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1. Introduction

Nowadays, the efficient conversion of biomass and/or biomassderived feedstocks into high value chemicals or liquid fuels is of great interest due to concern over the depletion of fossil fuels and to leverage sustainable development.^{1–3} As one of the top twelve platform chemicals, sorbitol, which was easily obtained from glucose hydrogenation, has achieved increasing attention^{4,5} and has been transformed into liquid alkanes, polyols, and isosorbide.⁶ Moreover, isosorbide, a useful fine chemical synthesized from intramolecular dehydration of sorbitol, has been widely applied in various fields such as medicines and polymers.^{7,8} In particular, the addition of isosorbide comonomer might remarkably enhance the glass transition temperature of PET polymer for its high temperature application.^{9,10}

Hence, a great deal of effort has been devoted to investigate isosorbide production from sorbitol. In recent years, mineral acids such as H_3PO_4 , H_2SO_4 and HCl were first studied under homogeneous reaction conditions. Fleche *et al.* indicated that sorbitol was successfully dehydrated into isosorbide with 77% yield using H_2SO_4 as catalyst at 135 °C.¹¹ Although a high yield of isosorbide was achieved, these liquid acids possessed several drawbacks from the standpoint of environment, safety, corrosivity, separation and operating cost. Based on these



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The dehydration of sorbitol to isosorbide over an environmentally benign cellulose-derived solid acid catalyst (CCS) has been investigated in order to develop a sustainable process for isosorbide production. The as-prepared CCS sample contained large amounts of -COOH, phenolic hydroxyl and $-SO_3H$ groups and presented satisfactory catalytic activity, isosorbide selectivity and recyclability under water-free conditions. Various methods such as BET, XPS, TG, SEM, FT-IR and pyridine adsorption were conducted to characterize the CCS catalyst in order to elucidate the possible catalyst structure–performance relationship. The results of FT-IR and pyridine adsorption revealed that most of the acid sites contained in CCS catalyst were assigned as strong Brönsted sites, which were crucial for catalytic sorbitol dehydration into isosorbide. When further compared to the conventional solid acid catalyst (niobic acid), the investigated CCS catalyst in this study was considered as one of the promising alternatives to the highly efficient catalysts for isosorbide production from sorbitol.

considerations, heterogeneous solid acid catalysts have been regarded as potential alternatives for liquid acids.^{12,13} These types of catalysts could be easily separated and recovered after the reaction and be used repeatedly several times. Therefore, it was remarkably desirable to select solid acids as catalysts to heterogeneously catalyze the dehydration reaction of sorbitol to replace conventional mineral acids. To date, a great variety of solid acids such as metal(iv) phosphates, sulfated tin oxides, zeolites, sulfated titania, Amberlyst-15, superhydrophobic mesoporous acid and silicotungstic acid have been investigated as catalysts for isosorbide production from sorbitol sequential dehydration.7,8,14-17 Compared to the homogeneous mineral acid catalysts, heterogeneous solid acid catalysts contributed several advantages, such as safety in handling, easy separation from reaction system, good recyclability and less corrosion of the reactor.18,19 However, numerous developed solid acid catalysts still exhibited a lower activity, which then needs a higher temperature and longer reaction time to obtain a satisfactory isosorbide yield. Moreover, some catalysts such as zeolite and ion exchange resin presented less hydrothermal stability leading to structure distortion and leaching of acid sites with water and/or products.²⁰ Thus, it is still a great challenge and there remains a chance to develop an efficient, low cost solid acid catalyst with excellent recyclability for the dehydration of sorbitol at moderate conditions. More recently, a cellulose- and/ or glucose-derived carbonaceous solid acid catalyst, which was environmentally benign, of metal-free composition, cheaper and easy to separate, has generated great interest and been successfully applied on a relatively large scale.²¹⁻²⁹ Such a type of carbonaceous material could be readily synthesized by



