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Amberlyst 15 as a new and reusable catalyst for the conversion of cellulose into cellulose acetate

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ABSTRACT

The acetylation of cellulose using sulfonated Amberlyst 15 as a new and reusable catalyst was investigated. Optimization of the acetylation process was carried out by variation in the amount of added catalyst, acetic acid, and acetic anhydride as well as the reaction conditions, which includes reaction time and reaction medium. Cellulose acetate, with a degree of substitution (DS) value of 2.38 and yield of 54.1%, was obtained under the optimized conditions and characterized using Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis–derivative thermogravimetry (TGA–DTG), and differential scanning calorimetry (DSC). The sulfonated polymer catalyst could be easily recovered by centrifugation after acetylation. Both the fresh and recovered catalysts were characterized by means of FTIR, TGA–DTG, DSC, and scanning electron microscopy (SEM), and the recovered catalyst could be successfully reused without further treatment. It was found that Amberlyst 15 possessed excellent catalytic stability, no significant changes in the DS values, and consistent yields of cellulose acetate observed over four reaction cycles.

1. Introduction

Recently, the need to explore alternative sustainable energy sources has arisen because of the shortage of resources as a consequence of the over-exploitation of fossil fuels. Interest in the chemistry of biomass-derived compounds has led to efforts aimed at the use of lignocellulosic materials as alternative sources of chemicals and energy (Heguaburu et al., 2012). Cellulose is the most abundant non-food biomass and renewable carbon source on Earth, and is widely considered a long-term renewable fossil fuel alternative (El–Sakhawy & Hassan, 2007; Van de Vyver, Geboers, Jacobs, & Sels, 2011). The conversion of cellulose into useful chemicals has attracted significant attention in the fields of green and sustainable chemistry, and has prompted the development of friendly environmental technologies (Chheda, Huber, & Dumesic, 2007a,b; Lv et al., 2010; Rutkowski, 2011).

Cellulose is a useful starting material for chemical conversion with the aim of obtaining a variety of cellulose derivatives; esterification is a common chemical modification of cellulose (Edgar et al., 2001). Cellulose acetate is one of the most important organic acid esters of cellulose, and is widely applied in the manufacture of fibers films, paints, plastics, filters, dialyzers, and drugs; as a further benefit, cellulose acetate is potentially biodegradable due to its biologically labile cellulose acid ester linkage (Ass, Frollini, & Heinze, 2004; Edgar et al., 2001; Marson & El Seoud, 1999; Sereti, Stamatis, Pappas, Polissiou, & Kolisis, 2001; Yang, Wang, & Kuo, 2004). Generally, wood and cotton are the major material resources for the industrial acetylation of cellulose (Rodrigues Filho et al., 2008; Steinmeier, 2004). In recent years, low-cost lignocellulosic biomass has become an attractive renewable resource because of its availability in large quantities as a result of its widespread cultivation on a global scale. So far, few research works on the preparation of cellulose acetate from rice straw have been proposed (Fan et al., 2013b).

Cellulose acetates are mainly produced via vapor phase or solution processes, in which cellulose reacts with acetic anhydride in acetic acid solution by means of a strong acid such as sulfuric acid or perchloric acid as the catalyst (Kuo & Bogan, 1997; Steinmeier, 2004). Rigorous conditions are generally required, and cellulose triacetate with an average degree of substitution (DS) value above 2.8 is often obtained. These strong inorganic acid-catalyzed processes often result in problems of corrosion and large amounts of generated waste. Furthermore, cellulose triacetate with a higher DS value is impractical in terms of its use in direct commercial applications due to its limited solubility in common organic solvents (Cao et al., 2007). Partially substituted cellulose diacetate, having DS values ranging from 2.0 to 2.5 and good solubility in acetone, is usually obtained from the partial hydrolysis of cellulose

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triacetate and is more widely applied in industry. The partial hydrolysis of completely acetylated cellulose is generally required to obtain a desired hydroxyl content, which makes the process complicated and poorly reproducible as a result of the degradation of cellulose during hydrolysis (Cerqueira, Valente, Filho, & Burrows, 2009; Yang & Wang, 2003). Therefore, the need to explore greener methods for the preparation of acetone-soluble cellulose acetates is generally recognized. Furthermore, the avoidance of strongly acidic catalytic technologies and back-hydrolysis processes of completely acetylated cellulose is desired (Heinze & Liebert, 2001; Zugenmaier, 2004).

