



Esterification of levulinic acid with ethanol catalyzed by sulfonated carbon catalysts: Promotional effects of additional functional groups

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ABSTRACT

Analysis of literature data on acid-catalyzed esterification reaction of levulinic acid (LA) with ethanol (EtOH) has suggested that some sulfonated carbon catalysts exhibit higher active-site performance than other solid acid catalysts such as macroreticular resins bearing sulfonic acid groups, zeolites, mesoporous silica functionalized with alkyl- and arene-sulfonic acid groups. To elucidate factors that enable the higher performance of sulfonated carbon catalysts, a series of sulfonated carbon catalysts was synthesized by sulfonating various carbon materials whose concentrations of surface oxygen-containing functional groups, porous structure, and swelling ability differ significantly. The catalysts were tested not only in the liquid-phase esterification reaction of LA with EtOH but also in the reaction of acetic acid (AcA) with EtOH because the latter reaction serves as a test reaction to probe the performance of $-SO_3H$ sites with minimal influence by mass transfer limitation and to provide an insight into a role of γ -keto group of LA in catalysis. The results show that all catalysts exhibit nearly the same turnover frequency per $-SO_3H$ site in the esterification reaction of AcA with EtOH despite widely different structural properties. In contrast, the data indicate that neighboring functional groups such as $-COOH$ and $-OH$ facilitate the reaction of LA with EtOH presumably through hydrogen-bonding interaction between these surface functional groups and γ -keto group of LA. These results suggest a general design strategy to improve the performance of solid acid catalysts further by precisely tuning the distance between $-SO_3H$ sites and neighboring functional groups.

1. Introduction

Levulinic acid (LA) has been identified as one of the most important value-added chemicals derived from biomass [1]. Two functional groups (ketone and carboxylic acid) in LA render it as important building blocks for the production of various biomass-derived commodities [2,3]. In addition, LA has been produced in large quantity for years [2], and new processes have been recently developed [4], expanding its large-scale production.

Esters of LA have been used as ingredients for flavour and fragrance and tested as an additive for transportation fuels [5–8]. Ethyl levulinate, for example, can be produced by esterification of LA with ethanol (EtOH) or by ethanolation of furfuryl alcohol [9]. Like many other liquid-phase esterification reactions [10–13], esterification of LA with short-chain alcohols is catalyzed by both soluble and solid acid catalysts [5,6,8]. Mineral acids such as H_2SO_4 are cost-effective catalysts to produce ethyl levulinate via esterification reaction. However, solid acid catalysts provide advantages of ease of separation from reaction products and lack of corrosion of reactor materials. Therefore, various solid

acid catalysts including zeolites [14], resin catalysts [15], supported heteropoly acids [16], sulfonated ZrO_2 [17] or SnO_2 [14], organosilica or mesoporous silica incorporating $-SO_3H$ groups [18,19], and sulfonated carbons [20–22] have been investigated as a potential catalyst for this conversion.

Analysis of literature data on acid-catalyzed esterification of LA with short-chain alcohols has suggested that some sulfonated carbon catalysts [20,21] exhibit higher performance than other solid acid catalysts such as Amberlyst-15 (ion-exchange resin consisting of macroreticular polystyrene with strongly acidic sulfonic group) [14,18], SAC-13 (SiO₂-supported Nafion) [18], mesoporous silica (SBA-15) functionalized with alkyl sulfonic acid groups [18], zeolite Beta [14,23], and HY zeolite [14] when initial rates were calculated and compared per strong acid site quantified by NH_3 temperature-programmed desorption (TPD), base titration using NaOH aq. or other methods reported in the literature and summarized in Table S1 in the Supplementary information. Only limited types of acid catalysts (soluble *p*-toluenesulfonic acid (*p*-TSA) [8] and organosilica nanotubes functionalized with both heteropoly acid and ZrO_2 [16]) appear to