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incomplete carbonization of renewable cellulose followed by sulfonation. It has been generally accepted that the obtained carbonaceous solid acid that contained flexible polycyclic nanosheets with numerous phenolic hydroxyl, -COOH and -SO₃H functional groups presented better catalytic behaviour than conventional solid acid catalysts in acid-catalyzed reactions such as hydrolysis and esterification.^{30,31} Furthermore, the acidity of the carbonaceous materials was estimated to be comparable with the acidity strength of concentrated H₂SO₄ because some -SO₃H groups were linked by strong H-bonds, resulting in strong acidity due to mutual electron-withdrawal.22 It has been reported that both sorbitol conversion and isosorbide selectivity were greatly affected by the types and/or concentrations of acid sites on the catalyst surface together with their acidic strength.7 Moreover, the synthesis of carbonaceous-based solid acids with tunable acid sites is still in its infancy and has not been investigated in depth.³²⁻³⁵

Inspired by recent research work, a carbon-based solid acid catalyst with cellulose as a precursor was synthesized by a hydrothermal method and selected as an environmentally friendly and recyclable catalyst in sorbitol dehydration into isosorbide under solvent-free experimental conditions. Characterizations such as BET, XPS, TG, SEM, FT-IR and pyridine adsorption were further conducted to construct a relationship between the catalyst structural properties and its catalytic performance. The as-prepared solid acid exhibited promising properties with high isosorbide selectivity and stability. This study might shed light on the development of more efficient solid acid catalysts for the production of high value chemicals from biomass and/or biomass-derived feedstocks.

2. Experimental

2.1 Chemicals and reagents

Both microcrystalline cellulose and commercial niobic acid were purchased from Shanghai Aladdin Industrial Co. Ltd. All other chemicals were supplied by Tianjin Kermel Chemical Reagent Co. Ltd. and used without further purification.

2.2 Catalyst preparation

The cellulose-derived carbonaceous solid acid catalyst was synthesized by hydrothermal carbonization and sulfonation of microcrystalline cellulose. Typically, 3.0 g microcrystalline cellulose (50 µm) was first added into 60 mL deionized water under magnetic stirring. The resulting liquid mixture was then transferred to a Teflon-lined stainless steel autoclave (100 mL), heated to 230 °C and kept at this temperature for 2 h at autogenous pressure. After quickly cooling the autoclave to room temperature, the collected precipitate was repeatedly washed with hot water and dried overnight at 90 °C. The obtained black solid was then dispersed in 150 mL of concentrated sulfuric acid (>96%), heated to 150 °C and maintained at this temperature for 6 h with a continuous N₂ flow (30 mL min⁻¹) to introduce $-SO_3H$ functional groups. After quenching to room temperature, 1000 mL deionized water was slowly added into the liquid mixture and filtration

was performed. Finally, the filtered black precipitate was thoroughly washed with hot deionized water until no sulfate ions were detected in the effluent. The resulting material was dried in a vacuum oven at 60 °C for 12 h. The as-prepared cellulose-derived solid acid catalyst is denoted as CCS in the following discussion.

2.3 Catalyst characterization

The specific surface area of the catalyst was measured by the BET (Brunauer–Emmett–Teller) method. The measurement was conducted on an ASAP 2010 Micromeritics apparatus and consisted of nitrogen adsorption at -193 °C. Prior to measurement, the sample was first outgassed at 300 °C for 3 h under N₂ flow (50 mL min⁻¹).

Raman spectra were obtained using a Jobin-Yvon T64000 spectrometer with an Ar ion laser as the illumination source (532.08 nm) and a CCD detector cooled at -196 °C. The Raman spectra of the catalysts were recorded with the laser power below 0.7 mV in order to avoid laser heating influences.

The surface morphology and elemental mapping of the investigated catalyst were studied by scanning electron microscopy (SEM) on a JEOL JSM-6460LV equipped with energy-dispersive X-ray detection. The operational acceleration voltage was 15 kV. The sample was sputter coated with gold for 1 min before SEM characterization.