We have previously reported the acetylation of cellulose catalyzed by phosphotungstic acid ($H_3PW_{12}O_{40}{\cdot}6H_2O$), whereby partially substituted cellulose acetates having DS values ranging from 1.43 to 2.28 and good solubility in acetone were obtained (Fan et al., 2013b). However, a large amount of catalyst was required; moreover, the catalyst-to-cellulose molar ratio reached 20%, and the catalyst could not be recovered after the acetylation process. Thus far, solid sulfonic acid-based catalysts developed for the catalytic hydrolysis of cellulose include sulfonated activated carbon (AC-SO_3H) (Onda, Ochi, & Yanagisawa, 2008; Onda, Ochi, & Yanagisawa, 2009), amorphous carbon bearing SO_3H groups (Pang, Wang, Zheng, & Zhang, 2010, sulfonated CMK-3 catalyst (CMK-3-SO_3H) (Kitano et al., 2009; Pang et al., 2010; Suganuma et al., 2008), and sulfonated polymers (Fan, Liao, Fang, Wang, & Song, 2013a), most of which reveal excellent catalytic performance. Therefore, it is expected that sulfonated heterogeneous catalytic species may also exhibit excellent catalytic performances for the acetylation of cellulose.

Herein, with the aim of developing a new catalytic system for the direct production of cellulose diacetate, commercially available Amberlyst 15 containing the sulfonic acid group was employed as a recoverable catalyst for the acetylation of cellulose extracted from rice straw. Important factors affecting the catalytic performance of Amberlyst 15, including the amount of catalyst, acetic anhydride and acetic acid amounts, reaction solvent, and temperature were investigated. The recyclable performance of the sulfonated polymer catalyst was examined without further treatment after recovery.

2. Materials and methods

2.1. Materials

Amberlyst 15 was supplied by Aladdin Co. Ltd. (Shanghai, China). All other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Peking, China). They were of AR grade and used without further purification except acetic anhydride was redistilled prior to use.

2.2. Acetylation of cellulose

The extraction of cellulose from rice straw was reported in our previous work (Fan et al., 2013b). The acetylation of cellulose was carried out according to the method reported in the literature with a slight change (Biswas, Saha, Lawton, Shogren, & Willett, 2006). In a typical acetylation procedure, 2 g of cellulose (ca. 12.3 mmol anhydroglucose unit, AGU), 0.55 g of acetic acid, 5 g of acetic anhydride, 30 ml of dichloromethane (CH_2Cl_2), and 1.5 g of Amberlyst 15 were added to a 100 ml round-bottom flask. The mixture was brought to 45 °C for 10 h with vigorous stirring, and the reaction mixture was then cooled to room temperature and centrifuged. The clear solution in the upper layer was transferred into a flask, and the solvent was removed by rotary evaporation, yielding a membrane as crude product. The solid was then collected after addition of 60 ml deionized water to the membrane, followed by addition of 50 ml acetone to the residue before filtration. The filtrate was evaporated after stirring for 30 min, and the solid was dried overnight at 80 °C in a vacuum oven to give the desired product.

2.3. Recovery of Amberlyst 15

The residue at the bottom of the centrifuge tube was retrieved after separation of the reaction mixture, and the collected solid was dried at 80 °C under vacuum for 10 h. Amberlyst 15 was collected by passing through a Tyler screen with 80 mesh, and then washed with 3 × 10 ml portions of acetone and dried at 80 °C under vacuum.

2.4. Determination of DS value and yield of cellulose acetate

All of the acetylation reactions of cellulose presented in this work were performed in triplicate; both the DS values and yields of acetylated product are the averages of three runs. The DS values of the samples were determined by complete hydrolysis of the samples with sodium hydroxide (Meng & Li, 2004; Rodrigues Filho et al., 2008). The yield of cellulose acetate was calculated based on the complete replacement of hydroxyl groups by acetyl groups, and was calculated according to the following equation:

$$\text{Yield}\ \ (\%) = \frac{m_p}{m/162 \times 288} \times 100\% \qquad (1)$$

where m is the mass of cellulose added to the acetylated reaction; m_p is the mass of the acetylated product; 162 and 288 are the molecular weights (in g mol^{-1}) of AGU and cellulose triacetate, respectively.

2.5. Characterization

Fourier-transform infrared (FTIR) was carried out on an EQUINOX 55 spectrometer ranging from 4000 to 400 cm^{-1}. The solid samples were grounded with dried KBr powder, and compressed into a disc prior to analysis. Thermal analysis including thermogravimetry (TG) analysis and differential scanning calorimetry (DSC) was performed using a Perkin-Elmer TG-DSC 7 spectrometer under nitrogen at a heating rate of 10 °C min^{-1} in the range from room temperature to 800 °C. Approximately 10 mg of samples were used in each analysis and the gas flow rate was kept at 90 ml min^{-1}. The surface morphology of catalyst was obtained using Hitachi N–3000 scanning electron microscope (SEM).

