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A facile and efficient method to improve the selectivity of methyl lactate in the chemocatalytic conversion of glucose catalyzed by homogeneous Lewis acid

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ABSTRACT

A facile and efficient method to improve the selectivity of methyl lactate (MLA) in the chemical conversion of glucose in methanol catalyzed by homogeneous Lewis acid was established. The yield of MLA was efficiently improved through controlling the acidity of the reaction solution by neutralization of protons generated from the hydrolysis/methanolysis of $SnCl_4$. The mechanism of glucose conversion to MLA catalyzed by $SnCl_4$-NaOH was explored. The effects of the concentration of catalyst and substrate and the reaction temperature and time were systematically studied. The catalyst system of $SnCl_4$-NaOH can efficiently convert glucose, fructose, and sucrose to MLA with yields of 47%, 57%, and 51% at 160 °C for 2.5 h, respectively. The catalyst can be regenerated and reused at least three times in the conversion of glucose to MLA without significant loss of activity and selectivity.

1. Introduction

With the gradual consumption of fossil resources, more and more attention is paid to utilize abundant and renewable biomass resource to produce chemicals and fuels. Carbohydrates represent the largest fraction of the annual biomass production. Many platform molecules for producing chemicals and fuels have been synthesized from biomass-based carbohydrates [1–3]. Lactic acid (2-hydroxypropionic acid, LA) is one of the top biomass-based carbohydrate derived platform chemicals [4]. LA and alkyl lactates are widely used in food, cosmetic, chemical, and pharmaceutical industries [5–8]. The demand for LA and alkyl lactates increases annually as green solvent and material for synthesis of biodegradable polymer–polylactic acid [7,8]. Over 90% of the total LA produced worldwide is obtained by fermentation [4]. With the growing demand for LA and alkyl lactates, this biocatalytic route may play an important role in industry. Meanwhile, the development of novel chemocatalytic processes for the production of LA and alkyl lactates from carbohydrate feedstocks has also attracted much attention in recent years [4]. Glucose is the most abundant monosaccharide and the cheapest hexose, which make it a promising candidate as a raw material for the production of LA and alkyl lactates. Glucose could be transformed to lactic acid in subcritical or supercritical water with or without catalyst [9,10], but high temperature and pressure processes pose stress on the reactor. Solid catalysts such as molecular sieves (Sn-β, Sn-MWW, Sn-MCM-41, and Sn-SiO_2-C) [11–14], bases (MgO and hydrotalcites) [6,15], and mixed oxides (WO_3/ZrO_2, WO_3/Al_2O_3 and Al_2O_3-ZrO_2) [16,17] can also transform glucose to LA and alkyl lactate, but the preparation of the solid catalysts, such as Sn-β, is usually difficult and time-consuming. Furthermore, polar products strongly adsorb in catalyst pores leading to catalyst deactivation. Metal salts as Lewis acid catalysts show excellent catalytic performance in the conversion of carbohydrates to LA and alkyl lactate [18–20]. Moreover, these salts can be easily obtained from commercial resources. The transformation process of hexoses such as glucose to LA or alkyl lactate is complex, which is composed of multiple reactions. For example, the conversion of glucose in alcohol to alkyl lactate comprises isomerization between aldose and ketose, retro-aldol condensation to trioses, dehydration, addition, etc (Fig. 1) [11,14]. Moreover, some side-reactions are often concomitant with the main reactions during this process. For example, hexoses can also dehydrate to 5-hydroxymethylfurfural (HMF) and subsequently to its degradation and etherization products [21,22], which compete with the retro-aldol reaction of hexoses to trioses. The important intermediate product—pyruvaldehyde can react with alcohol molecules to form pyruvaldehyde dialkylacetal [14], which also affects the selectivity of alkyl lactate. Therefore, it is very important to inhibit the side-reactions for improving the

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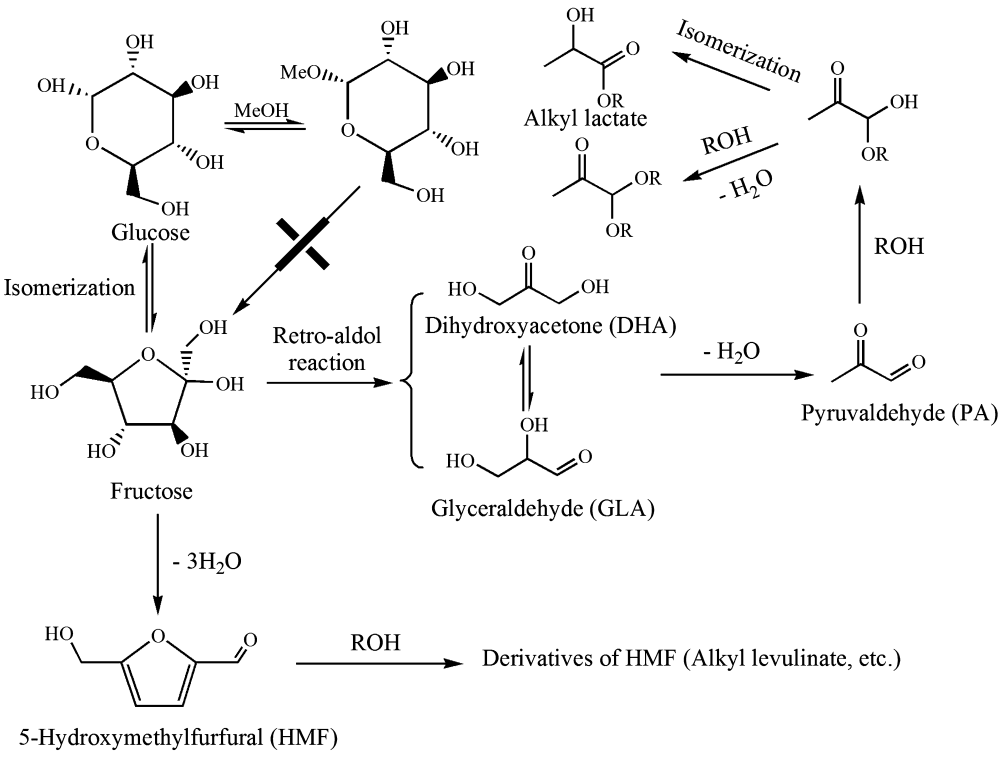