Thermogravimetric analysis (TGA) measurements were conducted on a TDA Q50 instrument in a N₂ flow (50 mL min⁻¹). The catalyst (10 mg) was placed in a quartz crucible and the temperature was increased from room temperature to 600 °C at a heating rate of 10 °C min⁻¹.

X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250 spectrometer equipped with an Mg-K_{α} X-ray source operating at 100 W. The charging effect was corrected by referencing the binding energy of C1s at 284.8 eV.

The functional groups over the surface of the CCS catalyst were detected by FT-IR spectra using the standard KBr disc method in the range from 400 to 4000 cm⁻¹ at 4 cm⁻¹ resolution on a Digilab FTS 3100 FTIR spectrometer. A mixture of catalyst and KBr (catalyst/KBr = 1/100, mass ratio) was pressed into self-supporting wafers (15 mm) for measurement.

The types of acid sites dispersed on the catalyst surface were further investigated by pyridine adsorption. Prior to the measurement, the catalyst (20 mg) was pressed into selfsupporting wafers (15 mm) and outgassed at 300 °C for 1 h under vacuum in order to remove the adsorbed impurities over the catalyst surface. After quenching to room temperature, the spectra were acquired as the background reference. Subsequently, pyridine vapor was introduced into the cell for 0.5 h followed by further evacuation for 0.5 h so as to remove the physically adsorbed pyridine. The catalyst was heated to 150 °C for 10 min and then another spectrum was acquired. The presented spectra were achieved by subtracting the spectra before and after pyridine adsorption. The ratio of the concentration of Brönsted acid sites to Lewis acid sites was calculated based on the ratio of the peak areas centered at *ca.* 1540 cm^{-1} and 1450 cm⁻¹, respectively, as reported in the literature.^{36,37}

The acidity of the CCS catalyst was studied by the NH_3 -TPD technique. Prior to NH_3 adsorption, the sample was also outgassed at 300 °C for 1 h in order to remove the impurities over the catalyst surface. After cooling down to 100 °C, NH_3 adsorption was carried out under a flow of NH_3/He (10 vol%, 50 mL min⁻¹) and maintained for 30 min. The flow was then switched to He (50 mL min⁻¹) so as to remove the physically adsorbed NH_3 . NH_3 -TPD was conducted in the He flow (50 mL min⁻¹) by increasing the temperature to 850 °C with a heating rate of 5 °C min⁻¹ when the desorbed NH_3 molecules were detected using online mass spectrometry (Inficon quadrupole). The quantities of desorbed NH_3 at different temperatures were calculated according to the relative areas of the deconvolution peaks from the spectra of desorbed NH_3 , as follows:

$$D = D_{\text{Total}} \times (A/A_{\text{Total}}) \times 100\%$$
(1)

where $D_{\text{Total}} \pmod{\text{g}^{-1}}$ is the total amount of desorbed NH₃; *A* is the area of a deconvolution peak and A_{Total} is the total areas of all the deconvolution peaks of the desorbed NH₃.

The content of $-SO_3H$ groups was also determined by acidbase titration following the procedures in previous reports.^{25,38} Typically, the catalyst (0.2 g) was added to an aqueous solution of NaCl (0.1 mol L⁻¹, 20 mL). The mixture was sonicated for 60 min and then magnetically stirred for 24 h at room temperature. After centrifugal separation, the obtained filtrate (5 mL) was titrated with aqueous NaOH (0.05 mol L⁻¹) with phenolphthalein as the indicator. The titration procedure was repeated three times and the average value was reported.

To identify whether sulfonate groups were successfully grafted onto the prepared carbonaceous solid acid catalyst, the sulfur content together with C and H concentration was determined by elemental analysis operated on an EURO EA 300 series elemental analyzer with flush combustion at 950 °C (O₂ flow of 20 mL min⁻¹). The catalyst (1.0 mg) was first placed in a tin can and automatically injected into the instrument. L-Cystine (C₆H₁₂N₂S₂O₄) was selected as the standard substance. The amount of $-SO_3H$ groups was estimated based on the S content.