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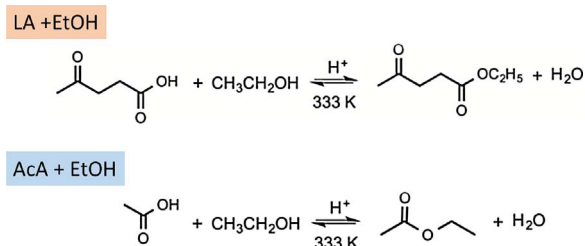
exhibit activity comparable to the sulfonated carbon catalysts. This analysis has raised questions about why some sulfonated carbon catalysts seem to perform better than others, and about whether there is a specific carbon catalyst performs better than others. In this work, we chose to investigate carbon-based catalysts for this reaction, aimed to address the second question, and thereby obtain a design principle to improve catalyst performance for this reaction further. Carbon-based catalysts potentially provide advantages because their porous structure and surface properties can be tailored by choosing the type of carbon materials and synthesis conditions of carbon precursors. In our previous work with phenolic-resin-derived carbon catalysts [24], we demonstrated that surface hydrophobicity and mesoporosity of catalysts can be tailored by synthesis conditions of precursor resins and their pyrolyzation temperature. In addition, we showed how these factors influence the performance of catalysts in three different acid-catalyzed reactions. In the current work, the type of carbon materials has been expanded to traditional carbon catalysts based on activated carbon and carbon nanotubes as well as graphite oxides and carbohydrate-based catalysts, which have become more common recently [13,20,25].

Challenges to achieve this goal include complex interplays of effects of porous structures, surface hydrophobicity/hydrophilicity, and swelling ability of some catalysts [25] that is also common in ion-exchange resin catalysts but challenging to evaluate its effect on overall performance [26]. Thus, we sought a way to resolve these effects by synthesizing a set of sulfonated carbon catalysts from various carbon sources, and conducting a test esterification reaction of acetic acid (AcA) with EtOH in addition to that of LA with EtOH (Scheme 1). We chose the reaction of AcA with EtOH because it can be considered as prototypical for esterification reaction, and the reactants are small enough to minimize effects of mass transfer limitations (kinetic diameter of AcA is reported to be 0.436 nm [27]). In addition, by comparing the data for the reaction of LA with that of AcA, we anticipated that we can investigate the effect of γ -keto group of LA on catalysis. We compare catalyst performance by apparent initial turnover frequency (TOF) rather than rate per catalyst mass to compare active-site performance and to minimize effects of product water on $-\text{SO}_3\text{H}$ groups [28,29]. We report our findings that additional surface functional groups such as $-\text{COOH}$ and $-\text{OH}$ groups in some carbon catalysts (carbonaceous catalysts) facilitate the reaction of LA with EtOH.

2. Experimental

2.1. Materials

Levulinic acid (97%), acetic acid (99.7%), ethanol (99.5%), D-glucose, cellulose, 0.01 N NaOH aq., and 0.01 N HCl aq. were purchased from Wako Pure Chemical Industries Ltd. Resorcinol (99.0%), formaldehyde (36.0 wt% aq.), sodium carbonate (99.8%), 1 N HCl aq., *tert*-butyl alcohol (99.0%), and sulfuric acid (98%) were purchased from Tokyo Chemical Industry Co. Ltd. Activated carbon (Norit GAC 1240W), Amberlyst-15 (hydrogen form), and multi-walled carbon nanotubes (SMW210, Sigma-Aldrich, BET surface area = $350\text{ m}^2\text{ g}^{-1}$) were purchased from Sigma-Aldrich Japan. Natural graphite powder (z-5F) was received from Ito Graphite Industry Co. Ltd.



Scheme 1. Esterification reactions tested in this work.

