conversion of cellobiose occurred. Unexpectedly, 5.5 % of cellobiose isomerized into sucrose in the $Fe_3O_4@SiO_2$ catalytic system. Both *o*-chlorophenol and sodium benzene sulfonate showed good catalytic activity for the hydrolysis of cellobiose. Sodium benzene sulfonate exhibited better catalytic activity and *o*-chlorophenol showed better selectivity for glucose. Interestingly, DMNC displayed the best catalytic activity and selectivity for glucose. The conversion of cellobiose and yield of glucose reached 95.3 and 91.1 %, respectively. Compared with *o*-chlorophenol and sodium benzene sulfonate under the same condition for the catalytic system of DMNC, the conversion of cellobiose and yield of monosaccharide are enhanced by 32 and 36 %, respectively. In natural β-glucosidases, the key step of hydrolysis of cellobiose is the simultaneous actions of attack on C_1 and inducing $O_{1-4'}$ by two groups of carboxylic acids.[31,32] In this work, the role of the *o*-chlorophenol group may be different from that of benzene sulfonate. The inductive effect between the *ortho* Cl atom and the H atom on the hydroxy group of phenol led to the easy attack of the O atom of phenol on C_1 of cellobiose (Fig. 2a). For benzene sulfonate, the O atom possesses strong nucleophilic ability, and could attack the C_1 of cellobiose (Fig. 2b). For DMNC, it is possible that *o*-chlorophenol and benzene sulfonate synergistically induce $O_{1-4'}$ and attack C_1 in the β-1,4-glycosidic bonds as illustrated as Fig. 2c, which is similar to the catalytic mechanism of natural β-glucosidases.[33] To better understand the catalyst DMNC, some experimental results and reaction conditions were compared with those of other reports in Table 2. As seen in Table 2, this work's catalytic system is slightly more effective than that of SO_3H0.3-Ph-SNT and obviously more effective than those other catalytic systems reported in Table 2. Also seen from Table 2, compared with other catalytic systems, this work's catalytic system used a relatively lower temperature and catalyst concentration. Moreover, different from the other reported reaction conditions of acidity (generally pH < 2), the pH value of this work was 4.0, which is a mild condition.

Effect of pH

In the absence of catalyst, the effect of pH on conversion of cellobiose at 130°C is shown in Fig. S3 (Supplementary Material). From Fig. S3, it can be seen that the hydrolytic breakage of glucosidic bonds is slow in aqueous solution in the range of pH 3.0–8.5. However, when pH < 3, the high concentration of H^+ can clearly promote the hydrolysis of cellobiose. In the presence of DMNC, the effect of pH on the reaction was investigated. As shown in Table 3, the pH had an obvious influence on both the rate of reaction and selectivity of the product. The conversion of cellobiose decreased with increasing pH, especially under the condition of pH < 5.0. At pH > 6.0, sucrose appeared. At pH 4.0, the DMNC displayed excellent catalytic activity (95.3 % conversion after 6 h) and the best selectivity for glucose (95.5 %).

Effect of Temperature

Cellulose is stable and difficult to hydrolyze under mild conditions owing to the large activation energy of its hydrolysis reaction, and hence the hydrolysis is usually carried out at high temperature. However, a high temperature could lead to the degradation of glucose and fructose into small

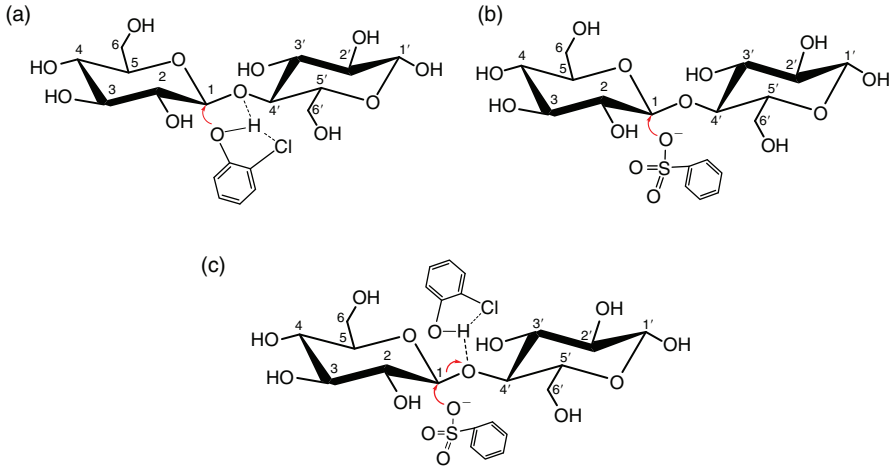


Fig. 2. Possible ways of attack of catalyst on cellobiose during hydrolysis: *o*-chlorophenol (a), sodium benzenesulfonate (b), and DMNC (c).