2.4 Experimental procedure

The catalytic dehydration of sorbitol was conducted in a stainless steel batch reactor (60 mL). Briefly, a mixture of 1.0 g sorbitol and 0.1 g powdered catalyst was poured into the reactor and purged with N2 for several times. Subsequently, the reactor was heated to the investigated temperature under magnetic stirring at 800 rpm. The reaction time was calculated when the reactor temperature reached the target one. After the reaction, the reactor was quickly cooled to room temperature in an icewater bath and an appreciable amount of water was added. The resulting mixture was filtered in order to separate the catalyst. Then, the obtained liquid solution was analyzed by HPLC (Wates e2695) equipped with UV and refractive index (RI) detectors and a Shodex SUGAR SC1011 column (8 \times 300 mm). The column was operated at 70 °C by a column heater and the operating temperature of detectors was 35 °C. Distilled water was used as the mobile phase at a flow rate of 0.6 mL min⁻¹. The injection volume was 10 µL of filtered (25 µm), undiluted sample. Sorbitol conversion and isosorbide selectivity were calculated as follows:

$$C_{\text{sorbitol}}\% = (\text{moles of reacted sorbitol/moles of initial sorbitol}) \times 100\%$$
 (2)

$$S_{\text{isosorbide}}\% = (\text{moles of carbon in the produced isosorbide/}$$

moles of carbon in the reacted sorbitol) $\times 100\%$
(3)

2.5 Procedure for recycling the catalyst

The recyclability of the CCS catalyst was investigated for the dehydration of sorbitol to estimate the catalyst stability. The reactions were repeatedly conducted under identical experimental conditions as mentioned above. After each run, the aged catalyst was filtered and thoroughly washed with hot deionized water and dried at 90 °C overnight for the next reaction.

3. Results and discussion

The physical and chemical properties of the as-prepared CCS catalyst were investigated by a series of characterization methods. The surface area and pore volume were 4.11 $m^2 g^{-1}$ and 0.055 cm³ g⁻¹, respectively, calculated from BET measurement. A slight decrease was observed when compared to the values of untreated microcrystalline cellulose (6.93 m^2 g^{-1} , $0.072 \text{ cm}^3 \text{g}^{-1}$). The decrease of pore diameter might be because of the existence of a large amount of surface functional groups over the catalyst surface after the hydrothermal and sulfonation processes.31 The hydrothermal carbonization process accelerated the cellulose structure to undergo dehydration, decomposition, hydrolysis and a rearrangement reaction to form a polycyclic aromatic structure embedded with active -COOH and -OH groups, which supplied sufficient active sites for sulfonation. Hence, the following sulfonation treatment resulted in the incorporation of -SO₃H sites into the carbonaceous material. These surface sites could occupy the pores leading to the decline of surface area and pore volume.



Fig. 1 Raman spectrum of the CCS catalyst.

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Fig. 1 shows the Raman spectra of the CCS catalyst. It was clearly observed that a distinct pair of characteristic peaks centred at ca. 1347 (D band) 1596 cm⁻¹ (G band) was observed. Normally, the D band is assigned to amorphous structured carbon because of carbon sheet stacking or incomplete carbonized catalyst structure,39 whereas the G band is attributed to the sp² C-C stretching vibration (E_{2g} mode) of well-structured carbon.⁴⁰⁻⁴² The intensity ratio of the peaks (I_D/I_G) might be associated with the degree of crystallinity of the carbonaceousbased solid acid.43 Notably, the larger intensity of the D band revealed that the as-prepared material possessed more amorphous structure, which was favourable for the grafting of sulfonic acid groups to achieve a large concentration of -SO₃H groups on the catalyst surface.⁴⁴ Furthermore, the large $I_{\rm D}/I_{\rm G}$ value of CCS catalyst might be attributed to the decline of the average size of sp² carbon caused by the addition of -SO₃H groups.⁴⁵ The abovementioned results indirectly supported the successful grafting of -SO3 groups after sulfonation treatment of incompletely carbonized cellulose.

