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Research paper

Magnetic hydrotalcites as solid basic catalysts for cellulose hydrolysis

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ABSTRACT

Magnetic Mg–Fe–CO_3 hydrotalcites (LDHs) with different Mg/Fe molar ratios were prepared and their microstructure and surface chemical properties were characterized. The particles were used to hydrolyze cellulose with β-1,4-glycosidic bonds. The catalytic activity relating to the electron–hole pairs, basicity, crystallinity and specific surface area depended on the Mg/Fe molar ratio. The LDH with Mg/Fe molar ratio of 3.0 (LDH-3) possessed the best crystallinity, the strongest ability to trap electrons, the highest basicity and specific surface area, exhibiting the highest catalytic activity in the cellulose hydrolysis. It could be because of the high crystallinity and basicity, especially plentiful strong basic sites, made the LDH-3 a strong ability to trap electrons leading to great affinity for β-1,4-glycosidic bonds of cellulose. The LDH-3 showed a maximum yield (46.5%) of soluble reducing sugars with high glucose selectivity (84.4%) at 150 °C for 24 h. Moreover, the solid catalyst could be easily separated and possibly reused.

1. Introduction

Cellulose is the most abundant and renewable carbon source which constitutes a large fraction of the lignocellulosic materials found in the world. Its efficient use is essential for the supplement of biofuels and biomaterials (Klemm et al., 2005; Ragauskas et al., 2006; Himmel et al., 2007; Zhou, 2011; Cheng et al., 2012). Cellulose gives rise to monomeric glucose upon hydrolyses through various processes catalyzed by enzymes or mineral acids. The enzymatic process takes place under mild reaction conditions, but it is slow and the enzyme cost is high. The traditional dilute acid hydrolysis process is operated at elevated temperature under high pressure, and the hydrolysis is a low efficiency. Hydrolysis with concentrated sulfuric acid can be operated under less harsh conditions, but requires expensive corrosion-resistant reactors and has major waste disposal problems. These processes have significant drawbacks such as separation of products and catalysts, corrosion hazard, and severe controls of enzymes, waste fluids, and reaction conditions (Zhang and Lynd, 2004; Kontturi and Vuorinen, 2009; Fang et al., 2011; Gliozzi et al., 2014). The heterogeneous catalysts can result in catalyst reuse and waste stream reduction, and make the process of industrial production environmentally benign and economical because of their non-corrosiveness and easy separation from products. The biomass carbon sulfonic acids (BC-SO_3H) as solid acid catalysts show about 25% yield of reducing sugars under microwave irradiation (Wu et al., 2010). At the same time, zeolites also show high glucose selectivity under hydrothermal condition (Onda et al., 2008). Especially in our previous works, Mg–Al–CO_3 hydrotalcites as solid base catalysts have high catalytic activities for the cellulose hydrolysis with hydrolysis yield of 47.4% and glucose selectivity (85.8%) (Fang et al., 2011). Hydrotalcites, layered double hydroxides (LDHs), consist of positively charged brucite-like layers with anionic species in the interlayer, forming neutral clay materials. LDHs possess homogeneous interdispersion of elements, high specific surface area, and the most important, strong basic properties which make them to be very attractive for catalytic applications (Zeng et al., 2008; Debecker et al., 2009; Wang and O'Hare, 2012; Rives et al., 2014). However, the separation and recovery of hydrotalcites from the reaction products are still difficult. Magnetic solid base catalyst can be separated easily from the reagents by an external magnetic field, which can effectively prevent catalyst loss and improve its recovery rate during separation process (Wang et al., 2008; Tang et al., 2012). To the best of our knowledge, there is little literature concerning the cellulose hydrolysis by magnetic Mg–Fe–CO_3 hydrotalcites.

Taking the aforementioned factors into account, a series of magnetic Mg–Fe–CO_3 hydrotalcites with various Mg/Fe molar ratios were synthesized and tested for cellulose hydrolysis. The characterization of the Mg–Fe–CO_3 hydrotalcites was studied with XRD, FT-IR, SEM, BET, particle size distribution, CO_2-TPD and contact angle measurement as well as the cyclic voltammetry, and the relationship between microstructure and catalytic performance was discussed, which might give fundamental insight into the catalytic mechanism of the catalyst.