Table 2. Comparison of various reported catalytic systems for the conversion of cellobiose

System	Conversion of cellobiose [%]	Yield of glucose [%]	Selectivity of glucose [%]	Ref.
Fe_3O_4-RGO-SO_3H[A]	66	61	92	[2]
Fe_3O_4@nSiO_2@mSiO_2-SSFBI[B]	—	53.9	—	[19]
SO_3H0.3-Ph-SNT[C]	92	88	95.7	[34]
Acidified carbon[D]	50	21	42	[35]
Hβ zeolites[E]	76	69	91	[36]
DMNC[F]	95.3	91.1	95.5	this work

[A]Reduced graphene oxide functionalised with magnetic Fe_3O_4 nanoparticles and –$PhSO_3H$ groups. The S content of the catalyst was 0.63 mmol g^{-1}, and the total acid density was 1.23 mmol g^{-1}. Reaction conditions: 30 mg cellobiose, 10 g L^{-1} Fe_3O_4-RGO-SO_3H, 3 mL H_2O, 150°C, 3 h.
[B]Magnetic perfluoroalkylsulfonylimide-functionalised silica. 120°C, 4 h, 0.3 g cellobiose, 3 mL distillation water, catalyst amount 25 mol-%, acid loadings were 0.61 mmol g^{-1}.
[C]Phenylene-bridged sulfonic organosilica nanotubes with different acid contents were synthesised through the –SH oxidation of sulfhydryl organosilica nanotubes. Reaction conditions: 20 mL deionised water, 0.2 g cellobiose, substrates: acid active sites = 14, 150°C, 2 h, 2.5 MPa nitrogen.
[D]Activated carbon is functionalised by different treatments with sulfuric acid and hot water. 200°C, 25 bar, 100 mg catalyst, 0.5 mL min^{-1} of 0.03 M cellobiose solution.
[E]Reaction conditions: 50 mg cellobiose, 10 g L^{-1} Hβ, 5 mL H_2O, 150°C, 6 h.
[F]Difunctional magnetic nanocatalyst. pH 4.0, 130°C, 6 h, 0.02 mol L^{-1} cellobiose, DMNC was 3.49 g L^{-1}.

Table 3. Conversion of cellobiose and distribution of products at various pH[A]

pH	Conversion of cellobiose [%]	Yield of monosaccharide			Yield of sucrose [%]
		Glucose [%]	Fructose [%]	Total [%]	
3.0	100	87.5	—[B]	87.5	—
3.5	100	90.6	—	90.6	—
4.0	95.3	91.1	—	91.1	—
4.5	92.2	81.6	2.6	84.2	—
5.0	83.6	71.2	2.3	73.5	—
5.5	47.1	24.7	—	24.7	—
6.0	33.7	21.6	—	21.6	3.5
7.0	27.8	16.5	—	16.5	7.7
8.0	25.89	11.8	—	11.8	10.1

[A]Reaction conditions: 130°C, 6 h, 0.02 mol L^{-1} cellobiose, and 3.49 g L^{-1} DMNC.
[B]— represents no product.

molecular substances and result in low selectivity of monosaccharide.[37,38] In this work, we found that the catalytic reaction showed good selectivity for glucose (> 95 %) when the temperature was low (130°C), as shown in Fig. 3. From Fig. 3, it can be seen that the conversion of cellobiose increased with increasing temperature and reached 100 % at 140°C. Above 130°C, glucose degraded and led to lower selectivity.

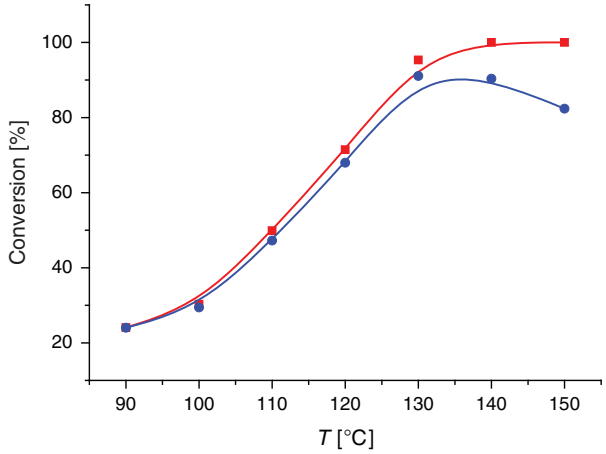


Fig. 3. Plots of conversion of cellobiose (■) and yield of glucose (●) versus reaction temperature, pH 4.0, 6 h.