Elemental analysis also revealed that the composition of the CCS catalyst was CH_{0.709}O_{0.404}S_{0.0455}, suggesting the successful incorporation of S into the carbonaceous material derived from the incomplete hydrothermal carbonization of microcrystalline cellulose. As compared to the untreated microcrystalline cellulose (CH_{1.704}O_{0.821}), the decline of H and O contents might be due to the combined results of dehydration and carbonization. In the XPS spectrum of the CCS catalyst (Fig. 2), a single S 2p peak was observed at around 168 eV suggesting that all S atoms of the CCS sample were presented in the form of -SO₃H groups, which was in agreement with previous reports.46 This revealed that sulfonation of incompletely carbonized carbon successively occurred in concentrated sulfuric acid to form sulfonic acid groups. Thus, the probable density of -SO₃H groups in the cellulose-derived catalyst could be calculated based on the S content in the catalyst composition. The value was ca. 2.2 mmol g^{-1} , which led to strong acidity in the CCS catalyst. The acid density was also comparable with the previous work.47 This might be a positive factor for the dehydration of sorbitol. The density of the -SO₃H acid sites estimated by the titration



Fig. 2 XPS spectrum of the CCS catalyst.

method was around 2.05 mmol g^{-1} , which was in good agreement with the result of elemental analysis. The slight deviation (6.8%) indicated that a small amount of the –SO₃H sites might be located within the catalyst matrix.

The morphologies of the untreated microcrystalline cellulose and CCS catalyst were also characterized by the SEM technique. As shown in Fig. 3, fresh microcrystalline cellulose was fibrous with fibre diameters of around 25 μ m and its surface was smooth. After hydrothermal treatment at 230 °C, the carbonaceous material exhibited a relatively rough surface and a looser structure with more nanopores because of the swelling influence of water.⁴⁸ Interestingly, the fibrous structure



Fig. 3 SEM images of (A) microcrystalline cellulose, (B) cellulose after hydrothermal treatment, (C and E) CCS catalyst and (D) mixed, (F) S, (G) C, (H) O elemental mappings of CCS catalyst.

of cellulose was disrupted and many carbon spheres with diameters in the range of 100–200 nm appeared, indicating the incomplete carbonization of cellulose in the hydrothermal conditions. With the further influence of sulfonation, a significant morphological change of carbonaceous material was observed. The catalyst surface became more rough and the average diameter of carbon spheres decreased to 20–40 nm. Fig. 3 also shows the elemental mappings of the whole region (Fig. 3E) for the various elements, which were investigated: C, O and S. It could be clearly seen that S was uniformly dispersed on the surface of the CCS catalyst meaning highly dispersed –SO₃H groups, which was favourable for the interaction of reactant and acid sites.

In order to identify the functional groups bonded to the surface of the investigated solid acid catalyst, FT-IR characterization was conducted and the result is presented in Fig. 4. The presence of -SO₃H groups in the CCS catalyst was directly evidenced by the FT-IR result. The vibration bands observed at ca. 1049 and 1164 cm⁻¹ were assigned to SO³⁻ stretching vibrations and O=S=O stretching vibrations in -SO₃H groups, respectively, suggesting that the resulting carbonaceous material contained the -SO₃H groups in good agreement with the result of the abovementioned element analysis.21 Moreover, the peaks centered at *ca.* 1632 and 1709 cm^{-1} were attributed to the C=C and COO- stretching vibrations, respectively, suggesting the existence of polycyclic aromatic rings, which were formed from the incomplete carbonization of the microcrystalline cellulose substance.49,50 The adsorption peaks in the range of 1400–1600 cm⁻¹ were assigned to the stretching vibration of the imidazole ring embedded in the polymer matrix. On the other hand, another clear band at 3431 cm⁻¹ corresponded to the -OH stretching vibration in phenolic hydroxyl (-OH) and -COOH groups formed during the process of carbonization and sulfonation.⁵¹ A broad band at 2200–2520 cm⁻¹ (shown in the inset in Fig. 4) could be attributed to an overlap of the bending mode (Fermi resonance) of -OH-O= connected via a strong H bond, as shown in the strong liquid Brönsted acid CF₃SO₃H, indicating that a number of the -SO₃H groups were in close proximity to each other.52 All the abovementioned results elucidated

that the as-prepared CCS catalyst contained a large amount of various surface functional groups such as -OH, -COOH and $-SO_3H$ groups, which is different from conventional solid acids with single functional groups.