3. Results and discussion

3.1. Characterization

3.1.1. FTIR

3.1.1.1. FTIR spectra of the fresh and recovered catalyst. FTIR spectra of the fresh and recovered Amberlyst 15 catalyst after the fourth run are given in Fig. 1. The wide peak at 3426 cm^{-1} in Fig. 1a is ascribed to the O—H stretching vibrations in the —SO_3H groups grafted to the poly(styrene-*co*-divinylbenzene) backbone as well as to the absorbed moisture (Gutch, Shrivastava, & Dubey, 2007). The weak peak at 2926 cm^{-1} is assigned to the asymmetric C—H stretching vibration in —CH_2— units (Tang, Huang, Ou, Chen, & Chen, 2011). The peaks in the ranges 1413–1641 and 672–906 cm^{-1} are characteristic of vibrations of the benzene ring skeleton and the out-of-plane bending vibrations of C—H groups in the substituted benzene styrene ring, respectively. The peaks at 1128 and 1038 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of —SO_3^- groups, respectively. The characteristic peaks resulting from the stretching vibrations of C—H in —CH_2— units, —SO_3^- groups, and aromatic moieties were still present in the spectrum of the recovered catalyst as shown in Fig. 1b; worthy of note is that no new peaks were observed. Thus, it is reasonable to

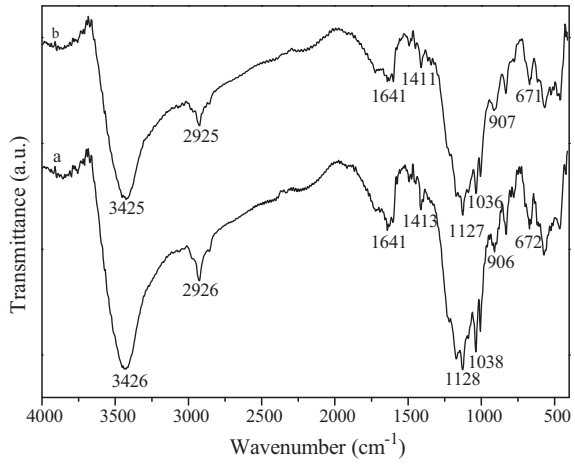

Fig. 1. FTIR spectra of Amberlyst 15 catalyst (a) fresh and (b) recovered catalyst after the fourth run.

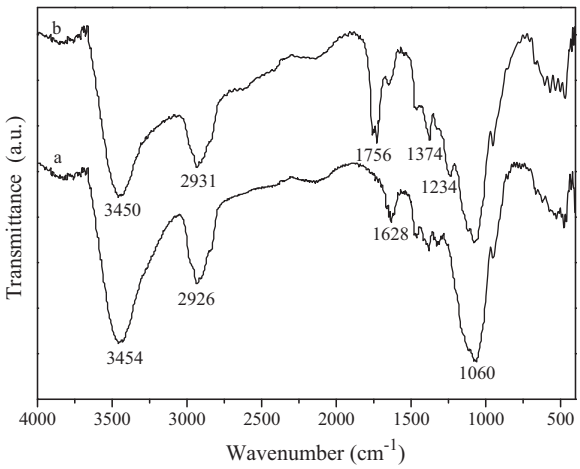

Fig. 2. FTIR spectra of (a) cellulose and (b) cellulose acetate.

conclude that almost no chemical change occurred to the Amberlyst 15 catalyst during the acetylation process.

3.1.1.2. FTIR spectra of cellulose and cellulose acetate. The FTIR spectra of cellulose and acetylated cellulose with a DS value of 2.38 are shown in Fig. 2. The dominant absorption peaks around 3454 and 2926 cm^{-1} in Fig. 2a of cellulose are attributed to the stretching vibrations of O—H group and C—H bonds in $—CH_2—$ units, respectively. New peaks presented in Fig. 2b at 1756, 1374, and 1234 cm^{-1} are correlated to the stretching vibrations of the C=O group, C—H bonds in the $—O(C=O)—CH_3$ group, and —CO— in the acetyl group, respectively (Cao et al., 2007), confirming that the hydroxyl groups were substituted for acetyl groups during the acetylation reaction.

