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Full Length Article

Experimental and kinetic study of glucose conversion to levulinic acid in aqueous medium over Cr/HZSM-5 catalyst

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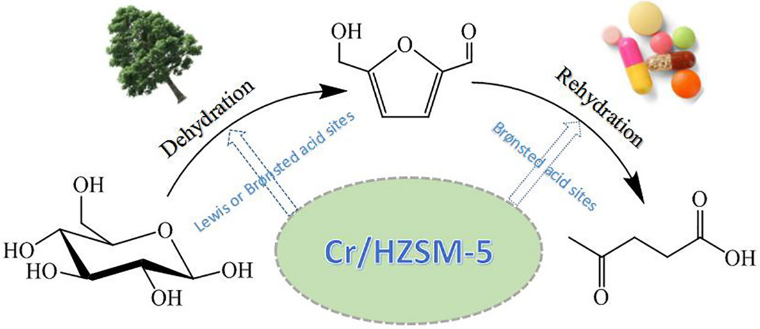
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a series of Cr modified HZSM-5 catalysts were synthesized, characterized, and tested for the conversion of glucose to levulinic acid (LA). The results showed that the catalyst with larger surface area, high acid density, and appropriate ratio of Lewis acid to Brønsted acid seemed beneficial for LA production from glucose. The highest LA yield of 64.4 mol% was obtained from 100 mol% glucose conversion at 180 °C for 180 min with 0.75 g 8%Cr/HZSM-5 catalyst. Furthermore, a simplified kinetic analysis which based on the pseudo first-order model was also developed to describe the behavior of glucose conversion to LA, and the results showed that the conversion of glucose to LA was a sequential reaction which consisted of glucose dehydration and HMF rehydration. The activation energy for glucose dehydration and HMF rehydration over 8%Cr/HZSM-5 catalyst were 69.1 and 54.0 kJ/mol, respectively, significantly lower than those over HZSM-5, which would be attributed to the impregnation of Cr into HZSM-5 enhancing the catalyst Lewis acid, and thus finally accelerated the glucose conversion through glucose-fructose isomerization, however, excessive Lewis acid also resulted the glucose into byproducts. Finally, the recycling experiments indicated that the Cr/HZSM-5 catalyst can be reused for at least four times with the activity loss less than 13.1%. It can be concluded that the Cr/HZSM-5 catalyst is an efficient and stable catalyst for LA production from glucose in aqueous media.

1. Introduction

Due to a lack of resource sustainability of fossil fuels as well as negative environmental effects from emissions, research is being done to find a liquid fuels for use as a gasoline replacement [1]. Biomass, the only sustainable source of organic compounds and has been proposed as the ideal material for the production of durable fuels and chemicals [2,3]. The carbohydrates present in the biomass can be depolymerized

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into sugar firstly, and then further converted into various chemical platforms, such as furfural, hydroxymethylfurfural (HMF), lactic acid, and LA [4–7]. LA is a versatile building block containing a carbonyl group and a carboxyl group, thus can be used as the raw material for further synthesis of various high-value chemicals. For example, hydrogenation of LA with molecular hydrogen or other hydrogen donors produces gamma-valerolactone (GVL), which can be used as liquid transportation fuel replacing ethanol in gasoline-ethanol mixture [8]. Esterification of LA with low-carbon alcohol (such as C_1 or C_2 alcohols) produces levulinic esters, which can be widely used in the food industry, as solvents or plasticizers [9,10]. Besides, LA also can be served as a feedstock for the production of liquid hydrocarbon fuels through a number of catalytic routes [11].

Generally, the conversion of carbohydrate into LA can be divided into three steps. Firstly, carbohydrate was hydrolyzed into water-soluble glucose with acidic medium, then the generated glucose was dehydrated into HMF, and subsequently the formed HMF was further converted into LA and formic acid (FA) with two molecules of water [12,13]. In the earlier cases, homogeneous Brønsted acids, such as H_2SO_4, HCl, and H_3PO_4, were often used as acidic medium for glucose conversion to LA. However, low LA yield and prolonged reaction time were often reported in these studies [14–16]. Recently, we have proposed a synergic catalytic mechanism for the glucose conversion to LA through coupling of H_3PO_4 and $CrCl_3$ as a mixed catalyst. The results showed that the combination of this Brønsted and Lewis acids in a single pot overcomes equilibrium limitations of glucose-fructose isomerization leading to acceleration glucose conversion and thus finally enhancing the LA yield in a shorter reaction time [17]. However, directly use of this homogenous mixed H_3PO_4-$CrCl_3$ catalyst still involves several problems such as equipment corrosion, environment pollution, and difficult recycling. Therefore, immobilizing these Brønsted and Lewis acids on the same solid supporter is highly recommended owing to solid acids absence of corrosiveness, environmentally friendly and easy to recovery [18].

