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Preparation of a novel carbon-based solid acid from cocarbonized starch and polyvinyl chloride for cellulose hydrolysis

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ABSTRACT

A novel carbon-based solid acid was successfully prepared by sulfonation of cocarbonized starch and polyvinyl chloride (PVC). The characterization results show that this catalyst possesses all characteristics of traditional carbon-based solid acids (CSAs). The differences are that chlorine from PVC is covalently bonded to edges of aromatic carbon sheets as new active groups, and ether (C–O–C) and aliphatic ($-CH_2-$) bridges are formed during the cocarbonization process which are derived from oxygen in starch and alkyl in PVC, respectively. Chlorine groups can adsorb cellulose hydroxyl groups strongly and bridge bonds make the carbon framework fully stretch, which reduces hindrance between SO_3H groups and glycosidic bonds to promote the catalytic performance in cellulose hydrolysis experiments. Furthermore, the durability results indicate that this catalyst has good stability.

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1. Introduction

Carbon-based solid acids (CSAs), the amorphous carbons consisting of aromatic carbon sheets bearing active sites such as SO_3H, OH, and COOH groups [1–4], have attracted a great deal of attention due to their favorable characteristics such as high acid densities, stability and recyclability [3,5], which are widely used in biodiesel synthesis and cellulose hydrolysis. However, compared with the esterification for biodiesel production, the efficiency of cellulose hydrolysis is unsatisfactory mainly because the interaction between CSA and cellulose is not strong enough. Although phenolic OH groups bonded to CSA have the ability to adsorb cellulose [6,7] and rich-phenolic hydroxyl CSA derived from phenolic residue has improved this ability [8], the adsorption effect is not efficient for breaking the hydrogen bonds in cellulose. Therefore, it is imperative to introduce the high affinity group for cellulose onto CSA in order to enhance the interaction between cellulose and catalyst.

Although many efforts have been devoted to the depolymerization of cellulose [2,7,9–11], little attention has been paid to strengthen the interaction between catalyst and cellulose. Recently, Li and Pan [12] synthesized a sulfonated chloromethyl polystyrene resin, containing cellulose binding sites (–Cl) and catalytic sites ($-SO_3H$), to design to hydrolyze microcrystalline cellulose into glucose, and the degradation of this catalyst was observed in experiment of Yabushita et al. [13]. From the standpoint of polymer chemistry, this is due to the thermal stability of resins is relatively poor, and it cannot be used at a higher temperature for a long time. The electronegativity of chlorine is strong enough to form hydrogen bonds with OH in cellulose, which should be advantageous to cellulose hydrolysis. As a chlorine-containing resin, Polyvinyl chloride (PVC) can be carbonized through the liquid phase during heat treatment with elimination of massive amounts of HCl [14], causing an obvious weight loss at higher temperature [15]. The residual amount of Cl is negligibly small due to the complete dehydrochlorination of PVC during carbonization [16]. If an appropriate method is adopted, chlorine-rich PVC can be served as a relatively cheap and widely available source of chlorine.

In this paper, a novel CSA was prepared by sulfonation of cocarbonized starch and PVC, aiming to introduce chlorine onto the robust supporter and improve the yield of CSAs. In order to evaluate the impact of Cl on CSA, PVC was cocarbonized with starch by adjusting the percentage of PVC in the feedstock. This chlorine functionalized carbon-based solid acids (CCSAs) prepared at different PVC ratio (10%, 20%, 30%, and 40%) are denoted as *x*-CCSA, where *x* is the PVC ratio. With pretreated microcrystalline cellulose [17] as the substrate, the hydrolytic activity of the catalysts was evaluated by the yield of reducing sugar, and the interaction between cellulose and Cl bonded to the CCSA was investigated.

