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Short communication

Impacts of acidity and textural properties of oxidized carbon materials on their catalytic activity for hydrolysis of cellobiose

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ABSTRACT

Hydrolysis of cellobiose was investigated in the presence of oxidized carbon materials with different textural properties and concentrations of surface acidic groups. Specifically, oxidized microporous activated carbon, graphite-like mesoporous Sibunit carbon, and graphite-like multi-walled carbon nanotubes were studied. Catalytic activity was found to correlate with the concentration of surface acidic sites. Activated carbon oxidized with HNO_3 at 130 °C exhibited superior catalytic activity due to highest acidity of this material. The catalytic performance was predominantly dependent on acidity, while textural properties only played a minor role, and no mass transfer limitations were observed for microporous catalysts.

1. Introduction

Sustainable process developments require the utilization of renewable resources by means of efficient and environmentally-benign technologies. Hence, a valorisation of cellulose through production of conventional and novel platform chemicals is currently the focus of numerous investigations [1–5]. Cellulose is the major constituent of lignocellulosic biomass, highly available e.g. as part of agricultural residues or pulp and paper waste streams. The valorisation of cellulose via platform chemicals includes (1) depolymerisation yielding glucose followed by (2) further upgrading of glucose into desirable products. Importantly, the efficient cellulose hydrolysis still remains challenging, although soluble monosaccharides can be transformed into a wide range of products applying appropriate reaction cascades [1–5]. Hydrolysis of cellulose can be performed biotechnologically or catalyzed by Brønsted acids. However, the use of enzymes is restrained by high costs, while the application of soluble acids is associated with a high corrosive potential and possible salt formation. Solid acidic materials are very promising for hydrolysis of cellulose as easily recyclable catalysts with low corrosion potential. However, a one-step hydrolysis of cellulose to glucose is challenging due to the highly resistant crystalline structure of the substrate [6]. As an alternative, cellulose can be pre-treated e.g. with super-critical water [7,8] or milled after impregnation with acids [9]. Such procedures convert water-insoluble cellulose into a mixture of water soluble oligomers. The latter can be hydrolysed in the presence of solid acidic catalysts [10].

Since depolymerisation of poly- and oligo-glucans is very complex due to numerous intermediates, cellobiose is often considered as model substrate for hydrolysis. Cellobiose is β-D-glucosyl-(1->4)-β-D-glucose, i.e. a disaccharide comprising of two β-D-glucopyranosyls connected by a β-1,4-glycosidic bond. Generally, cellobiose is very stable against hydrolysis compared to other disaccharides such as sucrose or maltose [10]. As a result, hydrolysis of cellobiose in the presence of a solid catalyst requires relatively harsh reaction conditions: the mass ratio of catalyst-to-substrate usually equals or even exceeds 1, temperatures over 100 °C are used, and the reaction typically lasts for several hours [10–14]. Despite high acidity, zeolites or ion-exchanged resins demonstrated poor activity for hydrolysis of cellobiose [10]. In the presence of a sulfonated chloromethyl polystyrene resin, hydrolysis of cellobiose was complete within 2–4 h at 100–120 °C, but 250 mg catalyst was used converting 100 mg of substrate [12]. In the presence of sulfonated silica, hydrolysis of cellobiose proceeds much faster [15,16]. However, sulfonated mesoporous silica as catalyst underwent a significant loss of the specific surface area under reaction conditions [17]. Functionalized carbons are

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promising water-tolerant materials that also demonstrated high catalytic performance for hydrolysis of glucans. Acidic groups on the surface of carbon materials can be induced by oxidation or sulfonation of carbons. Relatively high activity of carbon catalysts for hydrolysis of glucans was explained by favourable adsorption of glucan units on the carbons due to binding of substrates to surface oxygen-containing groups [13,18,19] and CH-π interactions between hydrogen of the glucan and arene rings of the carbon materials [20]. Carbon-based catalysts were successfully tested for cellulose hydrolysis producing glucose in 26–75% yield [17,18,21–29]. In several studies, cellobiose was used as model substrate for studying the hydrolysis of β-1,4-glycosidic bonds. For example, Hara et al. reported that a sulfonated carbon material produced by carbonization of cellulose [13,14] outperforms Amberlyst 15 in terms of activity and stability for hydrolysis of cellobiose [13]. When using sulfonated carbonized cellulose as catalyst, 70% yield of glucose was obtained within 9 h of reaction at 100 °C [13]. Ormsby et al. reported 75% yield of glucose based on cellobiose obtained over sulfonated biochar within 6 h at 120 °C. However, the sulfonated biochar was deactivated due to leaching of sulfonic groups [11]. Oxidized carbons are potentially more stable than sulfonated carbons, since the former do not undergo leaching of the surface active sites under hydrothermal conditions. Thus, Zhao et al. successfully recycled graphite oxide as catalyst for hydrolysis of cellobiose 4 times producing glucose in 58–68% yield at 150 °C within 24 h [28]. To summarize, studying hydrolysis of cellobiose as model substrate helps getting insight into hydrolysis of cellulose. Nevertheless, though carbon materials exhibit good catalytic performance for hydrolysis of cellobiose, little is known about the structure-activity relationships for the catalysts of this process. Therefore, this work aimed at understanding the role of textural properties and catalyst acidity for cellobiose hydrolysis in the presence of oxidized carbon materials.