TG analysis was selected to determine the thermal stability of the investigated CCS catalyst. As shown in Fig. 5, the asprepared material was thermally stable below 270 °C with only a slight weight loss (*ca.* 4.3%). This loss was probably due to the evaporation of adsorbed water from the catalyst surface. Furthermore, a large weight loss occurred in the higher temperature region ranging from 270 °C to 350 °C, assigned to the thermal decomposition of the surface functional groups and the destruction of the carbonaceous material's structure.⁵³ Hence, it could be elucidated that the CCS catalyst exhibited the satisfactory thermal stability and might be used below 270 °C. In this study, experimental conditions for the catalytic dehydration of sorbitol were operated below 220 °C. Thus, the asprepared carbon material was suitable for this reaction.

To further elucidate the acid types on the CCS catalyst and the ratio of strong Brönsted and Lewis acid sites, pyridine adsorption was carried out and the collected spectra are presented in Fig. 6. The result clearly depicts the co-existence of Brönsted and Lewis acid sites in the CCS catalyst. Briefly, an intense peak at ca. 1541 cm⁻¹ due to the N-H bending of the pyridinium ion was the characteristic adsorption peak of pyridine on Brönsted acid sites. Another comparatively less intense band at *ca.* 1450 cm⁻¹ was assigned to pyridine adsorption on Lewis acid sites. A sharp peak located at *ca.* 1490 cm^{-1} was attributed to the combined adsorption of a pyridine molecule on Brönsted and Lewis acid sites.54 The commercially available niobic acid, a typical industrial inorganic solid Brönsted acid, was also investigated for comparison purposes. The DRIFT spectra of the commercial niobic acid exhibited almost identical peaks except that the intensities of the bands of the CCS catalyst were much larger than the values of the commercial niobic acid, i.e., the amount of the acid sites in CCS catalyst was considerable higher than those in niobic acid. In addition, the ratio of Brönsted acid sites to Lewis acid ones calculated based on the peak areas centred at *ca*. 1541 cm^{-1} and *ca*. 1450 cm^{-1} , respectively, resulted in the following order: CCS (7.8) >



Fig. 4 FT-IR spectrum of the CCS sample.



Fig. 5 TG curve of the CCS catalyst.



Fig. 6 Py-FT-IR spectra of the CCS catalyst and commercial niobic acid.

commercial niobic acid (1.4). Hence, the abovementioned FT-IR data revealed that most of the acid sites (~84%) in the CCS sample belonged to strong Brönsted acid sites, which was a positive factor for the dehydration reaction. Upon further heating to 450 °C, the band at *ca.* 1540 cm⁻¹ was still clearly observed for the CCS catalyst, indicating its strong acidity. Based on the previous literature,⁷ both sorbitol conversion and isosorbide yield were greatly affected by the quantity of Brönsted acid sites. Therefore, the catalyst with higher amount of Brönsted acid sites might give rise to better catalytic performance in mild experimental conditions.

NH₃-TPD characterization was also conducted to assess the total acidity of the CCS catalyst. In general, the various NH₃-desorption temperatures elucidate the different strengths of the acid sites. Normally, the higher NH₃-desorption temperature corresponds to the stronger acidity. The acid sites might be denoted as weak, medium strong and very strong sites at NH₃-desorption temperatures of 150–300 °C, 300–400 °C and above 400 °C, respectively, and the amount of acid sites was associated with the peak areas of the NH₃-TPD curves.^{55,56}



Fig. 7 NH₃-TPD profile of the CCS catalyst.