3.1.2. Thermal analysis

3.1.2.1. Thermal analysis of the fresh and recovered catalyst. Fig. 3a–c shows the representative TG, DTG, and DSC curves, respectively, of the fresh and recycled catalyst after the fourth run. Fig. 3a indicates that the mass loss of the samples was composed of three steps; this was further verified by observation of three peaks in the DTG curves given in Fig. 3b. In the first step, the mass loss observed within 200 °C is associated with the removal of physically adsorbed molecular water (Gutch et al., 2007; He, Li, Hu, & Wen, 2008; Li, Cheng, & Yang, 2009). In the second step, the mass loss in the range of 200–400 °C may be attributed to the depolymerization of polystyrene chains (Ciopec et al., 2013) and the decomposition

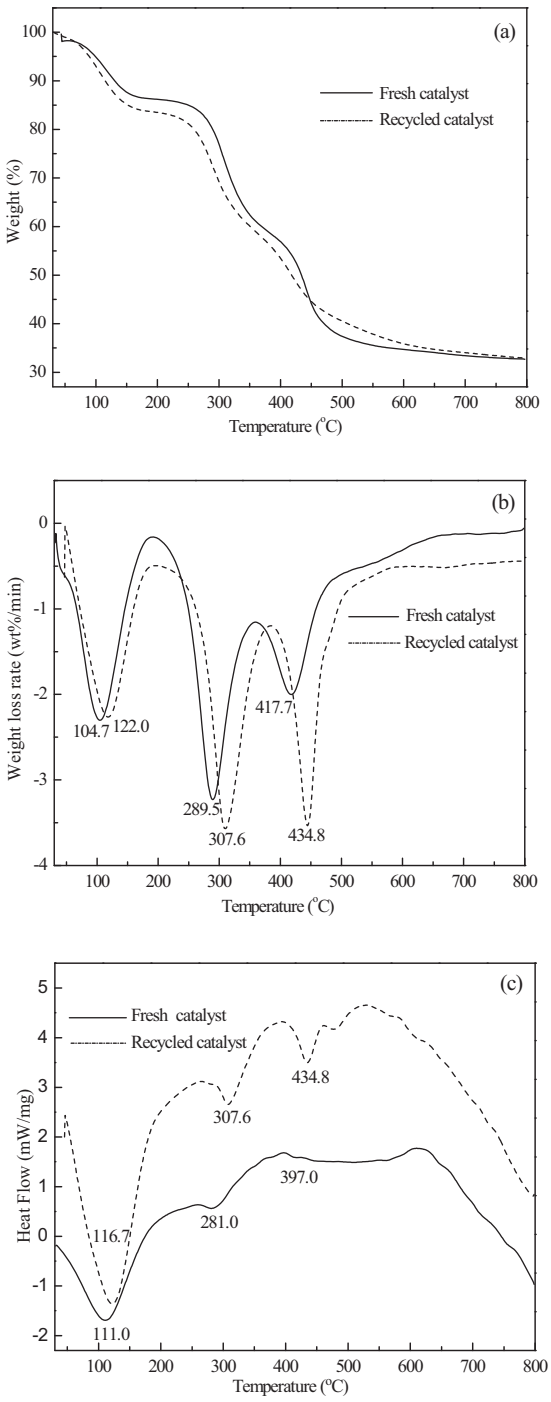

Fig. 3. TG, DTG and DSC curves of the fresh and recovered catalyst after the fourth run (a) TG, (b) DTG and (c) DSC curves.

of sulfonic acid groups. In the third step, the mass loss is mostly attributable to breakdown of the polymer backbone, while degradation of divinylbenzene takes place above 400 °C (Ciopec et al., 2013; de Santa Maria et al., 2008). The results in Fig. 3a indicate that the mass loss of the recycled catalyst was slightly less than that of the fresh catalyst. The total weight losses of the fresh and recycled catalysts were 66.74 and 60.91%, respectively; these losses are thought to result mainly from the physically adsorbed molecular water at around 110 °C (16.01% in the fresh catalyst and 11.11% in the recycled catalyst) as shown in Fig. 3a.

Three obvious endothermic peaks appeared around 111.0, 281.0 and 397.0 °C in the DSC plots of both fresh and recycled catalysts

presented in Fig. 3c, which are in accordance with the three steps of mass loss in the TG curves. However, the endothermic peaks of the recovered catalyst shifted to a slightly higher temperature compared to those of the fresh catalyst. This result may be due to a small amount of unreacted cellulose and acetylated product adhered on the surface of the recovered catalyst. This can be further illustrated by slight differences in the heat enthalpy of decomposition of these particles; 597.2 and 601.6 J g^{-1} for the fresh and recovered catalyst after the fourth run, respectively.

The plots in Fig. 3 clearly indicate that the thermal decomposition pathways of both the fresh and recycled catalyst are extremely similar, with the exception of slight differences in the mass losses and degradation temperatures, confirming that no obvious changes took place in the composition and thermal stability of the catalyst after the acetylation process.