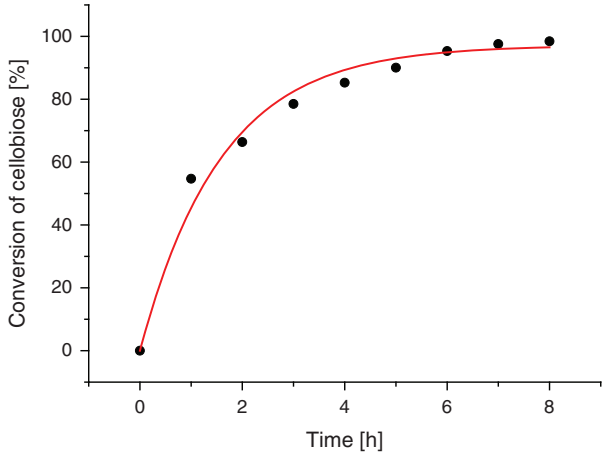


Fig. 4. Plots of conversion of cellobiose versus reaction time at pH 4.0 and 130°C.

Reaction Kinetics

The varieties of conversion of cellobiose and yield of glucose with time at pH 4.0 and 130°C are shown in Fig. 4 and Fig. S4 (Supplementary Material). From Fig. 4, it can be seen that the conversion of cellobiose could reach 95.3 % after a 6 h reaction time at 130°C, and it can also be found that the catalytic conversion of cellobiose showed an apparent first-order kinetic process. The solid curve fitted according to first-order kinetics was in agreement with experimental data, as shown in Fig. 4. Glucose will be generated and subsequently degrade slowly with time, which leads to the decrease of yield of glucose after 6 h (Fig. S4). Based on the reaction kinetic characteristics, the apparent first-order kinetic constant (k_{obs}) can be calculated. Hence, the activation energy (E_a) for conversion of cellobiose was evaluated as 88.3 kJ mol^{-1} according to the Arrhenius plot of ln k_{obs} versus $1/T$, as shown in Fig. S5 (Supplementary Material). It was reported that the activation energy (E_a) of the hydrolysis of cellulose was in the range of 110–260 kJ mol^{-1}.[39–41] The E_a value of the catalytic reaction was less than those reported, which indicated that the DMNC particles were an excellent catalyst for the breakage of the β-1,4-glycosidic bonds under relatively mild conditions.

Reusability of DMNC

The reusability of the DMNC was investigated in the hydrolysis of cellobiose for a reaction time of 6 h at pH 4.0 and 130°C. After each reaction, the DMNC catalyst was separated from the reaction mixture using an external magnet. The used catalyst was washed with water and dried in a vacuum oven at 60°C for 12 h. The recovered DMNC was then used for the next reaction run under the same conditions. As depicted in Fig. 5, no obvious decrease in catalytic activity was observed after five successive reaction runs. The yield of glucose was still more than 85 %, suggesting that DMNC exhibited excellent catalytic stability and recyclability.

Hydrolysis of Cellulose

The good catalytic ability of the nanocatalyst for the hydrolytic breakage of β-1,4-glycosidic bonds encouraged us to further investigate the catalytic hydrolysis of cellulose. We employed DMNC to catalyse the hydrolysis of pretreated cellulose filter paper and microcrystalline cellulose (MCC). The experimental results showed that filter paper and MCC were dissolved at 60.4

Fig. 5. DMNC cycle for cellobiose hydrolysis.

and 53.9 % (m/m), respectively, after 10 h of reaction at pH 4.0 and 130°C. The yields of total reducing sugar for the hydrolysis of filter paper and MCC were detected as 49.2 and 45.7 %. The selectivity of total reducing sugar was 81.5 and 84.8 %. The results displayed that the DMNC can efficiently catalyse the hydrolysis of cellulose by hydrolytic breakage of the β-1,4-glycosidic bond under mild conditions. Comparably, the hydrolysis of cellulose usually needs a high temperature because of the high activation energy of the reaction and thus results in further degradation of reducing sugars under high temperature conditions.[42,43] In this study, we suggest a green technology to achieve a satisfactory reducing sugar yield under relatively mild conditions by using a recyclable functional magnetic nanocatalyst.