2.2. Syntheses of catalysts

Catalysts were synthesized by sulfonating carbon materials using sulfuric acids under N_2 atmosphere. Graphite oxides (GO) were synthesized by oxidizing natural graphite powder (z-5F) by Hummers method [30]. Pyrolyzation of glucose and cellulose was conducted by heating 1.0 g of D-glucose and cellulose powder, respectively, in $100\text{ mL min}^{-1}\text{ N}_2$ to 673 K at a ramp rate of 5 K min^{-1} and holding the temperature at 673 K for 15 h. The resultant materials are designated as Glu and Cel, respectively. Hydrothermal treatment of glucose was conducted by heating a D-glucose solution (1 g/mL) in a sealed 23-mL Teflon-lined autoclave at 453 K for 24 h under static conditions. The resultant material is designated as HTGlu. Four different carbon gels (CG) were synthesized by pyrolyzing two different resorcinol-formaldehyde resins at different temperatures [24,31]. The resins were synthesized at a molar ratio of resorcinol (R) and sodium carbonate (C) of 50 and 200, and pyrolyzed at 673 or 1273 K. The resultant materials are designated as CG-x-y where x and y represent a R/C ratio and pyrolyzation temperature, respectively. CGs were sulfonated as reported previously [24]. Activated carbon (AC), multi-walled carbon nanotubes (CNT), GO, Glu, Cel, and HTGlu were sulfonated by heating them in concentrated H_2SO_4 at 353 K for 15 h, followed by deep washing with distilled water. Sulfonated materials are designated by adding S at the beginning of each name. For example, sulfonated AC and CNT are designated as SAC and SCNT, respectively.

2.3. Characterization of catalysts

Surface functional groups of the carbon catalysts were characterized by IR spectroscopy. Measurements were performed in a transmission mode under dynamic vacuum using a JASCO FT/IR-6100 Fourier transform spectrometer with a spectral resolution of 4 cm^{-1} . Acidic functional groups of the carbon catalysts were quantified by Boehm titration [32]. The standardization of NaOH solutions was performed using potassium hydrogen phthalate as the primary standard and phenolphthalein as the indicator. The carbon and oxygen concentrations in the catalysts were determined through CHN analysis (CHN: MICRO CORDER JM10, J-SCIENCE LAB Co.) while their sulfur concentrations were determined by ion chromatography analysis (Dionex ICS1600, Thermo Fisher Scientific Inc.) both at the Global Facility Center of the Creative Research Institution at Hokkaido University. The carbon and oxygen concentrations obtained from the elemental analysis were corrected after the moisture content of carbon catalysts was determined by thermogravimetric analysis (TGA), which assumed that the weight loss below 373 K arises from desorption of physisorbed water. Powder X-ray diffraction of carbon materials were measured on a Rigaku RINT Ultima IV with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$) and a D/teX Ultra detector. Data were collected in a continuous mode over $5 \leq 2\theta \leq 60^\circ$ in 0.05° step width with a scan speed of 0.16° s^{-1} . TG measurements were conducted on a Shimadzu TGA-50 thermogravimetric analyzer by heating approximately 10 mg of a catalyst in a platinum crucible to 1073 K at 10 K min^{-1} in a $20\text{ cm}^3\text{ min}^{-1}\text{ N}_2$ flow. The textural property of catalysts was characterized through nitrogen adsorption measurements. The adsorption isotherms were collected at 77 K on an adsorption apparatus BELSORP-mini II (MicrotracBEL Co.). Prior to analysis, samples were heated at 523 K in a $30\text{ mL min}^{-1}\text{ N}_2$ flow for 4 h. The surface areas of the catalysts were calculated by the Brunauer-Emmett-Teller (BET) method [33] in a relative pressure range of 0.05–0.3. The micropore volume (V_{micro}) of catalysts was calculated from N_2 uptake at $P/P_0 = 0.15$. The mesopore volume (V_{meso}) of catalysts was calculated by subtracting V_{micro} from the total volume calculated from N_2 uptake at $P/P_0 = 0.98$. Mesopore size distributions were determined by applying the Dollimore-Heal method [34] to the adsorption branch of isotherms.

To evaluate hydrophilicity of catalyst surface, water vapor adsorption isotherms were measured at 298 K on an adsorption apparatus

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