Catalytic Conversion of Glucose to Levulinic Acid Using Zeolite Immobilized Ionic Liquid as Catalyst

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ABSTRACT

Concerns towards diminishing fossil resources compel the chemical industry to explore alternatives for basic chemical productions. Carbohydrates derived biomass are promising alternatives for sustainable supply of fuels and valuable chemicals due to their abundant and relatively inexpensive properties. Carbohydrate such as glucose is a compound from which various bio-based chemicals can be derived. Among those chemicals, levulinic acid (LA) has received significant attention as platform chemicals for synthesizing a broad range of bio-based fuels. The conversion of carbohydrates to LA have been conducted in water in the presence of various catalysts, including homogeneous and heterogeneous catalysts. In this study, a new zeolite immobilized ionic liquid (HY-IL) catalyst has been explored for catalytic conversion of glucose to LA. The catalyst was prepared by immobilizing an acidic ionic liquid; 1,4 methylsulfonic acid imidazolium tetrachloroaluminate ([MSIM][$AlCl_4$]) into HY zeolite with weight ratio 1:2 of ionic liquid to zeolite. The synthesized [MSIM][$AlCl_4$] was characterized using CHNS elemental analysis to validate the prepared [MSIM][$AlCl_4$]. Meanwhile, the parents HY zeolite and HY-IL were characterized using N_2 physisorption and temperature desorption of ammonia (NH_3-TPD) to determine their surface area and acidity, respectively. From the characterization results, the prepared [MSIM][$AlCl_4$] was validated, the surface area of HY-IL was decreased, while the acidity of HY-IL was increased compared to the parent HY zeolite. The catalytic testing were conducted at 160 °C for 5 h using 0.4 g of catalyst and 0.4 g of glucose. HY-IL gave the highest LA yield (21%) compared to parent catalysts; [MSIM][$AlCl_4$] (23%) and HY zeolite (traces). The high catalytic performance of HY-IL was due to its high concentration of active acid sites compared to HY zeolite. This study demonstrated the potential of zeolite

ISBN : 978-602-73367-0-4

immobilized ionic liquid as a catalyst for biomass transformation to platform chemicals under mild process condition.

Keywords: *Levulinic acid; ionic liquid; glucose dehydration; zeolite; zeolite immobilized ionic liquid*

1.0 INTRODUCTION

Concern about energy demand is increasing due to the depleting of fossil fuel supplies. This stimulate the need to find an alternative for the fossil resources. Biomass has been identified as one promising alternative for fuels and chemicals productions due to its abundant and renewable feedstock (Bevilaqua et al., 2013). Levulinic acid (LA), a versatile chemical that can be derived from biomass, is an important basic chemical with various potential uses such as fuel additives, polymer, solvent, food additives, and pharmaceutical agents (Peng et al., 2010). Several acid catalysts; homogeneous and heterogeneous, have been employed for LA production such as mineral acid, metal chloride, and zeolite (Bevilaqua et al., 2013; Peng et al., 2010; Zeng et al., 2010). Each catalyst has its own disadvantages and drawback. For instance, zeolite suffered from poor catalytic activity due to its low acidity (Zeng et al., 2010). Thus, modification of catalyst is essential to improve its catalytic activity.

Ionic liquid have received considerable attention in many fields due to its unique characteristic such as low vapor pressure and high thermal stability (Bali et al., 2012). It is often referred to designable solvent as it physical properties can be tuned by changing their cation and anion. Several studies have been reported for LA production involving ionic liquid (Ren et al., 2015; Shen et al., 2015). The concern towards the exorbitant price of ionic liquid is prevalent. The high price limits the use of ionic liquids in large scale reactions. Thus, the quantity of ionic liquid for reaction purposes should be reduced. As such, the practicability of supported ionic liquid catalysts (SILC) has been introduced to reduce the quantity of ionic liquid (Mikkola et al., 2007). Herein, a new type of SILC was prepared, namely HY zeolite immobilized ionic liquid catalyst (HY-IL). The parent and prepared catalyst were characterized and further employed as catalyst for glucose conversion to LA.

