Highly efficient conversion of glucose into methyl levulinate catalyzed by tin-exchanged montmorillonite

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ABSTRACT

Tin-exchanged montmorillonite catalysts were prepared by an ion exchange method and examined as solid acid catalysts. The synthesized catalysts were characterized by X-ray fluorescence spectroscopy, inductively coupled plasma optical emission spectroscopy, N_2 adsorption—desorption analysis, powder X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, NH_3 temperature-programmed desorption analysis, and pyridine adsorption Fourier transform infrared spectroscopy. Subsequently, the catalysts were examined for use in the conversion of glucose into methyl levulinate in methanol. A high yield of methyl levulinate of 59.7% was obtained upon conversion of 0.3 g glucose in 24 g methanol over 0.15 g catalyst at 220 °C under 2 MPa N_2 for 6 h. The recyclability of the catalyst was also examined, and the conversions of glucose and methanol remained mostly unchanged under repeated usage of the catalyst in five catalytic runs; in contrast, the yield of methyl levulinate decreased slightly. The excellent catalytic performance of the tin-exchanged montmorillonite catalyst was attributed to a combination of the presence of a large amount of acidic sites and balanced amounts of Lewis and Brønsted acid sites on the catalyst.

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1. Introduction

Biomass, a renewable carbon resource, is a promising alternative to diminishing fossil resources for the provision of chemicals and fuels [1,2]. However, currently, the development of economical, efficient, and environmentally friendly technologies to convert biomass into chemicals and fuels represents a huge challenge. Recently, the transformation of carbohydrate biomass into value-added chemicals, such as 5-hydroxymethylfurfural [3,4], levulinic acid [5], and levulinate esters [6], has drawn enormous attention. Levulinate esters, such as methyl levulinate, ethyl levulinate, and butyl levulinate, are used as additives for the transportation fuels, as substrates for various condensation and addition reactions, and as feedstock in the flavoring and fragrance industries [7].

Levulinate esters can be produced from various materials, such as sugars (xylose, fructose, glucose) [8—24], cellulose [25—35], and even raw biomass materials [36]. Much effort has been devoted to improve the production of levulinate esters from carbohydrate biomass. To date, various homogeneous and heterogeneous catalysts have been developed to convert biomass materials into levulinate esters. Mineral acids, metal salts, and sulfonic acid-functionalized ionic liquids (SO_3H-ILS) have been used as efficient homogeneous catalysts for biomass alcoholysis to methyl levulinate. For instance, Peng et al. [13] reported the use of sulfuric acid at low concentrations (≤ 0.01 mol L^{-1}) as a catalyst for the conversion of glucose into methyl levulinate at 200 °C in methanol; a methyl levulinate yield of 50% was obtained. Saravanamurugan et al. [14] reported the use of SO_3H-ILS in the catalytic transformation of sugars to ethyl levulinate. Specifically, the ILS displayed a high catalytic activity toward the conversion of fructose into ethyl levulinate, achieving a yield of 77%. However, the catalyst was not effective in the conversion of glucose because of the high stability of the glucose rings. Conversely, glucose was converted into ethyl-*d*-glucopyranoside (63% yield) primarily, with a lower yield of ethyl levulinate. Zhou et al. [15] demonstrated the efficacy of $Al_2(SO_4)_3$ as a catalyst in the alcoholysis of glucose and a methyl levulinate yield of 64% was obtained at 160 °C. In another study, a mixed acids system containing both Brønsted and Lewis acids was examined and displayed superior performance in the alcoholysis of cellulose

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and glucose. Tominaga et al. [27] used a triflate salt as a Lewis acid and an organic acid as a Brønsted acid to synthesize methyl levulinate from cellulose and glucose. Specifically, methyl levulinate (75% yield) was obtained from cellulose using $In(OTf)_3$ and 2-naphthalenesulfonic acid as the catalyst system at 180 °C for 5 h. In contrast, a lower methyl levulinate yield of 58% was obtained from glucose using $In(OTf)_3$ as the sole catalyst at 160 °C. Although the above-exemplified homogeneous catalysts are effective for the conversion of carbohydrate biomass into levulinate esters, the catalysts are difficult to separate and recycle, thereby making the process potentially costly.

Various solid catalysts have been used to produce levulinate esters from carbohydrates. Peng et al. [17] investigated ZSM-5, NaY, H-mordenite, $Zr_3(PO_4)_4$, SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, and TiO_2 as solid acid catalysts in the conversion of glucose into methyl levulinate in near-critical methanol. Methyl levulinate was produced with a yield of 33% when the reaction was conducted at 200 °C for 2 h using SO_4^{2-}/TiO_2 as the catalyst. Saravanamurugan et al. [19] employed H-USY as a catalyst to obtain methyl levulinate from glucose, and methyl levulinate esters were obtained with a yield of ~49% at 160 °C for 20 h. In a subsequent study, Zhou et al. [22] investigated the catalytic performance of H-USY treated with nitric acid for use in the conversion of glucose in methanol; methyl levulinate was obtained with a yield of 54% at 180 °C for 20 h. Xu et al. [23] reported the use of sulfated montmorillonite as an efficient catalyst in the conversion of glucose and achieved a methyl levulinate yield of 48% at 200 °C for 4 h. Recently, Kuo et al. [24] reported that acidic TiO_2 nanoparticles exhibited superior activity and selectivity towards methyl levulinate from glucose in methanol, methyl levulinate was obtained with a yield of 61% at 175 °C for 9 h. However, the catalyst deactivated gradually during recycling.