HZSM-5, as a kind of H-type zeolite, has been extensively studied as the catalyst or catalyst support for various dehydration reactions owing to its large amount and strength of Brønsted acid sites [19–21]. Besides, its special three-dimensional channel structure, high specific surface area, and good thermal stability were also beneficial for various catalytic reactions [22]. However, by using HZSM-5 alone as catalyst for glucose dehydration reaction, the low LA yield has been reported during previous literatures [23,24]. This condition can be attributed to the absence of Lewis acid site of the catalyst, which means the glucose feedstock cannot be isomerized to fructose and thus finally resulted the low LA yield. In addition, the low acid density of the HZSM-5 catalyst could also be the reason for the low LA yield. Therefore, modification of HZSM-5 catalyst with Lewis acid to form a new catalyst might improve the catalytic properties and enhance the LA production at adequate process conditions.

Given the shortages of HZSM-5 zeolite in above discussion, a series of Cr modified HZSM-5 catalysts were prepared by impregnation method and evaluated for the conversion of glucose to LA in this study. Furthermore, in order to understand the relationship between catalyst physicochemical properties and catalytic activity in the production of LA from glucose, both the Cr modified HZSM-5 catalysts and HZSM-5 parent were characterized by XRD, FTIR, AAS, N_2 absorption, NH_3-TPD, and Py-FTIR. Besides, the kinetic model of glucose conversion to LA catalyzed by both Cr/HZSM-5 and HZSM-5 were also developed and the corresponding kinetic parameters were calculated based on the experiment data. Finally, the reusability of the Cr/HZSM-5 catalyst was also investigated in this study.

2. Experimental

2.1. Materials

Glucose (99.5%) used as feedstock in this study was supplied by Sigma-Aldrich and dried to constant weight prior to use. Catalyst precursors HZSM-5 and $CrCl_3 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd., China and used as received. Standard reagents such as glucose, HMF, LA, and FA were all supplied by Sigma-Aldrich and used without any further pretreatment.

2.2. Catalyst preparation

The Cr/HZSM-5 catalysts were prepared by wet impregnation method [25]. Firstly, $CrCl_3 \cdot 6H_2O$ aqueous solution and HZSM-5 zeolite powder with certain weight ratio of Cr^{3+} to zeolite were mixed and stirred at room temperature for 3 h. After impregnation, the mixtures were dried at 105 °C for 12 h, and followed by being ground to powder. Finally, the catalysts were calcined in air at 550 °C for 6 h with a linear heating ramp of 2 $^{\circ}C \cdot min^{-1}$.

2.3. Catalyst characterization

X-ray diffraction (XRD) of the HZSM-5 parent and Cr/HZSM-5 catalysts were performed in a Bruker D8 advance diffractometer and the 2θ angle between 5 and 90°. Infrared spectra of HZSM-5 parent and Cr/HZSM-5 catalysts were recorded from a Fourier-transformed infrared spectrophotometer (FTIR). The samples for analysis were mixed with KBr. Thirty-two scans were taken from 4000 to 400 cm^{-1}. Thermal gravimetric (TG) analysis was performed at a heating rate of 10 $^{\circ}C \cdot min^{-1}$ from 30 to 700 °C in flowing air using a WCT-2 thermal analyzer. Surface area, pore size, and pore volume of HZSM-5 parent and Cr/HZSM-5 catalysts were calculated based on N_2 adsorption–desorption isotherms at 77 K. Acid type of HZSM-5 parent and Cr/HZSM-5 catalysts were evaluated by an in situ FTIR using pyridine as probe molecule (Py-FTIR). Acid properties of HZSM-5 parent and Cr/HZSM-5 catalysts were quantified by temperature programmed desorption with ammonia as the probe molecule (NH_3-TPD).

2.4. Catalyst performance

Experiments for glucose conversion were performed in a 100 ml batch reactor which supplied by Parr Instrument Company and equipped with a mechanical stirrer and electric heater. Prior to the reaction, 1 g glucose together with 50 ml distilled water and a certain amount of catalyst were loaded into the reactor, and then heated to a designed temperature within 20 min. The temperature was controlled with ± 1 °C of the set value via a modular controller and the agitation speed was fixed at 800 rpm. The initial time ($t = 0$) for the reaction is taken once the desired reaction temperature is reached. During the reaction, about 1–2 ml of sample was collected via the sampling line at certain time. After reaction, the mixture was cooled to room temperature and separated by centrifugation. The supernatant liquid was filtered with 0.22 μm nylon syringe filter and followed to analysis by high performance liquid chromatography (HPLC) and total organic carbon analyzer (TOC). The solid residue was washed with water and ethanol for several times, and then dried at 105 °C overnight for the next run or analysis.

2.5. Product analysis

The concentrations of LA, FA, and HMF in the reaction liquid were quantified by HPLC with an UV-detector via a C_{18} column at 35 °C. The mobile phase applied was an acetonitrile: phosphoric acid-sodium dihydrogen phosphate buffer solution (pH 2.6) = 1:9 (v/v) with a flow rate of 0.6 $ml \cdot min^{-1}$ [17]. The concentration of residual glucose in the