As shown in Fig. 7, the NH₃-desorption profile of the CCS catalyst started from ca. 150 °C and then rapidly increased to maximum peak (ca. 210 °C) together with another big hump at around 350 °C. Then, it progressively declined until 800 °C. The peak in the NH₃-TPD profile might be resolved into several deconvolution peaks, indicating the existence of acid sites with various strengths. Notably, the peak at ca. 201 °C was associated with the hydrogen-bound ammonia (weak); moreover, the partial contribution of physically adsorbed NH₃ could not be ruled out. Another two peaks (ca. 340 and 478 °C) corresponded to the medium strong and very strong acid sites,⁵⁶ respectively. The presented very strong acid sites were attributed to the -SO₃H groups, whereas the weak acid sites were assigned to the -OH groups on the catalyst surface. The quantity of desorbed ammonia at distinct temperatures was calculated according to the areas of the deconvolution peaks (eqn (1)) and resulted in the following order: weak sites (0.8 mmol g^{-1}) < medium strong sites (1.8 mmol g^{-1}) < very strong sites (1.5 mmol g^{-1}). The total concentration of strong sites was ca. 80%, highly in line with the previous result of pyridine adsorption, revealing that most of the acid sites on the surface of the CCS catalyst belonged to strong acid sites.

Considering the results of the previous reports,57-59 the possible reaction mechanism of sorbitol dehydration into isosorbide mainly consists of two sequential steps: sorbitol was first dehydrated to form monocyclic sorbitans such as 1,4sorbitan, 2,5-sorbitan and 1,5-sorbitan; then, isosorbide was produced from another dehydration reaction occurring on 1,4sorbitan instead of other sorbitans. The effect of reaction parameters on isosorbide yield, including catalyst dosage and reaction temperature, was investigated to assess the catalytic performance of the CCS catalyst. First, a blank test was carried out to elucidate the catalyst role in isosorbide production from sorbitol. In the absence of catalyst, only a slight sorbitol conversion (\sim 7%) without any detectable isosorbide was observed at 160 °C. In contrast, with the addition of CCS catalyst, both sorbitol conversion and isosorbide selectivity remarkably increased to ca. 63% and 35%, respectively, at 160 °C. The main observed products were isosorbide, 1,4-sorbitan together with trace amount of 1,5-sorbitan by-product. Other non-identified compounds are denoted here as 'unknown'. As shown in Fig. 8, 100% sorbitol conversion was achieved when the reaction temperature was above 190 °C. As to the isosorbide selectivity, it was still affected by further increasing the reaction temperature. Isosorbide selectivity steadily increased from 160 °C to 200 °C and then slightly decreased at 220 °C. The maximum value of isosorbide selectivity (67%) was obtained at 200 °C. In addition, the gradual decrease of sorbitan selectivity upon heating elucidated the occurrence of the consecutive dehydration of sorbitol to isosorbide, suggesting that sorbitan acted as an intermediate, which was in good agreement with the previous result.⁵⁷ At 220 °C, the unknown humin by-products, which might be formed from oligomerization and/or self-polymerization of isosorbide or crosspolymerization between sorbitan and isosorbide,57 were observed to increase leading to the decrease of isosorbide selectivity.



Fig. 8 Effect of reaction temperature on sorbitol conversion and isosorbide selectivity using CCS catalyst (sorbitol: 1 g; catalyst: 0.1 g; reaction time: 1 h).

Catalyst dosage greatly controlled the reaction kinetics and it was necessary to optimize this factor in order to achieve the satisfied selectivity to the targeted product.⁶⁰ The effect of catalyst amount on the dehydration of sorbitol was investigated (Fig. 9). When the weight ratio of CCS catalyst to sorbitol was 0.04, both 85% sorbitol conversion and 46% isosorbide selectivity could be obtained at 200 °C after 1 h reaction. Then the isosorbide yield progressively increased upon increasing the ratio from 0.04 to 0.12 that a high value of 68% could be achieved for 1 h. With adding more catalyst, increase of isosorbide yield was limited. In contrast, a slight decline of isosorbide selectivity was observed, which might be due to the excess acid sites resulting in the formation of humins by-product.

