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# Modified solid acids derived from biomass based cellulose for one-step conversion of carbohydrates into ethyl levulinate

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## ABSTRACT

A series of metal salt-modified carbon catalysts had been prepared to study the selective transformation of various carbohydrates into ethyl levulinate in an ethanol medium. The specific textural and chemical characteristics of prepared carbon samples were identified by Raman, XRD, XPS,  $\text{NH}_3$ -TPD, FT-IR and nitrogen physisorption. Various parameters such as ethanol/water volume ratio, NaCl addition, reaction temperature, and catalyst dosage played a great role in ethyl levulinate production. A desirable ethyl levulinate yield of 58.0 mol% with a highest ROF (rate of ethyl levulinate formation per gram of catalyst per hour) value of 2148.3  $\mu\text{mol}/(\text{g}_{\text{cat}}\cdot\text{h})$  was achieved at 468 K over  $\text{FeCl}_3$  modified carbon catalyst with respect to fructose conversion. The recycling experiments revealed that the sulfonated carbon catalysts exhibited relatively satisfied activity and stability.

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## 1. Introduction

With the gradual depletion of fossil resources and further deterioration of global environment, direction towards utilization of renewable biomass resources as good candidates for sustainable production of biofuels and chemicals has gained increasing interest in recent years [1–8]. As a kind of biomass-derived intermediate platform chemicals, levulinate esters including ethyl, methyl, or butyl levulinate are usually obtained from biomass resources via direct acid-catalyzed alcoholysis of carbohydrates, one-pot alcoholysis of furfural and its derivatives, and esterification of levulinic acid, which can be used as solvents, fragrances, additives for gasoline and diesel transportation fuels [9–11].

Typically, mineral acids and metal salts, such as HCl,  $\text{H}_2\text{SO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$ , were widely adopted to produce levulinate esters with desirable yields [12–14]. However, these catalysts also presented obvious deficiencies, such as corrosion, product separation, and catalyst recycling. Thus, heterogeneous acid catalysts that can be easily separable and reusable over repeated cycles are still in great demand. Subsequently, a series of solid acid catalysts have been reasonably designed and applied in the catalytic production of levulinate esters, such as sulfated metal oxides, heteropoly acids, zeolites, ionic liquids [15–21]. For example, sulfonic acid functionalised SBA-15 was found to be active in the transformation of levulinic

acid, mono- and disaccharides into ethyl levulinate (EL). Almost 100% of levulinic acid conversion was achieved after 2 h of reaction at 390 K, and fructose gave higher yield of EL than that of glucose [15]. Baronetti et al. [16] reported the upgrade of levulinic acid into EL using reusable silica-included Wells–Dawson heteropolyacid as catalyst, and observed that the material still displayed good catalytic activity after three consecutive cycles. Sulfonated carbon nanotubes were also developed as catalysts for EL production, and it was found that concentration of acid sites formed on the nanotube surface played an important role in EL formation [22]. Yang et al. [23] synthesized hierarchical H-USY zeolite for the direct conversion of glucose into methyl levulinate, along with a yield of 54% produced. Although great progress has been made for levulinate esters synthesis, those solid acids are expensive and difficult to prepare. Therefore, extensive efforts have been devoted to developing heterogeneous and cost-effective catalysts for the transformation of biomass-derived feedstocks into levulinate esters.

Recently, sulfonated carbons, characteristic of low material cost, chemical inertness and good mechanical and thermal stability, are reported to show better performance in acid-catalyzed reactions of biomass utilization, such as fatty acids esterification [24–26], transesterification [27,28], saccharides dehydration [29] and cellulose hydrolysis [30,31]. For instance, Sievers et al. [30] found that sulfonated carbon catalysts with appropriate strong/weak acid sites could selectively hydrolyze cellobiose into glucose. Nata et al. [32] successfully prepared sulfonated carbonaceous spheres with high acidity, which displayed good capability to hydrolyze

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cornstarch. In addition, the highest TOF (turnover frequency) of  $109 \text{ h}^{-1}$  was observed in biodiesel production from oleic acid over sulfonated carbons, seven times than that of Amberlyst-15 [25].

Inspired by these findings, we synthesized a series of carbon-based catalysts for the direct transformation of carbohydrates into EL using biomass-derived cellulose as a precursor via a modified preparation involving metal salts impregnation, incomplete carbonization and high temperature sulfonation. Various metal salts modified carbon catalysts were also developed to find the most active one for EL production. Effects of varied experiment parameters were systematically investigated, including reduction temperature, catalyst loading, ethanol/water volume ratio, and so on. To our delight, EL yield had been significantly improved by around 20% for  $\text{FeCl}_3$  modified carbon catalyst that reached up to 58.0 mol% under the optimal conditions. Besides, the prepared sulfonated carbons exhibited good activity and stability in recycling experiments.

## 2. Experimental

### 2.1. Materials

Fructose (99%), cellobiose (98%), cellulose (25  $\mu\text{m}$ ), levulinic acid (LA, 99%), 5-hydroxymethylfurfural (HMF, > 99%), and EL (99%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). All other chemicals were supplied by Guangzhou Chemical Reagent Co. Ltd. (Guangzhou, China) and used without further purification.