Conclusions

A novel difunctional magnetic nanocatalyst with *o*-chlorophenol and benzene sulfonate active groups was prepared and used to catalyse the hydrolysis of cellobiose and cellulose under relatively mild conditions. The DMNC displayed excellent catalytic activity for the hydrolysis of cellobiose to glucose. The conversions of cellobiose and yield of glucose were 95.3 and 91.1 %, respectively, for a reaction time of 6 h at pH 4.0 and 130°C. MCC can also be efficiently hydrolyzed. MCC was

degraded by 53.9 % and 45.7 % reducing sugar was achieved at pH 4.0 and 130°C for 10 h. Compared with previously reported studies, the prepared nanocatalyst displayed several advantages for the hydrolysis of cellobiose, such as a higher conversion of cellobiose, yield of glucose, and less by-products achieved at low temperature (130°C) and high pH (4.0). The nanocatalyst is effective for the hydrolytic cleavage of β-1,4-glycosidic bonds in both cellobiose and cellulose. The activation energy for hydrolysis of cellobiose was evaluated as 88.3 kJ mol^{-1}. The magnetic catalyst could be easily separated and reused without significant loss of catalytic activity five times. This work provided an environmentally friendly method for the efficient hydrolysis of cellulose.

Experimental

Materials and Instruments

β-D-(+)-Cellobiose was of biological grade and purchased from the J&K Corp. Co. 3-Isocyanatopropyl triethoxysilane, 3-chloro-4-hydroxyaniline, sodium sulfanilate, fructose, glucose, sucrose, maltose, ferric chloride hexahydrate, ferrous sulfate heptahydrate, trisodium citrate dihydrate, ammonium hydroxide, and tetraethyl orthosilicate were purchased from the Kelong Reagent Co., and all of the reagents were of analytical grade and used after relevant purification. Acetonitrile was of chromatographically pure grade and purchased from the Adamas Co. Whatman 42 filter paper was purchased from the GE Healthcare Companies. MCC and phosphoric acid (85 %) were purchased from the Aladdin Biochemical Technology Co., Ltd

The methods used for characterization and reaction/product analysis include: NMR spectroscopy (AM-400, Bruker, Switzerland), TEM (JEM-2010, Japan Electron Optics Laboratory), VSM (MPMS3, Quantum Design, America), FT-IR spectroscopy (670FT-IR, Nicolet, America), UV-vis spectroscopy (UV-5300 spectrophotometer, Yuanxi Co., China), elemental analysis (Euro-EA-3000, America), and high-performance liquid chromatography (HPLC, LC-10T, Shodex, Japan, with an RI detector (RI-201R, Shodex, Japan) and a sugar-D chromatographic column).

Methods

The initial reaction solution, containing 0.1746 g cellobiose, 87.3 mg catalyst, and 25 mL of deionized water, was sealed and heated and kept at the desired temperature. Before sealing, N_2 gas was passed into the solution for 30 min. The magnetic catalyst was recovered by magnetic separation, washed, and vacuum dried. Concentrations of cellobiose, glucose, fructose, and other products in the reaction solution were determined quantitatively by HPLC with an external standard method by comparing to a standard sample. The pH was adjusted with H_2SO_4 or NaOH. On a carbon basis, the conversion of cellobiose X was calculated as $X=(C_0 - C_t)/C_0$. The yield of the monosaccharide Y_1 was calculated as $Y_1 = C_{1t}/2C_0$. The yield of sucrose Y_2 was calculated as $Y_2 = C_{2t}/C_0$. The selectivity of glucose S was calculated as $S = Y_1/X$, where C_0, C_t are the concentrations of cellobiose at reaction times $t = 0$ and t, respectively, and C_{1t}, C_{2t} are the concentrations of the monosaccharide and sucrose at time t, respectively.

The cellulose was pretreated with a modified method from the literature[44] as follows: 1 mL of deionized water and 3 g of MCC were added into a 50 mL round-bottomed flask. Phosphoric acid (30 mL of 85 %) was then slowly added to the flask with stirring. The decrystallization was carried out for 10 h with stirring in a water bath at 50°C and quenched by cooling in ice-water. Subsequently, the mixture was poured into 150 mL of deionized water with vigorous stirring. The formed precipitate was collected by filtration. The solid sample was washed with deionized water and acetone. Finally, the solid sample was vacuum dried at 50°C for 12 h. The Whatman 42 filter paper was pretreated using the procedures above.