A commercial solid acid (niobic acid) was also investigated for comparison purpose. From the results presented in Fig. 10, it could be clearly observed that the niobic acid sample only exhibited 81% sorbitol conversion with much less isosorbide selectivity (\sim 43%) at 200 °C. However, the formation of sorbitan by-product was much higher compared to the value for the CCS catalyst, which was in accordance with the previous reports that the catalyst with weak acidity produced a high concentration of sorbitan.⁷ It is also worth mentioning that beyond the amount of acid sites, catalytic performance was also greatly affected by the types of acid sites. The catalyst with a high quantity of



Fig. 10 Comparison of catalytic performance of CCS and commercial niobic acid in dehydration of sorbitol (blank: CCS; full: niobic acid. Sorbitol: 1 g; catalyst: 0.1 g; reaction temperature: 200 °C; reaction time: 1 h).

Brönsted acid sites was more efficient for sorbitol dehydration to isosorbide. As discussed in the results of pyridine adsorption, the amount of Brönsted acid sites contained in the CCS catalyst was almost eight times higher than the value of niobic acid. All the above results clearly point out that the investigated CCS catalyst could efficiently catalyze sorbitol dehydration.

The catalyst recyclability is regarded as one of the important factors of an efficient solid acid catalyst to reduce the operational cost. In the case of carbonaceous solid acid catalysts with $-SO_3H$ groups, the catalyst deactivation was mainly caused by the leaching of sulfur species during the reaction process. Hence, the stability of the CCS catalyst for the dehydration of sorbitol has also been tested with several runs at 200 °C. As shown in Fig. 11, isosorbide yield was observed to be almost similar after being repeatedly used for four times. Therefore, it could be concluded that the CCS catalyst was easily reused without any remarkable loss of performance. Elemental analysis of the product aqueous solution revealed that no remarkable leaching of S occurred during the recycle test. The elemental analysis result of the aged catalyst suggested similar amounts of $-SO_3H$ groups for the fresh and used catalysts (2.2



Fig. 9 Effect of catalyst dosage (reaction temperature: 200 °C, reaction time: 1 h).



Fig. 11 Recycle usage of the CCS catalyst. Sorbitol: 1 g; catalyst: 0.1 g; reaction temperature: 200 °C; reaction time: 1 h.





Fig. 12 FT-IR spectrum of the aged CCS catalyst.

mmol g^{-1} and 2.15 mmol g^{-1} , respectively). In addition, as presented in the FT-IR spectrum of the aged catalyst (Fig. 12), the characteristic peaks assigned to -SO₃H groups remained unchanged after four consecutive cycles. The difference compared to the fresh one was the decrease of the peak attributed to the -OH groups (weak acid sites). This might have no detrimental influence on the catalyst behaviour. In summary, it indicated that no dissociation and/or disruption of sulfuric groups occurred. It was noted that the electron-withdrawing -COOH groups incorporated in the carbon material could enhance the electron density between the C and S atoms while enhancing the catalyst stability even under the harsh reaction conditions.²² Thus, it could be concluded that this cellulosederived solid acid catalyst could be repeatedly used without significant loss in catalytic performance. This might be helpful to the R&D of highly efficient catalysts for isosorbide production.

4. Conclusions

The catalytic dehydration of sorbitol into isosorbide has been thoroughly investigated under water-free conditions over a cellulose-derived solid acid catalyst. Based on the characterization result, most of the acid sites contained in the prepared catalyst were strong Brönsted acid sites that were much more than the value for the conventional solid acid (niobic acid). A satisfactory sorbitol conversion and isosorbide selectivity could be achieved as high as 100% and 67%, respectively, at 200 °C for 1 h. Moreover, the catalyst was easily synthesized and could be repeatedly used without any significant loss in catalytic performance. In general, the investigated carbonaceous material is promising for replacing mineral acids for efficient production of isosorbide from sorbitol. In addition, the further development of a highly active catalyst might shed light on environmentally friendly chemical production, including biomass and/or biomass-derived feedstocks conversion.

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