3.1.2.2. Thermal analysis of cellulose and cellulose acetate. The thermal properties of cellulose and cellulose acetate with a DS value of 2.38 were next characterized using TG and DSC measurements, respectively, under a N_2 atmosphere, the results of which are shown in Fig. 4. It can be noticed from these plots that only one considerable weight loss event occurred between 300 and 400 °C in the TG curves of all samples. Correspondingly, the maximum decomposition temperatures of cellulose and cellulose acetate were observed at 346.8 and 360.8 °C, respectively (Fig. 4b). This phenomenon indicates that the thermal stabilities of the cellulosic materials are slightly affected by the acetylation. Total mass losses of 80.45% of cellulose and 86.15% of cellulose acetate with a DS value of 2.38 were also observed (Fig. 4a). This difference in the mass loss is possibly ascribed to the replacement of hydroxyl groups with acetyl groups (Shaikh, Pandare, Nair, & Varma, 2009).

The endothermic peak presented around 80 °C in the DSC plots (Fig. 4c) can be attributed to the evaporation of the adsorbed water; no other peak was observed in the DSC plot of cellulose likely due to the masking of a reversing event (such as glass transition) by its corresponding non-reversing event (such as enthalpic relaxation). A maximum endothermic peak located at 348.6 °C in the curve of cellulose acetate with a DS value of 2.38 was noted (Fig. 4b), which may be mainly related to degradation of the acetylated derivatives (Glasser, Samaranayake, Dumay, & Davé, 1995; Rodrigues Filho et al., 2008). The appearance of the peak at 348.6 °C reveals that the thermoplasticity of cellulose acetate is higher than that of cellulose.

3.1.3. SEM

The morphologies of the fresh and recovered catalysts after the first run were studied by SEM at various magnifications; the corresponding SEM photographs are presented in Fig. 5. It can be seen from the magnified images in Fig. 5a and b that the fresh catalyst exhibited a smooth surface; in contrast, many cracks were observed on the surface of the recovered catalyst at a low magnification. This can be ascribed to the poor mechanical strength of the commercial samples, which may not be sufficient to endure the violent stirring during the reaction. Fig. 5c and d reveal that the particles were agglomerated together at higher magnifications and that no other obvious change was observed after the reaction, indicating the micro-structure of the catalyst is not affected by the reaction. In addition, a small amount of white powder, likely composed of unreacted cellulose, could also be observed on the surface of the recovered catalyst, in accordance with the TG-DTG analysis given in Fig. 3.

3.2. Acetylation of cellulose

3.2.1. Investigation on the catalyst

We have investigated the catalytic activity of $H_3PW_{12}O_{40}{\cdot}6H_2O$ in our previous work (Fan et al., 2013b), in which acetone-soluble