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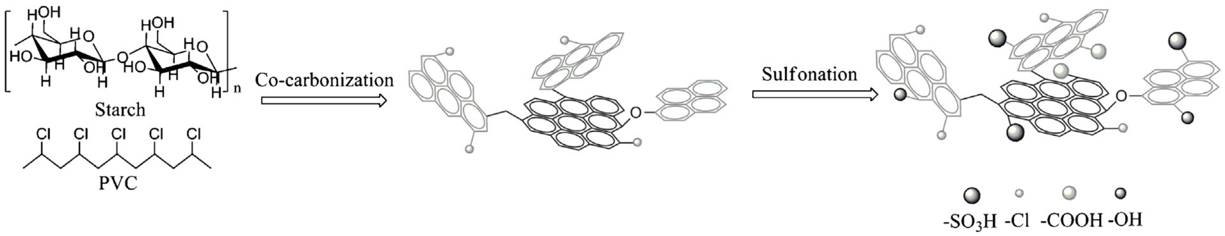

Fig. 1. Preparation of CCSA.

2. Experimental

2.1. Materials

Potato starch was analytical grade from Xi'an Guowei Starch Limited Company; Microcrystalline cellulose, trade name is AVICEL®PH-101; PVC was industrial grade from Taiyuan Chemical Plant; Glucose, cellobiose, hydrogen peroxide, concentrated sulfuric acid (98%), concentrated phosphoric acid (≥85%) and 3,5-dinitrosalicylic acid were of analytical grade.

2.2. Cellulose pretreatment

Prior to hydrolysis, microcrystalline cellulose was pretreated by concentrated phosphoric acid according to the method by Wei and Kumar [17].

2.3. Preparation of CCSA

Typically, starch and PVC, mixed uniformly with predetermined proportion, were cocarbonized for 10 h at 450 °C under N_2 to produce black solid precursors, which were then heated in concentrated sulfuric acid (98%) at 150 °C under N_2 for 6 h. Subsequently, the black slurry was cooled to room temperature and filtered. The residue was washed repeatedly in boiling deionized water until the filtrate was neutral and free from sulfate and chloride ions, and then dried in the oven at 80 °C overnight. The synthesis process of CCSA is shown in Fig. 1.

2.4. Determination of chlorine content

An analytical procedure, oxygen bomb combustion [18], has been developed for the dissolution of total chlorine in CCSA and then the chlorine contents were evaluated by turbidimetry.

2.5. Characterization

The X-ray diffraction (XRD) analysis of the CCSA was conducted on a Shimadzu XRD-6000 diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.15405$ nm) at 40 kV and 30 mA in the scanning angle (2θ) of 5–65° at a scanning speed of 8°/min. The Fourier transform infrared (FT-IR) spectrum was obtained by using a Shimadzu 8400 Fourier transform infrared spectrometer in the range of 400–4000 cm^{-1} with a 4 cm^{-1} resolution. The Carbon nuclear magnetic resonance (^{13}C NMR) spectrum was measured at room temperature using a Bruker 600 MHz AV-III spectrometer with magic-angle-spinning (MAS) at 4.5 kHz and the pulse length was 3.91 μS. X-ray photoelectron spectroscopy (XPS) was performed using ESCALAB250 spectrometer employing an Al $K\alpha$ X-ray source operating at 200 W. The photoelectron pass energies for wide and narrow scans were 150 eV and 60 eV, respectively. The base pressure of the XPS chamber was 10^{-7} Pa. All binding energies were referenced to the carbon C–H photopeak at 284.8 eV. The amount of produced glucose in filtrate was analyzed by a high performance liquid chromatography (HPLC) system equipped with Hypersil NH_2 column (250 × 4.6 nm) and RI detector (Shodex RI-201H) under the following conditions: flow rate, 1 ml min^{-1}; mobile phase, acetonitrile/water (4:1, V/V); column temperature, 40 °C. The amount of SO_3H groups was estimated through neutralization titration [19].

