

学 位 論 文 の 要 旨

専攻	安全システム工学 専攻	ふりがな 氏名	あせふ ばゆ Asep Bayu
学位論文題目	Production of High-Value Added Chemicals from Biomass-Derived Carbohydrates (バイオマス由来炭水化物からの高付加価値化学品の生産)		
<p>学位論文要旨</p> <p>Diminishing fossil-based carbon resources, especially petroleum oil, has attracted many researchers to find efficient processes for converting biomass and its derivatives into valuable carbon-based products such as fuels, chemicals and materials. One of attractive routes is via chemo-catalytic conversion of biomass-derived carbohydrates in various solutions such as ionic liquids (ILs), especially imidazolium-based type ILs. However, large application of ILs is limited by their relatively expensive prices, high viscosity (mass transfer limitation) and toxicity precursors. Also, the lack activity of some ILs in the presence of large amount of water also limits their applications only for depolymerization, isomerization and dehydration. In this dissertation work, I focused on developing new strategies to get more efficient and more environmental friendly catalytic systems for biomass-derived carbohydrates conversions. It includes 7 chapters.</p> <p>Firstly, aqueous glucose conversion with AlCl_3 as a catalyst was investigated in the presence of choline chloride (ChCl), a safe and cheap quaternary ammonium salt. About 34.2-38.4 mol% of levulinic acid (LA) and 39.6-44.2 mol% of formic acid (FA) were obtained from 10 wt% of glucose with AlCl_3 at 155 °C for 1.5 h. By combination of AlCl_3 with oxalic acid, LA and FA was achieved in the value of 51.7 mol% and 56.2 mol%, respectively. Kinetic study revealed that ChCl promoted catalytic activity of AlCl_3 in cascade reaction of glucose (<i>i.e.</i> isomerization, dehydration and rehydration) into LA and FA through enhancing fructose de-/rehydration rate. The activity was resulted from the generated bifunctional acids in the solution, <i>i.e.</i> aluminium/ChCl complex and the <i>in situ</i> formed Brønsted acid from the hydrolysis of AlCl_3, which was supported from the change of LA selectivity with the addition an excess amount of Brønsted acid. Despite its homogeneous reaction, this catalytic system was reused for several times. It is expected that such an aqueous ChCl based catalytic reaction system with Lewis acid can be widely applied for biomass-derived carbohydrates conversion.</p> <p>Secondly, ChCl was also found to promote catalytic activity of SnCl_2 in an aqueous system for the conversion of trioses, hexoses and cellulose into lactic acid (LacA). In the presence of ChCl, SnCl_2 was active to catalyze successive reaction of glucose (<i>i.e.</i> glucose-fructose isomerization, [3+3] retro-aldol of fructose into trioses and trioses de-/rehydration into LacA)</p>			

which was contrast with its worst activity in pure water (*i.e.* 47% and 7% of LacA selectivity at 155 °C for 1.5 h, respectively). It was resulted from the bifunctional acids formation in the solution, *i.e.* SnCl₂/ChCl complex and *in situ* generated Brønsted acid, which was indicated by the solubility enhancement of SnCl₂, the chemical shift of ¹¹⁹SnNMR spectra and the change of pH solution. Also, it was supported by the shift selectivity of glucose conversion into levulinic and LacA in water and ChCl aqueous solution at 190 °C, respectively. Kinetic study revealed that LacA formation was affected by temperature, in which, about 47%, 59% and 77% of LacA were achieved from glucose, fructose and trioses at 190 °C for 30 min. The result provided a new insight for the enhancement of the solubility as well as catalytic activity of tin chlorides in aqueous system.

Thirdly, a novel synthesis method for the preparation of Snβ-zeolite catalyst via immobilization of SnCl₂/ChCl on the commercial high silica β-zeolite was found, which indicated another versatility of ChCl in catalyst preparation field. This method was faster, facile, more environmental friendly and relatively cheaper when compared with the conventional hydrothermal synthesis and other post-synthetic methods using solid-state reaction or grafting in alcohol. A 1.3 wt% of Sn loading amount was found to be the optimum one, in which not only well disperse of Sn species was realized but also less inactive tin species were formed on zeolite. ChCl was also found to be responsible on opening silanol nest in the framework of β-zeolite. The obtained catalyst was effective and selective for sugar isomerization (*i.e.* 80-86% selectivity at 125 °C for 1-1.5 h) as commonly observed for Snβ-zeolite.

Finally, a promising strategy to apply imidazolium-based ILs for the heterogeneous catalysis conversion of biomass-derived carbohydrates was presented. A hybrid salt of 1-butyl-3-methylimidazolium and Keggin phosphomolybdate ([BMIM]₃PMO₁₂O₄₀) synthesized via ion exchange method was revealed to be an effective as well as selective solid catalyst for sugar epimerization reaction (*i.e.* 83-87% of selectivity at 78 °C for 1 h). The activity was comparable with its homogeneous acid H₃PMO₁₂O₄₀. This catalyst had promising criteria for its large application, *i.e.* easy to prepare from its commercial precursor (BMIMCl and H₃PMO₁₂O₄₀), water-tolerant and reusable without losing its catalytic performances. The regeneration of catalyst can be also easily realized by simply reoxidizing it with peroxide at mild condition (50 °C, 1.5-2 h) without destructing its structure.

These results provide new insights for the application of Lewis acid metal chlorides/ChCl aqueous system as alternative method for chemo-catalytic conversion of biomass-derived carbohydrates to some high-value chemicals and Lewis acid-based materials synthesis. Furthermore, the high activity and high selectivity of [BMIM]₃PMO₁₂O₄₀ on sugar epimerization reaction shows a promising application of imidazolium-based ILs in heterogeneous Lewis acid catalysis reaction for biomass-derived carbohydrates conversion.