For the hydrolysis of cellulose, the initial reaction solution containing 0.2 g of pretreated cellulose, 43.6 mg of catalyst, and 12.5 mL of deionized water was sealed and heated at pH 4.0. Before sealing, N_2 gas was passed into the solution for 30 min. The pH of the solution was adjusted with H_2SO_4 or NaOH. After 10 h of reaction, the magnetic catalyst was recovered by magnetic separation. The reaction mixture was centrifuged and the solid was vacuum dried and weighed. The centrifuged solution was analysed, and the concentration of total reducing sugar (C_{TRS}) in the solution was quantified by the dinitrosalicylic acid (*DNS*) *method* with a spectrophotometer.[45,46] On a carbon basis, the dissolution of cellulose D was calculated as $D=(m_0 - m')/m_0$. The yield of total reducing sugar (TRS) was calculated as $\mathrm{TRS} = C_{\mathrm{TRS}}V_0M/m_0$. The selectivity of total reducing sugar S was calculated as $S = \mathrm{TRS}/D$, where m_0, m' are the quality of cellulose at reaction time $t = 0$ and 10 h, respectively, M is the relative molecular mass of glucose units in cellulose ($M = 162$), and V_0 is the initial volume of the reaction solution.

Preparation of the Magnetic Nanocatalyst

Syntheses of 1-(3-Chloro-4-hydroxyphenyl)-3-(3-(triethoxysilyl)propyl)urea (**1**) and Sodium 4-(3-(3-(Triethoxysilyl) propyl)ureido)benzenesulfonate (**2**)

The synthesis of **1** is as follows: 3-isocyanatopropyl triethoxysilane (12 mmol) was added dropwise to 75 mL of $CHCl_3$ containing 3-chloro-4-hydroxyaniline (10 mmol) with stirring at room temperature. The mixture was then heated and refluxed for 10 h at 80°C and then cooled to room temperature. The product was separated by silica gel column chromatography, and a lavender crystalline product was obtained. Its identity was confirmed by ^{1}H NMR spectroscopy. δ_H (400 MHz, DMSO) 9.60 (s, 1H), 8.22 (s, 1H), 7.51 (s, 1H), 6.97 (d, *J* 8.8, 1H), 6.82 (d, *J* 8.7, 1H), 6.08 (s, 1H), 3.74 (q, *J* 7.0, 6H), 3.02 (dd, *J* 12.9, 6.7, 2H), 1.51–1.40 (m, 2H), 1.15 (t, *J* 7.0, 9H), 0.54 (t, *J* 8.4, 2H).

Compound **2** was prepared according to the literature.[47] Its identity was confirmed by ^{1}H NMR spectroscopy. δ_H (400 MHz, DMSO) 8.48 (s, 1H), 7.44 (d, *J* 8.6, 2H), 7.31 (d, *J* 8.6, 2H), 6.22 (t, *J* 5.6, 1H), 3.75 (q, *J* 7.0, 6H), 3.04 (dd, *J* 12.9, 6.7, 2H), 1.53–1.42 (m, 2H), 1.15 (t, *J* 7.0, 9H), 0.57 (dd, *J* 16.6, 8.0, 2H).

Preparation of DMNC

Fe_3O_4@SiO_2 nanoparticles (0.5 g) were ultrasonically dispersed in methanol (30 mL). A methanol solution containing **1** (0.22 g in 20 mL) and 20 mL of a methanol solution containing **2** (0.25 g) were added dropwise into the nanoparticle containing solution with stirring at room temperature. The mixture was heated and refluxed for 8 h at 80°C. It was then cooled to room temperature. The solid catalyst was separated from the methanol solution by magnetic adsorption with a magnet. The functional magnetic nanocatalyst was washed with methanol and dried in a vacuum dryer for 12 h at 60°C. The preparation DMNC is illustrated in Scheme 1.

To investigate the content of grafted functional groups on the magnetic nanocatalyst, the contents of N and S (1.41 % N, 0.83 % S) were quantified by elemental analysis. Thus, the amount of benzene sulfonate grafted on the magnetic nanocatalyst was calculated as 0.26 mmol $g^{-1}$and that of *o*-chlorophenol was 0.24 mmol g^{-1}.

Supplementary Material

Other experimental procedures, experimental results, and characterization data are available on the Journal's website.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgements

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 21273156).

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