Applied Catalysis A: General 473 (2014) 70–74

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

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

Shuguang Shen*, Bei Cai, Chunyan Wang, Huanmei Li, Guang Dai, Haifeng Qin

College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, PR China

ARTICLE INFO

Article history:
Received 26 July 2013
Received in revised form
21 December 2013
Accepted 29 December 2013
Available online 7 January 2014

Keywords:
Carbon-based solid acid
Cellulose
Cocarbonization
Chlorine
Heterogeneous hydrolysis

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.

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.

---

* Corresponding author. Tel.: +8603516010588; fax: +8603516010588.
E-mail addresses: shenshuguang@tyut.edu.cn, sgshen@sina.com (S. Shen).

0926-860X/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.12.037

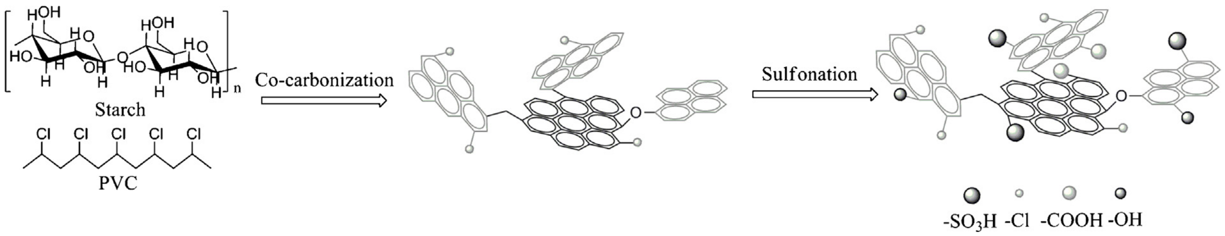

Fig. 1. Preparation of CCSA.

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

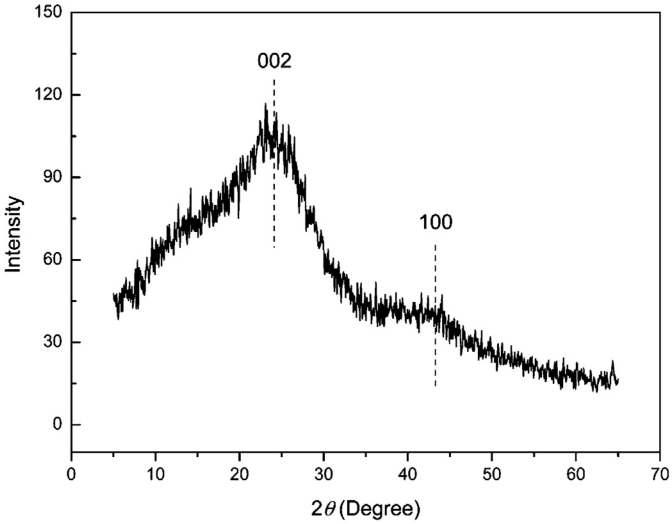

Fig. 2. XRD pattern of 40-CCSA.