Fig. 1. Proposed reaction pathway for the formation of different products from carbohydrates.

selectivity of the desired alkyl lactate in the conversion of glucose catalyzed by metal salts.

In this work, we report a facile and efficient method to improve the selectivity of methyl lactate (MLA) in the chemical conversion of glucose in methanol catalyzed by $SnCl_4$. Inorganic bases, such as NaOH, were utilized to neutralize the protons generated from the hydrolysis/methanolysis of $SnCl_4$. Using this method, the side-reactions were inhibited and the yield of MLA was improved effectively.

2. Experimental

2.1. Materials

Various metal salts including $SnCl_4{\cdot}5H_2O$, $SnCl_2{\cdot}2H_2O$, $SnSO_4$, $AlCl_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $CrCl_3{\cdot}6H_2O$, $Cr(Ac)_3$, $CoCl_2{\cdot}6H_2O$, $Co(Ac)_2{\cdot}4H_2O$, $ZrOCl_2{\cdot}8H_2O$, $MnSO_4{\cdot}H_2O$, $Mn(Ac)_2{\cdot}4H_2O$, NaCl, $MgCl_2$, and $SrCl_2{\cdot}6H_2O$, inorganic bases including NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, and $NH_3{\cdot}H_2O$, and H_2SO_4 (98%) were all purchased from commercial resources (AR grade). NaY (Si/Al = 2.55) was purchased from Nankai University, China. $Sn(OH)_4$ was prepared through precipitation of aqueous $SnCl_4$ solution with NaOH. Methanol (99.9%), naphthalene, glucose monohydrate, and sucrose were of analytic grade and purchased from Tianjin No. 3 Chemical Reagent Factory. Fructose (99%) was purchased from Aladdin Reagent Co. (China). Methyl lactate (> 98%, MLA) and methyl levulinate (> 99%, MLE) were purchased from TCI Shanghai, China. 1,3-Dihydroxyacetone dimer (97%, DHA) was obtained from J & K Scientific Ltd, China. All chemicals were used as purchased without further purification.

2.2. pH and UV-vis spectroscopy measurements of methanol solution of $SnCl_4$

The pH of methanol solution of $SnCl_4$ with different NaOH amounts was measured at room temperature on a PHS-3E pH meter (± 0.01 pH units) calibrated with standard buffer solutions. Here we used pH meter to measure the pH of the solution due to a small amount of water present in the solution, which was derived from (i) water of hydration in Sn halide; (ii) moisture absorbed by raw materials such as Sn halide, NaOH and methanol.

Ultraviolet-visible (UV-vis) electronic spectroscopic studies were done using a TU-1810 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., China) with 1 nm spectral resolution. Methanol was measured as reference/background spectrum. The methanol solutions of $SnCl_4$ with different amount of NaOH were prepared as follows. First, the methanol solutions of $SnCl_4$ and NaOH were prepared respectively. Then a certain amount of $SnCl_4$ solution and different amount of NaOH solution were decanted to other volumetric flasks. After dilution with methanol, the UV-vis spectra of these solutions with identical amount of $SnCl_4$ and different amounts of NaOH were recorded.

2.3. Catalytic reaction procedure and product analysis

An 80 mL teflon-lined stainless steel autoclave reactor was first charged with methanol (15 mL), and then a certain amount of carbohydrate and catalyst was added under stirring. After the autoclave was sealed, the atmosphere over the solution was replaced with N_2 for four times and then the pressure of N_2 was charged to 0.1 MPa. Subsequently, the reactor was heated to the desired temperature under stirring. When the reaction was over, the reactor was cooled down to the ambient temperature. The products in the reaction solution were identified by an Agilent 6890 N GC/5973 MS and a Shimadzu LC-20AT HPLC analysis system. Conversion of glucose was analyzed with the external standard method on a Shimadzu LC-20AT HPLC analysis system equipped with an Aminex HPX-87H column (300 × 7.8 mm) and refractive index detector (RID-10A). 0.005 M aqueous H_2SO_4 was used as the mobile phase, which had a flow rate of 0.6 mL/min. The column temperature was 40 °C. Yields of MLA and MLE were analyzed on a GC equipped with