2.0 MATERIALS AND METHODS

2.1 Materials

HY zeolite (SiO_2/Al_2O_3=30) was purchased from Zeolyst International Inc. 1-methylimidazole, chlorosulfonic acid (HSO_3Cl), D(+)-glucose monohydrate and aluminium chloride ($AlCl_3$) were purchased from Merck, Germany. Dichloromethane (CH_2Cl_2) was purchased from QRec, New Zealand. A standard analytical grade of LA (Merck) was used for analysis of desired product. Distilled water was used for the solution reaction.

2.2 Catalyst Preparation

2.2.1 Preparation of ionic liquid; [MSIM][Cl] and [MSIM][$AlCl_4$]

[MSIM]Cl] was prepared by adding HSO_3Cl dropwise to 1- methylimidazole in dry CH_2Cl_2 over a period of 5 min in ice bath. After the addition was completed, the reaction mixture was stirred for 2 hr, stand for 5min, then CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 and dried under vacuum to give [MSIM][Cl as a viscous pale yellow oil. For the synthesis of [MSIM][$AlCl_4$], $AlCl_3$ was added to [MSIM][Cl] over a period of 5 min at 50 °C. The reaction mixture then stirred for 1 hr at 50 °C to give [MSIM][$AlCl_4$] as white powder.

2.2.2 Preparation of zeolite immobilized ionic liquid

HY-IL was synthesized according to method described in literature (Arya et al., 2012). HY zeolite was added to a solution of [MSIM][$AlCl_4$] in water with weight ratio 1:2 of ionic liquid to zeolite. The mixture was stirred at 90 °C for 12 h. Finally, the catalyst was dried at 70 °C under vacuum to yield HY-IL.

2.3 Catalyst Characterization

The CHNS elemental analysis of ionic liquids; [MSIM][Cl] and [MSIM][$AlCl_4$] were characterized using Elemental Analyzer Vario MICRO Cube. The surface area of HY-IL and HY zeolite catalyst were determined according to the standard N_2 physisorption (Thermo Scientific, SURFER). Meanwhile, the acidity of HY-IL and HY zeolite were determined by temperature programmed desorption of ammonia (NH_3-TPD) using micrometrics Auto Chem II instrument.

2.4 Catalytic Test and Product Analysis

The catalytic conversion of glucose was carried out by dissolving glucose in distilled water and mixed with catalyst (1:1 of catalyst:glucose) in pressurized batch reactor. The reactor then preheated to a certain temperature. After the reaction was completed, the mixture was cooled to room temperature. All the samples were filtered and further analyzed using HPLC. The concentration of LA in product sample was determined by using HPLC (Agilent) under the following conditions: column = Aminex HPX-87H; flow rate = 0.6 ml/min; mobile phase = H_2SO_4 (5 mM); detector = UV210 nm ; retention time = 45min; column temperature = 60 °C. The concentration of sample was calculated using standard LA calibration curve with known concentrations. LA yield was calculated according to equation below:

$$\text{LA yield (wt \%)} = \frac{\text{LA amount (g)}}{\text{Initial glucose amount (g)}} \times 100\%$$

3.0 RESULTS AND DISCUSSIONS

3.1 Catalyst Characterization

The prepared [MSIM][Cl] is viscous pale yellow liquid, while [MSIM][$AlCl_4$] is a white solid. The elemental CHNS analysis results show similar calculated and found values, which validated the prepared ionic liquids. CHNS analysis (%): [MSIM][Cl]: Calculated C: 24.19, H: 3.53,N: 14.11, S: 16.12; Found C: 24.26, H: 3.52, N: 14.15, S: 16.17; [MSIM][$AlCl_4$]: Calculated C:14.48, H: 2.11, N: 8.44, S:9.65; Found C: 14.53, H: 2.10, N: 8.39, S:9.56.

The N_2 physisorption revealed the immobilization of ionic liquid to HY has reduced the surface area of zeolite from 1144.3 m^2/g (HY zeolite) to 415.6m^2/g (HY-IL). This decrement is due to the presence [MSIM][$AlCl_4$] at the intra-channel space in HY. By simple mixing IL solution and HY zeolite at 90°C, [MSIM][$AlCl_4$] was easily entering the inner channel of HY even though [MSIM][$AlCl_4$] was dissolved in water before mixing with HY zeolite.