2.6. Evaluation of hydrolysis performance

The catalytic performance of various catalysts was demonstrated through the hydrolysis of cellulose and cellobiose. For hydrolysis of cellulose, pretreated microcrystalline cellulose and CCSA with the mass ratio of 1:2 were added into a high pressure reactor in the presence of deionized water (10 ml), and then reacted at 150 °C for 6 h under magnetic stirring. After reaction, the yield of reducing sugar was estimated by the means of 3,5-dinitrosalicylic acid (DNS method) [20]. For hydrolysis of cellobiose, CCSA and 10 ml aqueous solution containing cellobiose (10 mg ml^{-1}) were heated at 120 °C for 6 h. Samples were drawn from the reaction mixtures and analyzed by HPLC.

3. Results and discussion

3.1. Characterization of catalyst

Fig. 2 shows the XRD pattern of CCSA. Two broad and diffuse peaks at 2θ angles of 20–30° and 40–50° are due to carbon (0 0 2) and (1 0 0) reflections, respectively. These diffraction patterns reflect that CCSA is an amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion. Structurally, the carbon framework of CCSA is approximately consistent with the others reported in the literatures [5,21,22]. Nevertheless, the peaks of the 0 0 2 and 1 0 0 reflections are changed slightly in their position and shape. This may be due to the differences in

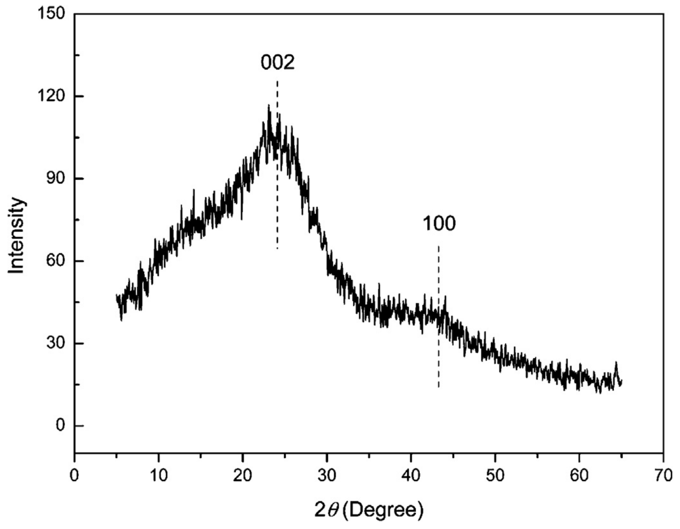

Fig. 2. XRD pattern of 40-CCSA.

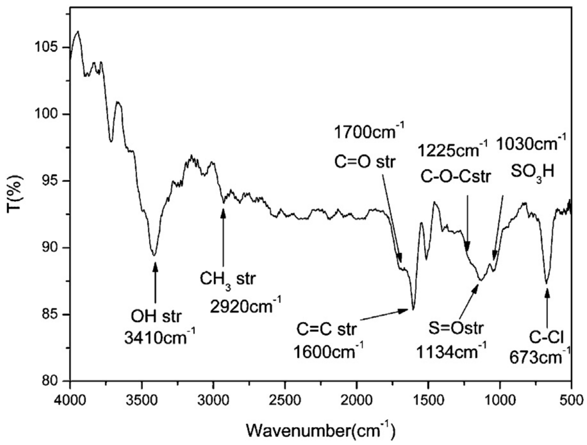

Fig. 3. FT-IR pattern of 40-CCSA.

