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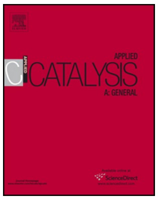

Esterification of levulinic acid with ethanol over sulfated Si-doped ZrO_2 solid acid catalyst: Study of the structure–activity relationships

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ABSTRACT

Esterification of levulinic acid with ethanol to produce ethyl levulinate was examined by using sulfated Si-doped ZrO_2 solid acid catalysts with enlarged surface areas and the relationships between the structural properties and catalytic performances were investigated. Structures of the catalysts were verified by XRD, nitrogen physisorption, FE-SEM, UV–vis and FTIR measurements. Acidity of the catalysts that substantially affect the catalytic activity was evaluated by NH_3-TPD measurement. Incorporation of Si atom into the lattice structure of ZrO_2 (up to 30 mol% Si per Zr atom) afforded high-surface-area SiO_2-ZrO_2 mixed oxides, and their sulfated forms provided increased numbers of sulfate anions and the associated acid sites. Several distinct correlations were found between the structural properties/acidities and catalytic activities, which suggested that (i) the number of accessible active acid sites and (ii) the accessibility of the organic reactants to the active sites play crucial roles in determining the overall activity. Among the catalysts tested, sulfated Si-doped ZrO_2 with optimum Si content (5.0–10 mol% Si per Zr) was found to be the best catalyst, the activity of which was far superior to that of the conventional sulfated ZrO_2. In addition, direct conversion of cellulosic sugars (glucose and fructose) into levulinate esters was also examined, in view of their practical applications in acid-catalyzed biomass conversion processes.

1. Introduction

Due to increasing global energy consumption and gradual depletion of fossil fuel resources, utilization of lignocellulosic biomass to produce chemicals, fuels, and energy has attracted considerable attention [1–3]. Various kinds of value-added platform molecules and biofuels can be produced from lignocellulosic biomass and its derivatives through gasification, fermentation, hydrogenolysis and chemical transformation [1–5]. Among those, levulinic acid (LA) and its esters are considered as one of the most promising platform chemicals that can be used for a range of derivatives in the biofuel, solvent, polymer and specialty chemicals markets [1–7]. LA is generally produced by acid-catalyzed hydrolysis of lignocellulosic biomass, including cellulose, glucose and fructose, and can catalytically be upgraded to levulinate esters [8–11], γ-valerolactone (GVL) [12–15], α-methylene-γ-valerolactone [16], olefins (via ring-opening and decarboxylation of GVL) [17,18], 2-methyl tetrahydrofuran (via 1,4-pentanediol) [19] and 5-nonanone (via pentanoic acid) [20] as well as diphenolic acid as an intermediate for the synthesis of epoxy resins and polycarbonates [21,22]. Levulinate esters are known to be useful as plasticizers and solvents, and have been suggested as fuel additives. For example, ethyl levulinate can be used up to 5 wt.% as a diesel miscible biofuel in regular diesel car engines, owing to the physicochemical properties similar to the biodiesel fatty acid methyl esters (FAME) [8]. Therefore production of these esters from cellulosic biomass offers not only a low-cost alternative route to their manufacture, but also a possibility to reduce the consumption of petroleum-derived fossil fuels.

The typical catalysts used for esterification of LA with alcohols are mineral acids such as HCl, H_2SO_4 and H_3PO_4 that can provide high yields of products within a short reaction period [23]. However, due to catalyst unrecyclability, harsh reaction conditions and operational problems (e.g., use of a large volume of base for neutralization and corrosion of equipment), replacement of such homogeneous catalysts by heterogeneous analogues that are easily separable and reusable over repeated cycles is highly desirable. For acid-catalyzed esterification, acid resins, heteropolyacids, zeolites, metal oxides, and metal salts among others have generally been claimed to be effective as heterogeneous acid catalysts. Several

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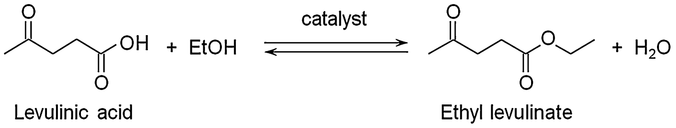

Scheme 1. Esterification of levulinic acid with ethanol.

types of heterogeneous acid catalysts have been applied to the esterification of LA with ethanol (Scheme 1) by Silva and co-workers, who demonstrated that sulfated mixed oxides (sulfated zirconia (SO_4^{2-}/ZrO_2), niobia (SO_4^{2-}/Nb_2O_5), titania (SO_4^{2-}/TiO_2) and stannia (SO_4^{2-}/SnO_2)) bearing a number of strong acid sites are good candidates for this reaction [8]. Owing to their strong acidity and excellent thermal stability, sulfated mixed oxides are known to have an ability to directly produce levulinate esters from cellulosic sugars in alcohol media [24,25].

