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One-pot synthesis of 5-hydroxymethylfurfural directly from starch over $SO_4^{2-}/ZrO_2–Al_2O_3$ solid catalyst

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ABSTRACT

The synthesis of 5-hydroxymethylfurfural (HMF) directly from starch was studied in dimethyl sulfoxide–water. The effects of catalyst variation, reaction time, water content, catalyst loading and temperature on the reaction were investigated. The $SO_4^{2-}/ZrO_2–Al_2O_3$ catalyst was found to act as a bifunctional catalyst with high activity for both hydrolysis and dehydration of starch. HMF yield of 55% was obtained after 6 h at 423 K for the reaction of starch (the molar ratio of water to glucose in starch is 44/1) over the $SO_4^{2-}/ZrO_2–Al_2O_3$ catalyst, which bears high acidity and moderate basicity with Zr/Al molar ratio of 1:1.

1. Introduction

With declining petroleum resources and rising environmental concerns, the production of energy and chemicals from renewable biomass has become an intense topic of applied and basic research. (Dodds and Gross, 2007; Rostrup-Nielsen, 2005) 5-Hydroxymethylfurfural (HMF), a versatile intermediate between biomass-based carbohydrates and petroleum-based industrial chemicals, has received much attention as an interesting platform molecule in biomass conversion. It can be converted to many value-added chemicals as well as liquid fuels that are compatible with the current infrastructure (Huber et al., 2005; Román-Leshkov et al., 2007; West et al., 2008). Different feedstock such as fructose, glucose, sucrose, inulin, cellulose, and starch, have been reported to give HMF at varying efficiencies (Tong et al., 2010; Zakrzewska et al., 2011).

Starch, one of the cheapest and most abundant renewable carbohydrates, can serve as a renewable and sustainable source of carbon for liquid fuels and chemicals (Röper, 2002). Starch is a glucose-based polysaccharide linked mainly by α-(1,6)- and α-(1,4)-glycosidic bonds (Stevnebø et al., 2006). The conversion of starch to HMF can be accomplished in two main steps: (1) hydrolysis of starch into glucose; (2) dehydration of the latter into HMF. Both the hydrolysis and dehydration reactions could be catalyzed by acid; as a result many acid catalysts have been used for the conversion of starch to HMF. Chheda et al. (2007) studied the use of HCl, H_2SO_4 and H_3PO_4 as Brønsted acid catalysts in a two-phase batch reactor. HMF yield of 36% was obtained. Some Lewis acids such as $SnCl_4$ (Hu et al., 2009b), $AlCl_3$ (Yang et al., 2012) and $CrCl_3$ (Zhao et al., 2007), could divide the dehydration of glucose into two steps: (1) isomerization of glucose to fructose; (2) dehydration of the latter into HMF. The conversion of starch catalyzed by $SnCl_4$ in ionic liquid medium, 1-ethyl-3-methylimidazolium tetrafluoroborate, gives 47% HMF yield (Hu et al., 2009b). Using $AlCl_3$ in H_2O–THF system affords 50% HMF yield from starch (Yang et al., 2012). Jae-An Chun (Chun et al., 2010) used HCl–$CrCl_3$ as co-catalysts for the conversion of starch to HMF, and a high yield of HMF (73%) was reported. Base catalysts can also catalyze the isomerization of glucose-to-fructose (James et al., 2010); thus, a mixed catalyst system that contains both an acid catalyst (H_3PO_4) and a base catalyst (pyridine) has also been used in the conversion of starch to HMF (Mednick, 1962). HMF yield of 44% was obtained in this mixed-acid–base system. The homogeneous Brønsted and Lewis acid catalysts affect both the hydrolysis and dehydration. However, there are some disadvantages of these catalysts including pollution, toxicity, and separation problems. Therefore, a low-toxicity, easy to handle heterogeneous catalyst is more desirable. Solid acid or acid–base catalysts have been used in the hydrolysis of starch (Yamaguchi and Hara, 2010; Matsumoto et al., 2011) and dehydration of glucose into HMF (Watanabe et al., 2005; Yan et al., 2009; Zhang and Zhao, 2011; Yang et al. 2010). Moreover, the basic sites on solid acid–base catalyst could also

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