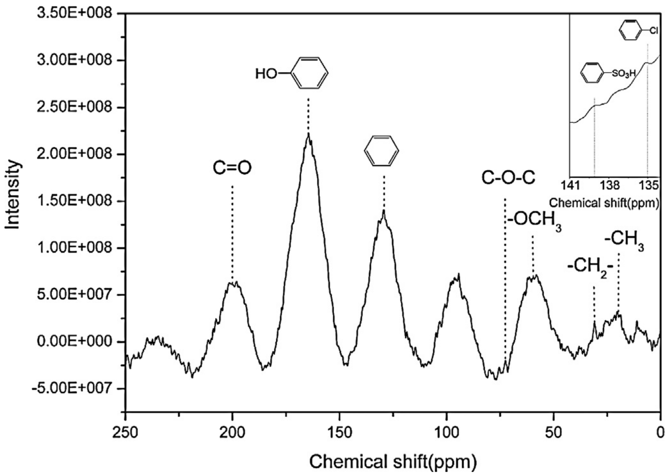

Fig. 4. ^{13}C NMR pattern of 40-CCSA.

carbonization mechanisms of starch and PVC, which impact the size and orientation degree of graphite crystallite.

The FT-IR pattern of CCSA is depicted in Fig. 3. The absorption bands at around 1134 cm^{-1} (O=S=O symmetric stretching) and 1030 cm^{-1} (SO_3 stretching modes in SO_3H) [23] are evidence that the as-prepared carbon materials were functionalized with catalytic sites (–SO_3H) on the surface. The peaks at around 3410 cm^{-1}, 1700 cm^{-1} and 1600 cm^{-1} are ascribed to stretching vibrations of O–H from phenols [21], C=O [24], and C=C, respectively, and these demonstrate that a large number of hydroxyl and carboxyl groups exist on amorphous carbons, which constitute its hydrophilic surface. In addition, ether bridges (C–O–C) between aromatic rings at the band of 1225 cm^{-1} [25] are observed in the FT-IR spectra standing for the cross-linking of condensed aromatic sheets. Clearly, a signal of C–Cl stretching vibration, which is never reported on CSAs, appears at around 673 cm^{-1}, implying that Cl atoms have been successfully introduced on carbon precursors during cocarbonization and still remain after sulfonation.

The ^{13}C NMR spectra (Fig. 4) of CCSA exhibits the resonance peaks at 129 ppm [26], 160 ppm and 200 ppm attributable to polycyclic aromatic carbon, phenolic OH, and COOH, respectively. Besides, a signal for sp^3-derived carbon at 20 ppm indicates that part of sp^3-carbons in starch and PVC are converted into aliphatic side chains (–CH_3) during the carbonization treatment. The signals at 73 ppm and 30 ppm are attributed to C–O–C and –CH_2– respectively, meaning that the carbon sheets are tethered via ether bridges or short aliphatic bridges. The peaks assigned to aromatic carbon bonded to Cl (ca. 135.1 ppm) or SO_3H (ca. 139.2 ppm) are obscured by the two broad peaks due to polycyclic aromatic carbon and phenolic OH.

The elements of C, S, O, and Cl are observed in the full-scan XPS spectrum (Fig. 5A) of CCSA, and the narrow-scans of S 2p and Cl 2p are conducted by using the XPS peak separation technique.

The narrow-scan XPS photopeak for S 2p of the CCSA is displayed in Fig. 5B. A single S 2p peak at 168 eV with a half-peak width of 2.1 eV is clearly observed in the spectrum of CCSA, assigned to SO_3H groups. It means that sulfonation of amorphous carbon is successfully achieved to form sulfonic groups in concentrated sulfuric acid, and all S atoms in the CCSA are contained in SO_3H groups [3,27].

The Cl 2p peak is resolved into two individual photopeaks in Fig. 5C, which are attributable to C–Cl (Cl 2p 3/2 binding energy of 200.0 ± 0.2 eV) [28], and C–Cl (Cl 2p 1/2 binding energy of 201.8 ± 0.2 eV) [29] separately, indicating that the new generated Cl groups are covalently bonded to sp^2-carbons of CCSA.