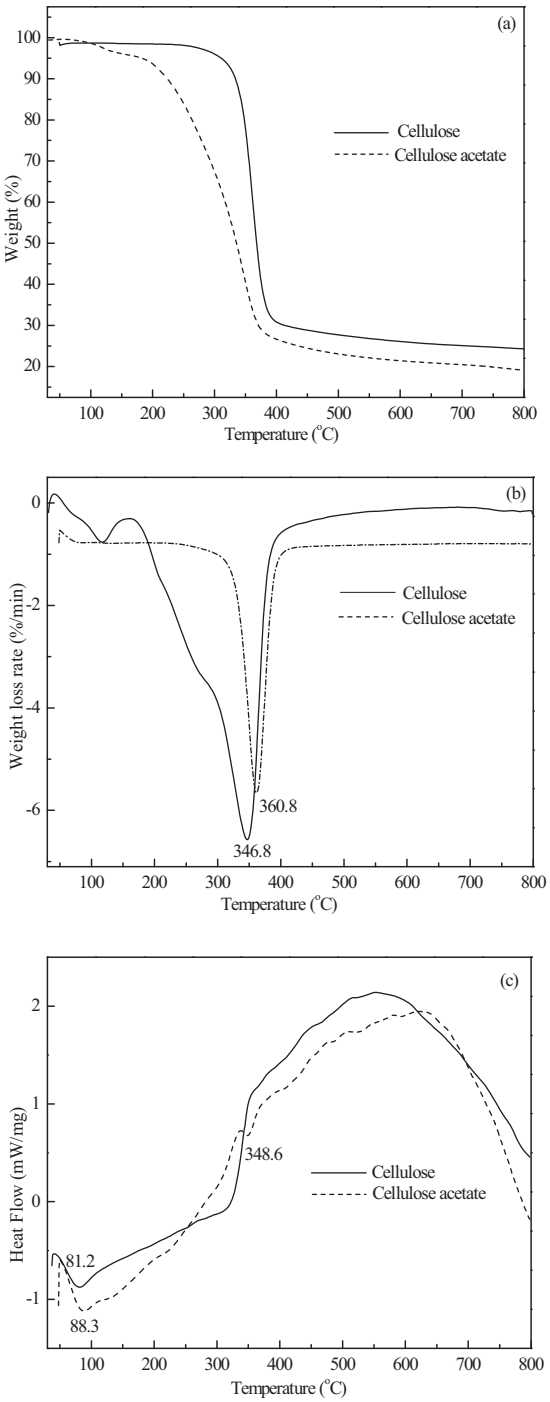

Fig. 4. TG, DTG and DSC curves of cellulose and cellulose acetate (a) TG, (b) DTG and (c) DSC curves.

cellulose acetate with a DS value around 2.2 was obtained. However, a large quantity of catalyst with respect to reagent mass was employed due to the high molecular weight of $H_3PW_{12}O_{40}{\cdot}6H_2O$. Accordingly, the catalytic performance of a smaller amount of $H_3PW_{12}O_{40}{\cdot}6H_2O$ was first investigated in this work (Table 1, entries 1–3). The results in Table 1 reveal that both the DS values and yields of cellulose ester dropped noticeably with a decreasing amount of $H_3PW_{12}O_{40}{\cdot}6H_2O$ (Table 1, entries 1–4).

The reaction was further carried out in the presence of Amberlyst 15 (Table 1, entries 5–9). Both DS values and yields of cellulose acetate were observed to increase in comparison to those obtained with an identical mass amount of $H_3PW_{12}O_{40}{\cdot}6H_2O$.

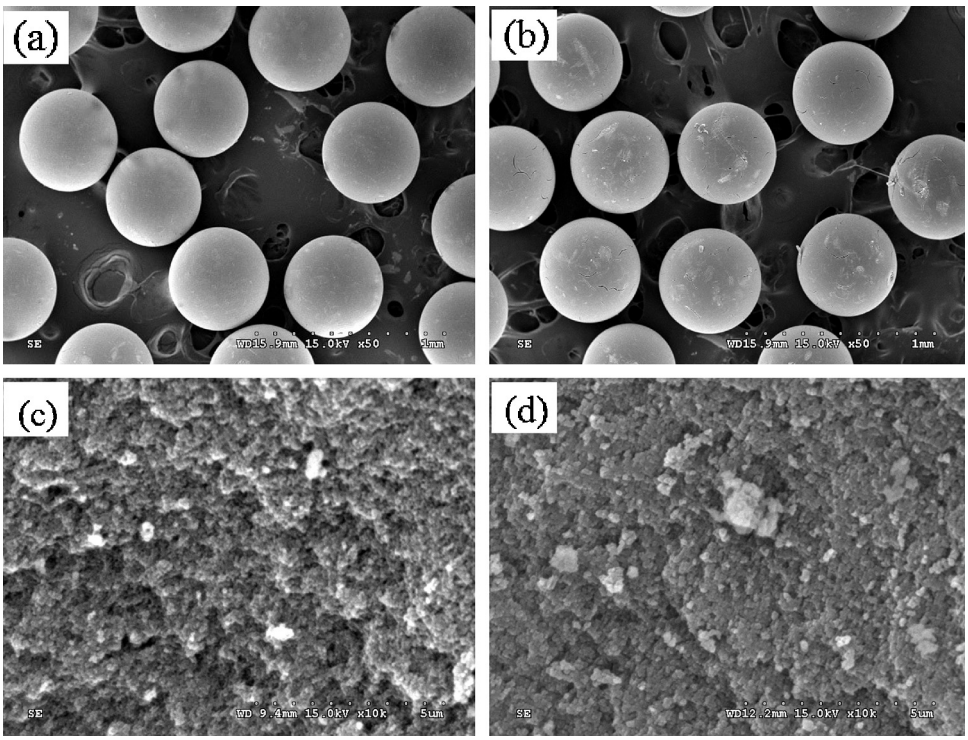

Fig. 5. SEM images of Amberlyst 15 catalyst (a) the fresh catalyst at 50 magnification; (b) the recovered catalyst after the first run at 50 magnification; (c) the fresh catalyst at 10,000 magnification and (d) the recovered catalyst after the first run at 10,000 magnification.