The TPD-NH_3 analysis disclose the acidity of HY zeolite and HY-IL were 2.293 and 9.301 mmol/g, respectively (Table 1). The catalyst acidity increased after immobilization of [MSIM][$AlCl_4$] to HY zeolite. Combination of sulfonic acid as anion and $AlCl_3$ as cation produce high acidity of ionic liquid. With the attachment of ionic liquid to zeolite, the total acidity of HY-IL higher compared to the fresh HY zeolite.

Table 1: Surface area and total acidity of catalysts

Catalyst	Surface area(m^2/g)	Acidity(mmol/g)
HY zeolite	1144.3	2.293
HY-IL	415.6	9.301

ISBN : 978-602-73367-0-4

3.2 Catalytic Performance

The catalytic performance of HY zeolite, [MSIM][$AlCl_4$], and HY-IL were tested for glucose conversion to LA. Glucose conversion catalyzed by HY-IL gave slightly higher LA yield compared to [MSIM][$AlCl_4$] (Fig. 1). However, when HY zeolite was applied as catalyst, only traces of LA was detected. Theoretically, catalyst with strong acidity is required to give high yield of LA (Lai et al., 2011). It is suggested that acidity of HY zeolite was not sufficient for LA production. Since HY-IL and [MSIM][$AlCl_4$] produce considerably high LA yield, it can be concluded that acid site from [MSIM][$AlCl_4$] is responsible for the production of LA from glucose. The amount of [MSIM][$AlCl_4$] and HY-IL used for all reactions are the same. Therefore, the use of HY-IL can minimize the amount of [MSIM][$AlCl_4$] used as catalyst. Besides, HY-IL is easy to separate from the reaction mixture and can be reused for next cycles. The reusability of HY-IL for glucose conversion to LA should be further studied.

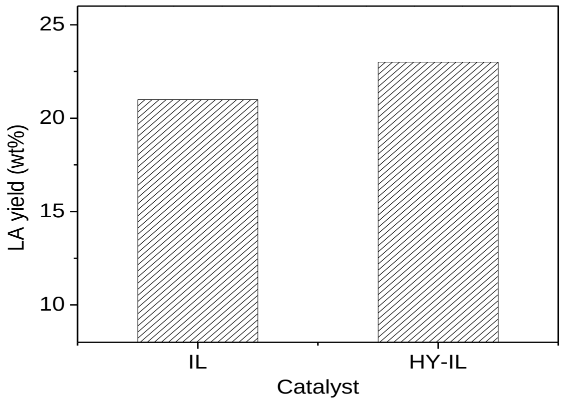

Figure 1: LA yield from glucose conversion using different catalyst (0.4 g catalyst, 0.4 g glucose, 40 mL H_2O, 160 °C, 5hr).

4.0 CONCLUSION

HY-IL has been synthesized and employed for catalytic conversion of glucose to LA. Immobilization of [MSIM][$AlCl_4$] to HY zeolite to give HY-IL has decreased the surface area but increase the acidity of HY zeolite. For reaction conducted at 160 °C for 5 hr, only traces amount of LA was detected using HY zeolite as catalyst. Meanwhile, HY-IL and IL gave 21 and 23% of LA yield, respectively. The high performance of [MSIM][$AlCl_4$] and HY-IL was due to the high catalyst acidity compared to HY zeolite. This study demonstrated the potential of HY-IL for biomass transformation to platform chemicals under mild process condition.

ACKNOWLEDGEMENT

The authors would like express gratitude for the financial support receive from Universiti Teknologi Malaysia under the research university grant 07H14, 08H62 and 02G36. Ministry of Higher Education (MOHE) also acknowledged for sponsoring one of the author, (MAABB) under MyBrain15 fellowship. NASR is a Researcher of Universiti Teknologi Malaysia under the Post-Doctoral Fellowship Scheme for the Project: Development of Nanocatalyst for Chemical Conversion to Fuels (vot no: 02E54).

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ISBN : 978-602-73367-0-4