3.2. *Catalytic performance for cellulose hydrolysis*

The differences of catalysts performance are closely related to not only the structure of catalysts but also the pretreatment methods and conditions of cellulose, which together determine the yield of reducing sugar. For this reason, we employed two commonly used CSAs to compare with CCSA. As shown in Fig. 6, reducing sugar yields from conventional glucose-derived CSA (GCSA) and starch-derived CSA (SCSA) are 37.2% and 36.8%, respectively, and their efficiency of cellulose hydrolysis is relatively low. Guo et al. [11,30] also recognized the same problems, consequently they used a combination of CSA and ionic liquids to obtain a higher reducing sugar yield. This method leads cellulose to dissolve in chloride ionic liquids, allowing it fully contact with acid sites on catalysts. To avoid the difficulties in products separation and recovery of ionic liquids, we attempted to immobilize chlorine on CSAs.

As shown in Table 1, when PVC was added in feedstock, the amount of Cl on catalysts increases with the increase of PVC ratio, and the amount of SO_3H groups is roughly the same among different catalysts. This means that the acidity of catalysts is little affected by the Cl content. However, from Fig. 6, it can be seen that the yield of reducing sugar increases remarkably with the increase of PVC content and the highest can reach 94.2%, revealing that the

Table 1
Catalytic performance for the hydrolysis of cellobiose over catalysts at 120 °C[a].

Catalysts	Amount of SO_3H/mmol g^{-1}	Amount of Cl in fresh catalysts/mg g^{-1}	Hydrolysis of cellobiose	
			Yield of glucose (%)	TOF
GCSA	0.855	–	44.06	0.241
SCSA	0.853	–	44.01	0.240
10-CCSA	0.858	2.73	44.21	0.240
20-CCSA	0.862	3.80	42.01	0.227
30-CCSA	0.863	5.51	44.52	0.241
40-CCSA	0.832	6.55	44.76	0.250

[a] Reagents and conditions: 0.2 g of catalyst, 0.1 g of cellobiose, 10 ml of water, 120 °C, 6 h.