Furthermore, the DS values and yields of cellulose acetate were evidently dependent on the amount of catalyst, with maximum values achieved using 1.5 g catalyst; a DS value of 2.27 and yield of 43.9% was obtained under the conditions (Table 1, entry 7), and was observed to decrease with a further increase in the amount of catalyst. From these results, it is reasonable to speculate that not only the acetylation of cellulose but also the degradation of cellulose acetate are enhanced by the addition of a larger amount of catalyst. The decomposition of cellulose acetate possibly occurs by scission of glycosidic linkages followed by pyranose ring rupture and acetic acid evolution resulting from partial deacetylation (Lucena, V de Alencar, Mazzeto, & Soares, 2003; Puls, Wilson, & Hölter, 2011). In addition, the acetylation of cellulose is generally accompanied by the formation of a small quantity of unstable cellulose, leading to the degradation of macromolecular cellulose into smaller molecular glycolipids (Chen et al., 2010). Thus, a decrease in the DS value and the yield of cellulose acetate was correspondingly observed.

Table 1
Acetylation of cellulose with various amount of Amberlyst 15.

Entry	Catalyst (g)	DS	Yield (%)
1[a]	1.0	1.16	7.6
2[a]	1.5	1.43	9.5
3[a]	2.0	1.65	12.3
4[b]	6.0	2.22	20.6
5[c]	0.5	0.68	11.2
6[c]	1.0	1.78	36.4
7[c]	1.5	2.27	43.9
8[c]	2.0	1.44	38.2
9[c]	2.5	0.93	14.5

Reaction conditions: 2 g of cellulose (ca. 12.3 mmol AGU), AGU: acetic acid: acetic anhydride = 1:0.8:4 (molar ratio), refluxed in 50 ml CH_2Cl_2 for 10 h.

[a] $H_3PW_{12}O_{40}{\cdot}6H_2O$ was employed as the catalyst.
[b] Reported in the literature (Fan et al., 2013b).
[c] Amberlyst 15 was employed as the catalyst.

3.2.2. Optimization of reaction conditions

Experiments were conducted by varying reaction time, solvent, and the amount of added acetic anhydride and acetic acid to reveal the influence of reaction variables on the acetylation of cellulose, the results of which are shown in Table 2. The results in Table 2 indicate that the DS values and yields of cellulose acetate were dependent on the reaction time (Table 2, entries 1–6). The DS values increased when prolonging the reaction time, but were almost kept constant when the reaction time was elevated up to 8 h, revealing only a moderate enhancement for the substitution of —OH group. Correspondingly, an increase in the yield of cellulose acetate was also observed with increasing reaction time in the range from 4 to 10 h (Table 2, entries 1–5). The observed drop in yield with a further increase in the reaction time beyond 10 h (Table 2, entries 5 and 6) is possibly due to the increased likelihood for the degradation of cellulose (Fan et al., 2013b).

Regarding the solvent, it was found that both the DS values and cellulose acetate yields were maximal using CH_2Cl_2 as the solvent with other conditions remaining constant (Table 2, entry 4); similar results were observed using acetone (Table 2, entry 7). A lower DS value of 1.03 and yield of 24.5% was observed in $CHCl_3$ (Table 2, entry 8). Almost no acetylation product was obtained in refluxing *N*-dimethylformamide (DMF); this result can be ascribed to the degradation of cellulose at higher reaction temperatures, as the boiling point of DMF is much higher than that of CH_2Cl_2. It is well known that the solubility of cellulose acetate is dependent on the degree of hydroxyl group substitution. Solubility tests revealed that the samples with DS values around 2.0 listed in Table 2 exhibited good solubility in acetone and CH_2Cl_2, but not in $CHCl_3$ and DMF, which possibly resulted in the differences in the DS values and yields of cellulose acetate.

The influence of the amounts of added acetic acid and acetic anhydride on the acetylation of cellulose was further examined in more detail as shown in Table 2. The yield increased monotonously as the amounts of acetic anhydride were increased until reaching

Table 2
Effect of reaction conditions on the acetylation of cellulose.

Entry	Acetic acid/AGU (molar ratio)	Acetic anhydride/AGU (molar ratio)	Time (h)	Solvent	DS	Yield (%)
1	0.8	4	4	CH_2Cl_2	1.82	16.2
2	0.8	4	6	CH_2Cl_2	2.03	26.9
3	0.8	4	8	CH_2Cl_2	2.24	35.9
4	0.8	4	10	CH_2Cl_2	2.27	43.9
5	0.8	4	11	CH_2Cl_2	2.25	32.8
6	0.8	4	12	CH_2Cl_2	2.28	25.3
7	0.8	4	10	Acetone	2.05	42.1
8	0.8	4	10	$CHCl_3$	1.03	24.5
9	0.8	4	10	DMF	–	–
10	0.8	3	10	CH_2Cl_2	1.83	39.5
11	0.8	5	10	CH_2Cl_2	2.38	48.6
12	0.8	6	10	CH_2Cl_2	2.35	52.8
13	0.8	7	10	CH_2Cl_2	2.38	54.1
14	0.4	4	10	CH_2Cl_2	2.37	33.9
15	1.2	4	10	CH_2Cl_2	2.19	45.3
16	1.6	4	10	CH_2Cl_2	2.15	47.8
17	2.0	4	10	CH_2Cl_2	1.77	51.3
18	2.4	4	10	CH_2Cl_2	1.39	52.2