### 2.2. Catalyst preparation

In a typical process, 5 g cellulose powder was added into metal chloride solution with a metal ion concentration of 10 mmol/L, and the mixture was first stirred at room temperature for 0.5 h. Then, vacuum rotatory evaporator was used to remove the water in the mixture, and the remaining sample was placed in a vacuum oven at 333 K overnight. After sufficient grinding, the impregnated cellulose with a metal content of 1 mmol/g was obtained. Subsequently, the final powder was further carbonized at 673 K for 1 h under  $\text{N}_2$  atmosphere to produce the metal modified cellulose-derived amorphous carbon. Notably,  $\text{FeCl}_3$ ,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{SnCl}_4$  and  $\text{CrCl}_3$  were used as metal chloride precursors for impregnating treatment. As for sulfonation treatment, the resulting carbon was mixed with 98%  $\text{H}_2\text{SO}_4$  (carbon mass to  $\text{H}_2\text{SO}_4$  volume ratio at 1:10), followed by heating at 423 K in a  $\text{N}_2$  atmosphere to introduce functional  $-\text{SO}_3\text{H}$  groups. Soon afterwards, the mixture was diluted with deionized water and cooled to room temperature slowly, which was followed by filtrating and washing with hot deionized water (348 K) until the sulfate ions were no longer detected in the washed water. Finally, the resulting catalyst, denoted as AC-M- $\text{SO}_3\text{H}$ , was dried at 338 K for 12 h. In addition, Fe-impregnated carbon without sulfonation was defined as AC-Fe. For comparison purpose, normal carbon catalyst (AC- $\text{SO}_3\text{H}$ ) was also synthesized in the same way without metal-impregnating.

### 2.3. Characterization

Powder X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer using  $\text{Cu K}\alpha$  radiation generated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Ultra system employing an  $\text{Al K}\alpha$  radiation source. The binding energies for each spectrum were calibrated with a C 1s spectrum of 284.6 eV. High-resolution spectra of S 2p and O 1s were recorded at pass energy of 40 eV and resolution of 0.1 eV per step, for quantitative measurements of binding energy. Fourier transform infrared (FT-IR) absorbance spectra were measured on a Nicolet iN10 FT-IR Microscope to identify the

functional groups on the aromatic carbon structure. Raman spectroscopy was carried out on a LabRAM HR800 (HORIBA JY, France) using a continuous laser source at 515.5 nm.

The Brunauer-Emmett-Teller (BET) surface area measurements were performed with  $\text{N}_2$  adsorption-desorption isotherms at 77 K (SI-MP-10, Quantachrome). Before test, the samples were degassed under vacuum at 393 K for 16 h. The morphological analysis for prepared catalysts was carried out using high resolution transmission electron microscopy (HR-TEM, JEM-2100HR). For sample preparation, a small amount of catalysts were firstly dispersed in ethanol solution, and then a drop of the suspension was placed onto copper grid, followed by evaporating the solvent. Field emission scanning electron microscopy (FE-SEM) images of the samples were performed on a scanning electron microscope (Hitachi, S-4800) operating at an acceleration voltage of 3 kV.

The total acid densities of prepared carbonaceous material, including  $-\text{COOH}$ ,  $-\text{OH}$  groups and  $-\text{SO}_3\text{H}$  groups, were determined by titration method using phenolphthalein as an indicator. The  $-\text{SO}_3\text{H}$  densities of sulfonated materials were calculated from sulfur content in the carbon samples according to elemental analysis. The surface acidities of the carbons were measured by ammonia temperature-programmed desorption ( $\text{NH}_3$ -TPD) on a Micromeritics Autochem II 2920 chemisorption analyzer [33]. Briefly, the sample was heated up to 423 K at a rate of 15 K/min and stayed for 2 h in a He flow to remove adsorbed impurities. Then the sample was cooled to 373 K for the adsorption of  $\text{NH}_3$ . After flushing with He for 0.5 h to remove physically adsorbed  $\text{NH}_3$ , the TPD data were collected from 373 K to 1173 K with a ramp of 10 K/min.

### 2.4. Synthesis of EL

The experiments of direct conversion of carbohydrates into EL were performed in a 50 mL stainless steel reactor equipped with digital temperature indicator and magnetic stirring. The reactions were conducted at a temperature range of 463–483 K, catalyst dosage of 16.7–83.3% (relative to substrate mass) and reaction time range of 1.5–3.5 h, respectively. After desired reaction duration, the reactor was quenched in an ice cool water bath to terminate the reaction. The liquid sample was filtered and collected for analysis.

### 2.5. Products analysis

The quantity of liquid samples in organic phase was analyzed by Agilent 6890 equipped with a flame ionization detector (FID) and a KB-5 capillary column (30.0 m  $\times$  0.32  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ) using nitrogen as the carry gas. The GC-MS analysis was recorded on Agilent 6890 GC/MS, equipped with a 30 m HP-INNOWax (0.25 mm internal diameter). The operating conditions for GC-MS were as follows: injector port temperature, 513 K; column temperature, initial temperature 333 K (5 min), gradient rate 10 K/min, final temperature 493 K (2 min).

The HPLC analysis of sugars, HMF and LA in aqueous phase was performed on Shimadzu LC-20AT equipped with an UV/refractive index detector and a Shodex Sugar SH-1011 column ( $\varnothing 8 \times 300 \text{ mm}$ ). 0.005 M  $\text{H}_2\text{SO}_4$  was used as the mobile phase at a flow rate of 0.5 mL/min, and the column temperature was 323 K.

The corresponding formulas for calculating fructose conversion and product yield were defined below:

Conversion (%) = [Mol of fructose converted/mol of fructose fed]  $\times$  100

Yield (%) = [Mol of product obtained/mol of substrate fed]  $\times$  100

In addition, ROF was defined as the rate of EL formation per gram of catalyst per hour.

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