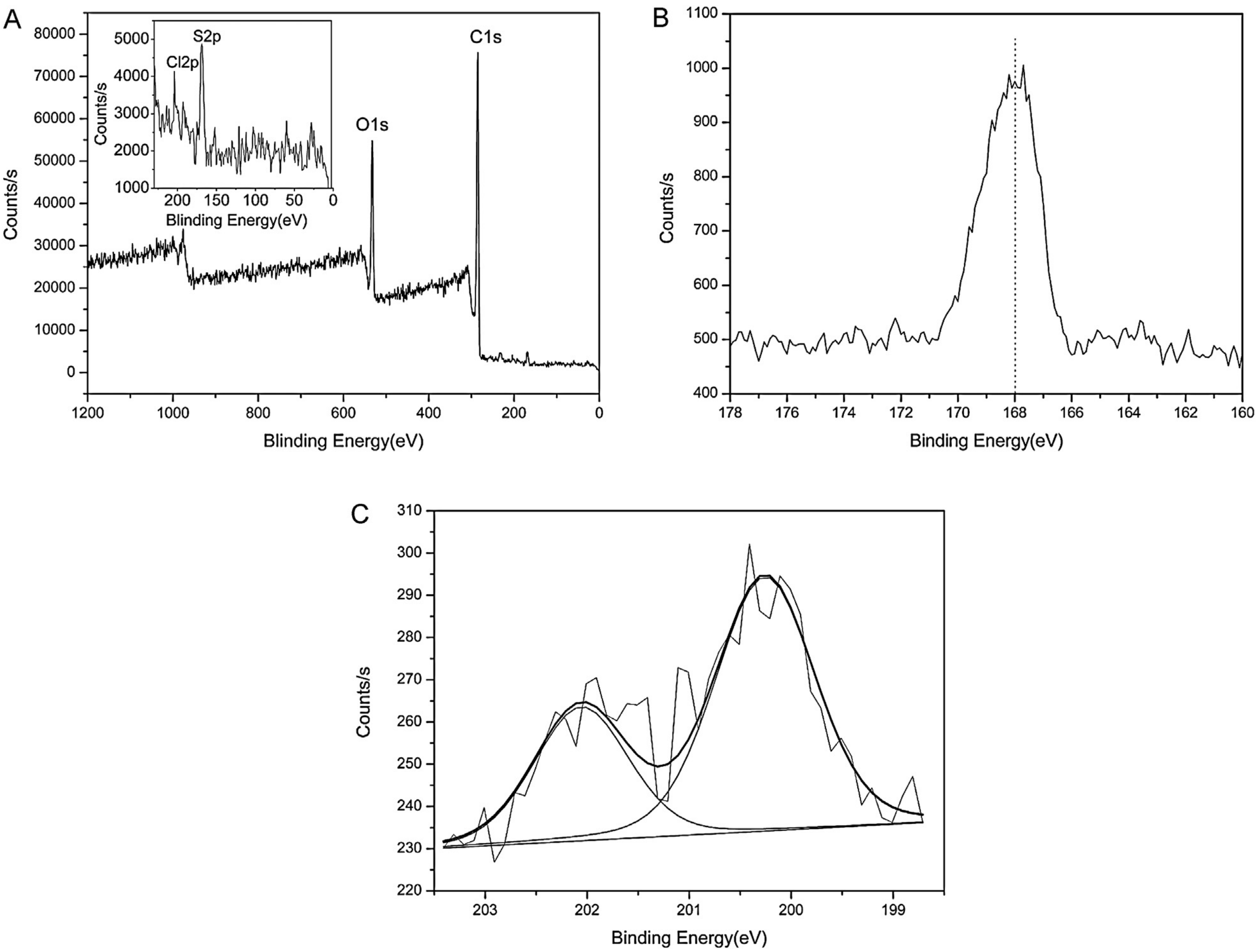

Fig. 5. (A) XPS pattern of 40-CCSA; (B) S 2p XPS pattern of 40-CCSA; (C) Cl 2p XPS pattern of 40-CCSA.

participation of Cl on CCSA significantly accelerates the cellulose hydrolysis.

In order to further verify the role of Cl, the hydrolysis of cellobiose over different catalysts was studied in aqueous solution and the results are shown in Table 1. Unexpectedly, there are negligible differences of glucose yield for various catalysts, suggesting that Cl groups fail to work on cellobiose hydrolysis. One reasonable explanation for this phenomenon is that cellobiose is a simple and water soluble molecule consisting of two glucose linked by a β-1,4-glycosidic bond, which has minimal problems in the interaction with catalysts.

The process (Fig. 7) of cellulose hydrolysis over CCSA is attributed to the strong electronegativity and small size of the Cl atom, which has high hydrogen bonds basicity. As electron donors, Cl atoms attack the cellulose hydroxyl protons, tending to form hydrogen bonds with cellulose. Upon interaction between cellulose and CCSA, the oxygen and hydrogen atoms from different hydroxyl groups are separated, leading to opening of the intra- and intermolecular hydrogen bonds of cellulose and finally exposing the glycosidic bonds within cellulose. On the other hand, these bridge bonds in CCSA can make the carbon framework fully stretch to reduce steric hindrance among SO_3H groups and glycosidic bonds. Consequently, SO_3H groups and glycosidic bonds are located close enough in space to permit the hydrolysis of cellulose.

At present, some studies have confirmed the good stability of conventional CSAs [19,31]. After Cl, a new functional group, is introduced onto CSA, the resonance effect exists in CCSA with the consequent delocalization of electrons through the aromatic rings, which can make the CCSA more stable. The durability of CCSA was examined by recycling the catalyst three times in cellulose hydrolysis. After each reaction run, CCSAs were recovered by decantation, washing, drying at 80 °C overnight with 99.0–99.5% recovery, and then reused in the next batch of hydrolysis at identical conditions. About 10–25% of Cl on CCSAs is leached after recycling three times.