2. Experimental

2.1. Chemicals and materials

Glucose anhydrous for biochemistry (Reag. Ph. Eur.) and HNO_3 (65%, puriss.) were provided by Merck. D-(+)-cellobiose of >98% purity was purchased from Alfa Aesar. NaOH of ≥98.8% purity from Geyer Chemsolute was used. Measure solution of 0.1N HCl was prepared using a standard ampoule from Geyer Chemsolute. Commercial carbon materials were used for functionalization. Active carbon (AC) AC FE-000082-001, article 101408, was supplied by Blücher. Mesoporous graphite-like carbon material Sibunit® (Sib) was obtained from Institute of Hydrocarbon Processing, Omsk, Russia. Carbon multi-walled nanotubes (CNT) with O.D. × L 6–9 nm × 5 μm and carbon content >95% were supplied by Sigma Aldrich. All the solutions were prepared in distilled water.

2.2. Catalysts preparation

Prior to functionalization, AC and Sib were ground in a Pulverisette 23 planetary ball mill (Fritsch). The fraction of the particles smaller than 100 μm was separated by sieving and used for further treatments. Oxidation of carbon materials with 65% HNO_3 was performed at 70 and 130 °C. 3 g carbon material and 150 mL of 65% HNO_3 were charged to a round-bottom flask with a back-condenser. The flask was placed into a thermostated oil bath and kept under stirring with a magnetic stirrer for 2 h. The oxidized materials were repeatedly washed with 10–20 L water until a constant pH was reached. The materials were filtered and dried overnight at 120 °C.

2.3. Catalyst characterization

Catalysts were characterized by low-temperature sorption of N_2 using a Quadrasorb SI Automated Surface Area & Pore Size Analyzer after preliminary outgassing under vacuum at 110 °C for 20 h. X-ray diffraction analysis (XRD) was performed on a D5000 Siemens XRD diffractometer with a CuKα X-Ray tube (λ = 1.54056 Å). The tube voltage and current were 45 kV and 40 mA, respectively. Diffraction patterns were collected in the 3–90° 2θ range, with 0.02° intervals and a step time of 1 s. The amount of acidic sites was determined by Boehm titration. 500 mg of a functionalized carbon or 2 g of a not-treated carbon were dispersed in an aliquot (10 or 20 mL) of 0.2 M NaOH and kept under stirring in a closed vessel overnight. Thereafter the solid was separated by filtration and 5 mL aliquot of basic solution was mixed with 25 mL 0.1 M HCl. The excess of HCl was back-titrated with 0.2 M NaOH with a Titroline alpha titrator unit (Schott). Transmission electron micrographs (TEM) were aquired using microscope JEOL, JEM-2200FS operating at high tension of 200 kV and electron probe diameter of 1 nm in scanning transmission (STEM) mode. The pH_{slurry} was determined according to a previously described procedure [30]. Distilled water was boiled prior to the analysis for removal of dissolved carbon dioxide and cooled down till room temperature. 5 mL water and 300 mg carbon samples were placed in plastic vessels and kept under stirring for 70 h to reach the equilibrium. Thereafter the carbon materials were filtered off and the pH of the filtrate was measured.

2.4. Catalytic test

Hydrolysis reactions were conducted in a 20 mL autoclave with glass inlet. A typical reaction mixture contained 300 mg catalyst, 300 mg cellobiose and 5 mL water. The reactions were carried out at 120 °C and ca. 30 bar nitrogen under stirring at 750 rpm. After the experiments, the reaction mixture was cooled down in an ice bath and filtered through a polyamide syringe filter (Chromaphil, polyamide, pore size 0.2 μm). For the recycling test, CNT-130 catalyst was separated from the reaction mixture by filtration, rinsed with water and dried overnight at 80 °C.

The reaction mixtures were analyzed by means of high-pressure liquid chromatography (HPLC) using a Shimadzu Prominence LC-20 system. HPLC analysis was carried out by using two successively connected Organic Acid Resin columns (CS-Chromatographie, 100 mm × 8.0 mm and 300 mm × 8.0 mm) connected via a 6 port switching valve. The columns were thermostated at 40 °C, the eluent (154 μL of CF_3COOH in 1L of water) was supplied at 1 mL min^{-1} flow rate. During the first 7 min after the injection, the eluent was supplied with pump A throw two successively connected columns and a refractive index (RI) detector. After that the valve switched the position and the elution continued for 18 more minutes through the columns separately. The eluent was pumped with the pump A through the first column (100 mm × 8.0 mm) and a photodiode array (PDA) detector with the detection wavelength of 270 nm for analysis of possible furan-derivatives as by-products. Simultaneously the elution was pumped through a second column (300 mm × 8.0 mm) and the RI detector with pump B in order to analyse cellobiose and glucose.

3. Results and discussion

Three commercial materials, namely activated carbon (AC), mesoporous graphite-like carbon of the Sibunit family (Sib) and graphite-like multi-walled carbon nanotubes (CNT) were studied. The abbreviations AC-pris, Sib-pris and CNT-pris denote the pristine materials. The graphitic structures of Sib-pris and CNT-pris along with the less ordered nature of AC-pris were confirmed by