Despite the progress made to date, the development of an efficient and environmental benign catalyst that can afford high yields of levulinate esters and good stability is still imperative for cost-effective conversion of biomass feedstocks.

Of particular interest, montmorillonite (Mt) has a large surface area, significant cation-exchange ability, expansible interlayer space, a good adsorption capacity, and flexible and tunable acidity. Mt is composed of aluminosilicate layers, where one octahedral alumina sheet is sandwiched between two tetrahedral silica sheets. In the aluminosilicate layers, partial isomorphous substitution of Si(IV) ions by trivalent metal cations and Al(III) ions by divalent metal cations causes a charge deficit. To balance this charge deficit, a number of exchangeable hydrated alkali and alkaline earth metal cations occupy the interlayer space of montmorillonite [37].Various types of metal cations can be readily introduced in the expansible interlayers. Metal cations-exchanged Mt comprises both Lewis and Brønsted acid sites that enable Mt to operate as an effective and environmentally benign heterogeneous catalyst in acid-catalyzed organic transformations with excellent product selectivity [38–42].

On the other hand, it has been reported that the incorporation of tin to the frame of zeolites results in highly efficient catalysts for converting monosaccharides or different biomass sources into high-valued chemicals [43,44].

In our previous study, various metal ion-exchanged Mt catalysts were examined in the conversion of glucose to methyl levulinate. We found that Al-exchanged Mt with well-balanced amounts of Lewis and Brønsted acid sites showed excellent activity and stability in this reaction [45]. In the present study, we demonstrate the excellent catalytic activity of tin-exchanged Mt toward the conversion of glucose in methanol—a methyl levulinate yield of ~60% was obtained. Moreover, the tin-exchanged Mt catalyst could be reused at least five times without significant losses in the product yield. Detailed process parameters including reaction time,

temperature, substrate amount, and the reusability of the catalyst were investigated in terms of catalytic performance. Moreover, different carbohydrate sources were studied.

2. Experimental

2.1. Chemicals

$SnCl_4·5H_2O$ (≥99%), D-glucose (≥99%), sucrose (≥99%), D-fructose (≥99%), starch (≥99%), cellobiose (≥99%), methyl formate (≥99.5%), and methanol (≥99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Microcrystalline cellulose (degree of polymerization 250, crystalline index 70%, and average particle size 20 μm) was obtained from Sigma-Aldrich. Methyl-glucoside (≥99%) was purchased from Aladdin Reagent Co. Ltd.. Methyl levulinate (≥99%) and methyl lactate (≥99%) were obtained from Tokyo Chemical Industry Co. Ltd.. Na/Mt was purchased from Zhejiang San-Ding Technological Reagent Co. Ltd. (China). Inulin (≥99%) and K10 Mt were purchased from Alfa Aesar.

2.2. Preparation of the catalysts

Ion exchange was used to prepare tin-exchanged Mt catalysts. In a typical synthesis, 1 g Na/Mt was ion-exchanged with 150 mL aqueous solution of $SnCl_4·5H_2O$ (12.9 mmol L^{-1}) at 60 °C for 12 h with stirring. The resulting slurry was filtered and repeatedly washed with deionized water until the pH of the filtrate was neutral. Subsequently, the sample was dried at 120 °C. The resultant product is denoted as Sn/Mt. Then, Sn/Mt was calcined at 300, 400, or 500 °C in static air for 3 h to obtain a series of Sn/Mt catalysts which are correspondingly denoted as Sn/Mt-300, Sn/Mt-400, and Sn/Mt-500. A similar method was used to synthesize tin-exchanged K10 Mt (Sn/K10).

2.3. Characterization of the catalysts

The relative content of each element in the catalysts was determined via X-ray fluorescence (XRF) spectroscopy on a Shimadzu XRF-1800 X-ray fluorescence spectrometer (40 kV, 95 mA). The tin content was more accurately determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Teledyne Leeman Labs Prodigy7 apparatus.

The specific surface areas and pore size distribution of the samples were obtained by N_2 adsorption–desorption measurements at −196.2 °C using a Micromeritics ASAP 2020M system. Prior to the measurements, the samples were outgassed at 150 °C for 4 h. The surface area (S_{BET}) values of the samples were calculated using the Brunauer–Emmett–Teller (BET) equation. The pore size distributions were derived from the desorption branch of the N_2 isotherms using the Barrett–Joyner–Halenda (BJH) method. The total pore volume (V_p) values were estimated by considering the nitrogen uptake at a relative pressure (P/P_0) of ~0.99. The average pore diameter (D_p) of the samples was calculated from the surface area and the total pore volume ($D_p = 4V_p/S_{BET}$).

The crystal structures of the catalysts were characterized by powder X-ray diffraction (XRD) on a Rigaku D/MAX2550VB X-ray diffractometer (35 kV, 40 mA) with a Cu Kα source. The diffraction patterns were recorded in 2θ ranging from 10° to 80° at a scan rate of 8° min^{-1} and from 2° to 12° at a scan rate of 1° min^{-1}. The UV–visible diffuse reflectance spectra were recorded on a Perkin-Elmer Lambd-950 spectrophotometer using $BaSO_4$ as a reference. The IR spectra were recorded on a Thermo Fisher Nicolet IS10 spectrometer using the KBr disk technique. The concentration of the sample in KBr was 1.0 wt%, and 0.1 g KBr was used in the preparation of the reference and sample disks. The chemical states