Reaction conditions: 2 g of cellulose (ca. 12.3 mmol AGU), 1.5 g of Amberlyst 15.

an acetic anhydride-to-cellulose molar ratio of 7 (Table 2, entries 4, 10–13). The DS value also increased with an increased amount of acetic anhydride, and was almost kept constant once the acetic anhydride-to-AGU molar ratio exceeded 5. The DS improvements observed with an increase in the amount of acetic anhydride is helpful to promote the equilibrium shift to the right (product) since the acetylation of cellulose is a reversible reaction, thus resulting in an increase in the DS value and yield of acetylation product. Theoretically, the completely acetylated product with a DS value of about 2.8 should be obtained if an excess of acetic anhydride is employed. However, the results in Table 2 revealed that the experimental DS values were much less than the theoretical DS value, even when an excessive amount of acetic anhydride was employed. This result can be ascribed to the loss of acetic anhydride in side reactions as well as the degradation of cellulose. Moreover, the accessibility of acetic anhydride to the polymeric hydroxyl groups may be affected by the aggregation among cellulose chains, which arises as a result of intermolecular bonding of cellulose (Ass, Frollini, & Heinze, 2004).

The results in Table 2 also show that the amount of acetic acid is an important factor for the acetylation of cellulose (Table 2, entries 4, 14–18). The yield increased as the amount of acetic acid was increased until reaching a molar ratio of acetic acid to AGU above 2.0, after which point it was kept nearly constant with further increases in acetic acid amounts (Table 2, entries 17 and 18). The existence of acetic acid causes changes in the microcrystalline structure of cellulose and plays an important role in the activation of cellulose acetylation, leading to the observed yield increases with an increase in the amount of acetic acid.

3.2.3. *Recycle performance of Amberlyst 15*

Amberlyst 15 was recovered after the reaction and reused without further treatment; the performances of the recycled catalyst are shown in Table 3. As can be seen, both the DS values and yields changed only minimally, indicating the Amberlyst 15 catalyst possesses a stable catalytic performance for the acetylation of cellulose. The results in Table 3 further confirm that no change occurred in the chemical structure and composition of the catalyst during the acetylation process, which is in accordance with the FTIR spectra and thermal analyses presented in Figs. 1 and 3, respectively. However, only about 35% of the catalyst based on the initial charged amount could be recovered after the fourth run. This reduction is attributed to catalyst fragmentation during the vigorous stirring due to its poor mechanical strength. This point could also be verified by the SEM image in Fig. 5b, in which clear cracks were observed in the recycled catalyst after the first run.

Table 3
Reused catalytic performance of Amberlyst 15.

Recycle	DS	Yield (%)
1	2.27	43.9
2	2.21	41.5
3	2.19	42.3
4	2.13	42.2

Reaction conditions: 2 g of cellulose (ca. 12.3 mmol AGU), AGU: acetic acid: acetic anhydride = 1:0.8:4 (molar ratio), 1.5 of Amberlyst 15, refluxed in 50 ml CH_2Cl_2 for 10 h.

4. Conclusions

The direct acetylation of cellulose to cellulose diacetate catalyzed by sulfonated polymer Amberlyst 15 was developed, and the products were characterized by FTIR, TG-DTG and DSC measurements. Amberlyst 15 was found to provide acceptable activity in view of the obtained DS values and yields of cellulose acetate. Both the DS values and yields were dependent on the amount of catalyst employed, added acetic anhydride and acetic acid, and reaction conditions including reaction time and reaction medium. Cellulose acetate with a DS value of 2.38 and yield of 54.1% was obtained under the optimized conditions. The sulfonated catalyst could be easily recovered by centrifugation after the acetylation reaction. Both the fresh and recovered catalysts were characterized using FTIR, TG-DTG, DSC, and SEM techniques, revealing no obvious changes in the chemical composition and structure of the catalyst during the acetylation process. The catalyst was reused without further treatment, and no significant difference in the DS values and yields was observed over four reaction recycles.

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