2. Experimental

2.1. Materials

Microcrystalline cellulose (particle size of 100 μm, density of 0.3 $g \cdot mL^{-1}$) was bought from Biobasic Inc. (Shanghai, China). The

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cellulose was pretreated by ball-milling (SHQM-0.4L, Chunlong Petroleum Instrument Co., Ltd., Jiangsu, China) using ZrO_2 balls (mass of 1.8 kg and diameter of 2 mm) with a spinning speed of 230 rpm for 24 h (Onda et al., 2009), and the ratio of ball to powder mass was 5:1. All the reagents/reactants were of analytical grade and solutions were prepared with deionized water.

2.2. Preparation of hydrotalcites

Magnetic Mg–Fe–CO_3 hydrotalcites (LDHs) with Mg/Fe molar ratio of 2.0–4.0 were prepared by the co-precipitation method, following the literature previously described (Kang et al., 2013; Zeng et al., 2014). The aqueous solutions containing $Mg(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ with various Mg/Fe molar ratios were separately placed into three-neck flasks. The metal salt solution was titrated to constant pH 9.3 using the solution containing 1.2 $mol \cdot L^{-1}$ NaOH and 0.1 $mol \cdot L^{-1}$ Na_2CO_3 at 40 °C with vigorous stirring. The pH was measured all along the reaction process with an industrial pH electrode (Mettler Toledo Delta 320). After the reaction was carried out for 2 h, the mixture was aged at 65 °C for 18 h. After cooling, the resulting slurry was filtered, washed with deionized water, and subsequently dried at 90 °C for 18 h. For convenience, the hydrotalcites with different Mg/Fe molar ratios of 2.0, 3.0 and 4.0 were designated as LDH-2, LDH-3 and LDH-4, respectively.

2.3. Preparation of LDH modified electrodes

The glassy carbon electrode (GCE) with a diameter of 3.0 mm was used as the substrate to grow the LDH film. Prior to the preparation procedure of the film, the GCE was successively polished to a mirror finish using 0.3 and 0.05 mm alumina slurries, respectively, followed by rinsing thoroughly with deionized water. After successive sonication in absolute ethyl alcohol for 3 min, the electrode was rinsed with deionized water and allowed to dry at room temperature. The LDH particles were dispersed in deionized water by an ultrasonic cleaner, and the dispersion solution (10 mL of 2.0 $mg \cdot mL^{-1}$) was dropped on the pretreated GCE and dried with infrared radiation heating for 3 min to obtain a LDH film-modified electrode. The modified electrode was designated as LDH/GCE. For convenience, the electrodes modified by LDH with Mg/Fe molar ratios of 2.0, 3.0 and 4.0 were also designated as LDH-2/GCE, LDH-3/GCE and LDH-4/GCE, respectively.

2.4. Characterization of hydrotalcites and voltammetric measurement

Powder X-ray diffraction (XRD) patterns were obtained in the 2θ range 5–70° using a Rigaku D/MAX-3C instrument (Japan) with CuKα source ($\lambda = 0.1541$ nm). Fourier transform infrared (FT-IR) spectrum was recorded on PerkinElmer Spectrum One B instrument (USA) using KBr pellet technique. The particle size distribution was determined using a Mastersizer 2000 laser particle size analyzer (Malvern Co., UK). The low-temperature N_2 adsorption–desorption experiments were carried out using a NOVA-e1000 system (Quantachrome Instruments, USA). Samples were outgassed at 110 °C in vacuum (1×10^{-4} Torr) for 8 h. The specific surface area (SSA) was calculated using the Brunauer–Emmett–Teller (BET) method based on the N_2 adsorption isotherms. Scanning electron micrograph (SEM) was obtained with a JEOL JSM-6700F instrument (Japan). Contact angle measurement was measured by means of sessile drop method with uncompacted powder stuck on a fixed glass support using a drop shape analysis system (DSA 100, Kruss Co., Germany). Temperature programmed desorption (TPD) was used to assess surface basicity of catalyst using an automated chemisorption analyzer (Chembet Pulsar, Quantanchrome Instruments, USA). 200 mg sample was exposed to a stream of 10% CO_2–He mixture at 400 °C for 2 h. The sample was cooled to room temperature and flushed with pure CO_2 for 1 h until saturation. The sample was heated from 100 to 800 °C at a heating rate of 10 $°C \cdot min^{-1}$ under a He stream flowing at 60 $mL \cdot min^{-1}$.

