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Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid

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ABSTRACT

A sulfonated carbon material was prepared by incomplete hydrothermal carbonization of glucose followed by sulfonation. The carbon material contained $-SO_3H$, –COOH, and phenolic –OH groups, and exhibited high catalytic performance for the hydrolysis of cellulose. A total reducing sugar (TRS) yield of 72.7% was obtained in ionic liquid 1-butyl-3-methyl imidazolium chloride at 110 °C in 240 min reaction time. The effect of water on the hydrolysis of cellulose in the catalytic system was studied. A water content of less than 2% in the ionic liquid promoted the formation of TRS, whereas a water content of greater than 2% lead to a decrease in TRS. The sulfonated carbon material catalyst was demonstrated to be stable for five cycles with minimal loss in catalytic activity. The use of an ionic liquid with functionalized carbon catalyst derived from glucose provides a green and efficient process for cellulose conversion.

1. Introduction

The hydrolysis of cellulose to obtain reducing sugars such as glucose is essential for using biomass in chemical processes, since the reducing sugars can be transformed into a wide range of important chemicals such as ethanol, 5-hydroxymethylfurfural and hexitols (Rinaldi and Schuth, 2009; Van De Vyver et al., 2011). However, conversion of cellulose offers great challenges due to its recalcitrant nature.

Thus far, many efforts have been devoted to the depolymerization of cellulose with mineral acids, bases, enzymes (Ramakrishnan et al., 2010), and supercritical water (Sasaki et al., 1998, 2000). Liquid acid catalyzed hydrolysis of cellulose is efficient, however, corrosion, waste disposal and solvent recycle make this method unattractive. The hydrolysis of cellulose with enzyme is efficient, but it is slow and sensitive to inhibitors such as furfural and 5-hydroxymethylfurfural. Depolymerization of cellulose in sub- or supercritical water is highly efficient and only requires reaction times on the order of several seconds, but the process gives a complex product distribution and generally has low glucose selectivity due to the high reaction temperature (Peterson et al., 2008).

Solid acid catalytic systems for cellulose hydrolysis have advantages of simplicity, and efficiency since they are easily separated from reaction products and they show good catalytic activity for many substrates. Various solid acids have been examined for cellulose hydrolysis, including ion-exchange resin (Qi et al., 2011; Rinaldi et al., 2008, 2010), heteropolyacids (Ogasawara et al., 2011; Tian et al., 2010), sulfonated activated carbon (Onda et al., 2008; Pang et al., 2010; Wu et al., 2010), and layered transition-metal oxides (Lai et al., 2011; Tagusagawa et al., 2010). In these research works, the hydrolysis of cellulose is generally carried out in water. Because cellulose is insoluble in water, only the acid sites at the exterior of the catalyst particle surface can apparently be reached by the solid substrate, which leads to low efficiency or the requirement to use long reaction time (24 h) and high reaction temperatures (>200 °C) to achieve sugar yields above 50% for hydrolysis of cellulose (Geboers et al., 2011).

Some attempts have been made on the hydrolysis of cellulose in ionic liquids, since cellulose has good solubility in chloride and acetate anion ionic liquids. Li and Zhao (2007) studied the hydrolysis of cellulose using a combination of a mineral acid and an ionic liquid, and obtained a total reducing sugar yield of 77% for a reaction temperature and time of 100 °C and 540 min, respectively, with 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]). Rinaldi et al. (2008) investigated the depolymerization of cellulose in [BMIM][Cl] with Amberlyst 15 DRY resin as catalyst, and obtained a reducing sugar yield of 28% at 100 °C in 5 h reaction time. Although these methods are improvements over the use of mineral acids alone, they are limited by the nature of the catalyst and its activity at the given conditions. Sulfonated carbon materials derived from activated carbon, sugar or cellulose are solid acid

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