A typical sulfated zirconia prepared by treatment with aqueous H_2SO_4 or $(NH_4)_2SO_4$ of dried zirconia powder, followed by calcination in air at 600 °C contains 1–4 S atoms/nm^2 (0.5–2.0 wt.% S) [26–30]. One of the main drawbacks of zirconia-based solid acid catalysts, however, is their low surface area (less than 100 m^2/g), which restricts the reaction interface, and thus most of the active sites are not accessible by reactants. Intensive research efforts have been recently devoted to the improvement of their textural properties, mainly by combining with some materials possessing high surface area such as silica. The combination of silica and zirconia not only increases the surface area of zirconia, but also improves its acidity and stability [31,32]. For the preparation of sulfated silica-zirconia materials, various methods have been developed, which include physical mixing of the component oxides [29], chemical solution decomposition method [31], incipient wetness impregnation method [33,34], co-precipitation method [35] and sol–gel method [36–39], however, these attempts sometimes result in equal or lower activities per gram of catalyst compared with the bulk material due to the limitation in Zr loading. On sulfated zirconia materials, developing efficient synthetic routes to improve the textural properties and to stabilize the acidic phase with high sulfur retention ability still remains a challenging topic, and it is scientifically important to study the relationships between the textural properties and catalytic performances, where a number of factors are working simultaneously.

To better understand the influences of textural and acidic properties of sulfated zirconia materials on their catalytic performances, we report here a systematic study of the structure–activity relationships using a series of sulfated Si-doped ZrO_2, with the objective of maximizing the final surface area, active site accessibility and the overall catalytic activity, in view of their practical applications in acid-catalyzed biomass conversion processes. A series of sulfated Si-doped zirconia with varied Si content are synthesized by co-precipitation and the subsequent impregnation method. The activities of the catalysts are evaluated by the esterification of LA with ethanol at 70 °C and are compared with that of the conventional sulfated zirconia. The recyclability and stability of the catalysts which are important for practical catalytic operations are also discussed. In addition, conversions of cellulosic sugars (glucose and fructose) directly into levulinate esters by acid-catalyzed solvolysis in methanol are also examined using a few selected catalysts.

2. Experimental

2.1. Preparation of sulfated Si-doped ZrO_2

A series of sulfated Si-doped zirconia with varied Si content were synthesized by co-precipitation method under basic conditions and the subsequent impregnation procedure [35,40]. Typically, 13.5 g of zirconium oxynitrate dihydrate ($ZrO(NO_3)_2 \cdot 2H_2O$; 99%, Wako Pure Chemical Ind. Ltd.) was completely dissolved in 500 mL of deionized water in a teflon flask to avoid the Si dissolution from glass containers. To this solution, 10 mL of ethanol solution containing a designated amount of tetraethylorthosilicate (TEOS; 95%, Wako Pure Chemical Ind. Ltd.) was added, and subsequently solution pH was adjusted to 9.0 by dropwise addition of 10% aqueous NH_3 solution (Wako Pure Chemical Ind. Ltd.) with homogenization at a rotation speed of 12,000 rpm using a homogenizer. The homogenization was continued for 30 min and the obtained gel was aged at room temperature for 48 h, followed by filtration, washing with 5 L of deionized water and drying at 100 °C overnight. The thus obtained solids were granulated, sieved and subsequently sulfated by impregnating 1.0 g of solid in 15 mL of 1.0 M sulfuric acid solutions for 1 h, followed by vacuum filtration, drying at 100 °C overnight and calcination in air at 600 °C for 3 h. The obtained samples were labeled $SO_4^{2-}/Si\textit{x}\text{-}ZrO_2$, where *x* denotes the atomic ratio of Si/Zr in the initial gel solution.

For comparison, a sulfated zirconia (SO_4^{2-}/ZrO_2) was prepared the same way as the above procedure except for the addition of silicon source.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku RINT 2000 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å) over the 2θ range from 10 to 80°. Nitrogen adsorption–desorption measurements were performed at −196 °C by using Micromeritics ASAP2020. The samples were degassed at 300 °C under vacuum for 4 h to vaporize physisorbed water prior to data collection. Specific surface areas were calculated by the BET (Brunauer–Emmett–Teller) method by using adsorption data ranging from $P/P_0 = 0.05$ to 0.30. The pore size distributions were obtained from the adsorption branch of the nitrogen isotherms by the BJH (Barret–Joyner–Halenda) method. The field emission scanning electron microscopy (FE-SEM) images were obtained with a HITACHI S-4800 equipped with an energy dispersive X-ray system (EDX; HORIBA, EMAX ENERGY), by which the elemental analysis was performed. The samples were observed without metal coating to observe genuine surface morphology. Infrared spectra were recorded with a JASCO FTIR-6300 instrument in the spectral range 2000–400 cm^{-1} under vacuum with a resolution of 4 cm^{-1} using the KBr pellet technique, where 2 mg of the sample was mixed with 200 mg of analytical grade KBr. A total of 128 scans were collected to obtain each spectrum. Diffuse reflectance UV–vis spectra were collected using a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere in the spectral range of 200–400 nm. Absorption spectra were obtained using the Kubelka–Munk function.

The acidity of catalysts was studied by temperature programmed desorption of NH_3 (NH_3-TPD) by using a BELCAT-B system (BEL Japan, Inc.). Approximately 100 mg of each sample was mounted in a quartz tube and was preheated under a He flow (50 mL/min) at 600 °C for 1 h, allowed to cool to 50 °C, and subsequently exposed to flowing 5% NH_3/He gas mixture (50 mL/min) for 1 h. After being purged at 50 °C for 0.5 h with He to eliminate weakly adsorbed NH_3, NH_3-TPD was carried out between 50 and 600 °C under a He flow (30 mL/min) with a ramping rate of 10 °C/min, and the desorbed NH_3 was quantified by an on-line thermal conductivity detector.

2.3. Esterification of levulinic acid with ethanol

Levulinic acid esterification was performed in a quartz glass reactor with a reflux condenser. Into a reactor were placed solid acid