Cyclic voltammetric (CV) measurements were performed with a CHI 660 electrochemical analyzer (Shanghai Chenhua Apparatus Co. Ltd., Shanghai, China) at a potential range of −0.2–1.2 V and a scanning rate of 100 $mV \cdot s^{-1}$ for 20 cycles. A conventional three-electrode system was used, including a LDH/GCE as the working electrode, a saturated calomel electrode (SCE) as reference electrode and platinum wire electrode as the auxiliary electrode. CV was carried out in the phosphate buffer (pH 9.0) containing 0.5 $mol \cdot L^{-1}$ $K_4[Fe(CN)_6]$ with saturated KBr solution as supporting electrolyte, using an alternating current voltage of 5.0 mV, within the frequency range of 1–10^6 Hz. After 20 CV cycles for a specific sample, there was little change between the peak shapes as well as the magnitudes in each cycle, indicating the excellent long-term stability of the LDH/GCE electrodes.

2.5. Cellulose hydrolysis with hydrotalcites

Pretreated cellulose (0.45 g), catalyst (0.50 g) and deionized water (150 mL) were loaded into a ZrO_2-lined autoclave with 500 mL (FCFD05-30, Jianbang Chemical Mechanical Co., Ltd., Shandong, China). The vessel was sealed, purged with nitrogen for 10 min to remove oxygen, and heated to 150 °C with stirring (400 rpm) for a specific time. The reaction mixture was filtered and washed using deionized water for three times. The filtrates were collected and subjected to the analysis of soluble reducing sugars (SRSs) using a total organic carbon analyzer (TOC-5000A, Shimadzu, Japan). The amount of glucose was conveniently analyzed on a Shimadzu HPLC-20A instrument (Japan) equipped with SCR-101C column and refractive index detector (RID-10A). Each sample was diluted with ultra-pure water before analysis to prevent the overloading of the column with organic solvents.

The reuse of the LDH-3 as a catalyst was carried out for 24 h every time. After the first reaction, the solid residue containing the catalyst and pretreated cellulose was separated from the hydrolytic solution by filtering and washing with deionized water. The filtrate was collected for SRS analysis. After drying the solid residue and supplementing some fresh milled cellulose in the residue, the mixture was used for the next hydrolytic reaction under the same conditions. Experiments were carried out by triplicate. The SRS yield and glucose selectivity were calculated as follows:

$$\text{SRS yield}(\%) = (\text{carbon mass of SRSs})/(\text{carbon mass of cellulose}) \times 100\%$$

$$\text{Glucose selectivity}(\%) = (\text{carbon mass of glucose})/(\text{carbon mass of SRSs}) \times 100\%.$$

3. Results and discussion

3.1. Characterization of Mg–Fe hydrotalcites

3.1.1. XRD

The powder XRD patterns for the magnetic LDH with various Mg/Fe molar ratios of 2–4 were shown in Fig. 1A. The three samples had the typical crystalline phase of a hydrotalcite with sharp and intense (003), (006), (009), (110) and (113) reflections. The interlayer distance ($d_{003} \approx 0.77$ nm) was a typical of CO_3^{2-} intercalated hydrotalcite. They showed the X-ray pattern of single phase LDH compound which matched totally with the standard hydrotalcite pattern, which was in good agreement with that of the previous reports (Cavani et al., 1991; Rives, 2001; Abdelkader et al., 2011). The crystallinity of the phase, however, depended on the Mg/Fe molar ratio. XRD pattern of the LDH-4 showed the presence of $MgCO_3 \cdot 3H_2O$ as an impure phase due to the increase of magnesium content. The LDH-2 and LDH-3 showed a single phase Mg/Fe LDH and no other crystalline phases were observed. Comparing with the LDH-2 and LDH-4, the diffraction