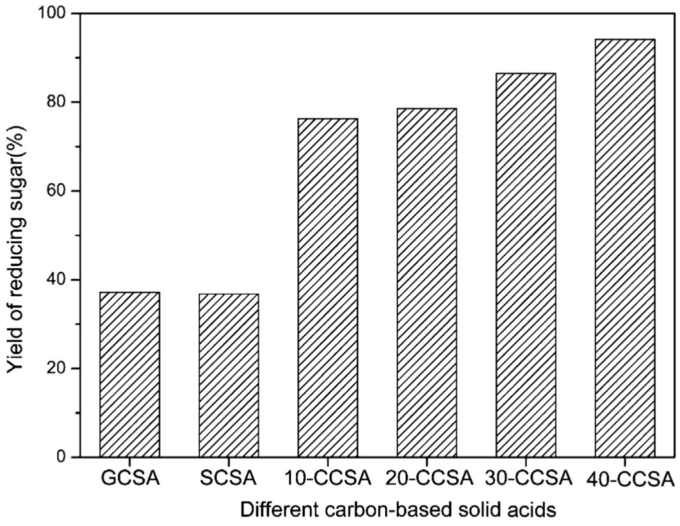

Fig. 6. Reducing sugar yield from different carbon-based solid acids.

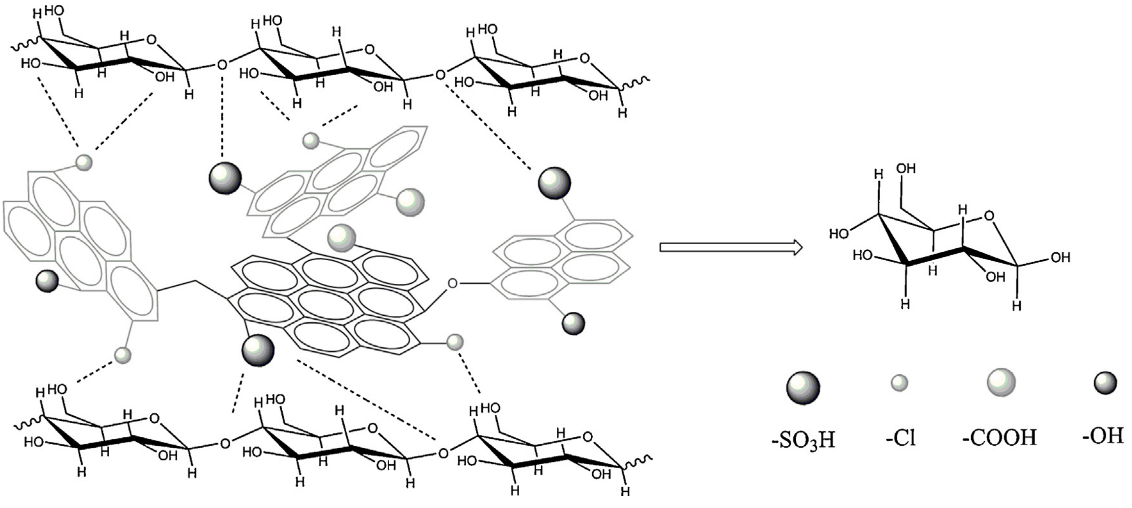

Fig. 7. The process of cellulose hydrolysis over CCSA.

As a result, the yield of reducing sugar from 40-CCSA is decreased from 94.2% to 90%, indicating the stability of CCSAs is needed to be further improved.

4. Conclusions

A novel carbon-based solid acid was successfully prepared by cocarbonization of starch and PVC followed by sulfonation, exhibiting strong potential for use as a replacement for conventional CSAs. The chlorine groups and bridge bonds derived from PVC and starch emerge as new parts of CSAs, which can form hydrogen bonds with cellulose and make the carbon sheets fully stretch, respectively. As a result, the accessibility of hydrolysis site (SO_3H) to glycosidic bonds is enhanced to stimulate the hydrolysis of cellulose. Furthermore, the durability experiments indicate that the CCSAs have good stability.

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