Short Communication

Solid acid catalysed formation of ethyl levulinate and ethyl glucopyranoside from mono- and disaccharides

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ABSTRACT

Sulfonic acid functionalised SBA-15 (SO$_3$H-SBA-15), sulfated zirconia and beta, Y, ZSM-5 and mordenite zeolite catalysts have been applied for the dehydration of sugars to ethyl levulinate and ethyl-D-glucopyranoside (EDGP) using ethanol as solvent and reactant. The SO$_3$H-SBA-15 catalyst showed a high catalytic activity for the selective conversion of fructose to ethyl levulinate (57%) and glucose to EDGP (80%) at 140 °C, whereas the disaccharide sucrose yielded a significant amount of both products. The SO$_3$H-SBA-15 catalysts were found to be highly active compared to the zeolites under identical reaction conditions.

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1. Introduction

The utilisation of biomass provides an attractive approach to meet the challenges concerned with the diminishing availability of fossil based resources such as coal, oil and natural gas [1]. Especially, the conversion of carbohydrates to bio-platform chemicals (e.g. lactic acid, succinic acid, levulinic acid, etc.) has become increasingly important since they are potential replacements in making alternative fuels and chemicals [2–4]. In this connection, the conversion of glucose to value-added chemicals is a key transformation because glucose is readily available in abundance as cellulose polymer. However, the selective hydrolysis of cellulose to monomeric glucose is one of the great economic bottlenecks of the processes [3]. Other important transformations in carbohydrate chemistry include, e.g. the dehydration of monosaccharides, fructose and xylose to make the non-petroleum based chemicals 5-hydroxymethylfurfural (HMF)/levulinic acid and furfural, respectively [3,5,6].

Solid catalysts are generally preferable in catalysis due to their easy separation, recyclability, wide range of thermal operating window and long-term stability. Zeolites are solid crystalline microporous materials with large surface area and strong acid sites. Despite these characteristics, they are not widely applicable materials for molecular transformations of bulky molecules due to their small pore size openings of typically 5 to 8 Å (micropores). Since zeolites only have few surface silanol groups, it is quite difficult to introduce functional groups into the

materials. However, Kresge et al. [7] have reported the synthesis of mesoporous M41S materials with very high surface area, and Zhao et al. [8] have later reported another mesoporous materials (SBA-15) with large surface area and thicker wall size between the mesoporous channels. These mesoporous materials have a large number of readily accessible surface silanol groups which facilitate further modification to immobilise acidic and basic functional groups into the walls of the mesoporous channels [9,10]. Introducing the alkyl and sulfonic groups into the MCM-41 silica matrix has been well investigated by Joaquin and co-workers. They found that it was possible to synthesise well-ordered MCM-41 materials bearing alkyl sulfonic groups and tune the pore size by changing the alkyl chain length [11]. Due to their corresponding interesting intrinsic properties, these functionalised mesoporous materials have found considerable attention in the field of catalysis [12–16].

It is well known that the dehydration of fructose can take place in the presence of homogeneous or heterogeneous acid catalysts or in the presence of ionic liquids as catalyst/reaction media [5,17,18]. The dehydration of fructose leads to formation of HMF which can be rehydrated to form levulinic acid in water. Since levulinic acid has been recognised as a bio-platform chemical, the direct conversion of sugars to levulinic acid or its esters has become of importance [19–21]. Numerous reports have focused on applying solid acid catalysts for the conversion of mono/disaccharides to HMF in the presence or absence of solvents. Most solid acid catalysts used for the transformation gave a rather low yield of levulinic acid [22–24]. However, recently, Peng et al. [25] reported that glucose can be directly converted to ethyl levulinate over sulfated zirconia catalysts with a moderate yield up to 30% at 200 °C. To produce levulinic acid, carbohydrates are traditionally

being treated with aqueous mineral acid (H_2SO_4 and HCl) at atmospheric pressure at 100 °C [26]. This method usually yields about 40% of levulinic acid, but the yield can be improved to 60–70% by continuous flow conditions at higher temperatures and pressures using H_2SO_4 as catalyst [27]. Major drawbacks using the mineral acid catalysts are, however, tedious work-up during the separation stages and difficult catalyst regeneration.

Recently, we found that sulfonic acid functionalised ionic liquids were highly promising catalysts for the selective transformation of fructose to ethyl levulinate and glucose to ethyl-D-glucopyranoside (EDGP) [28]. We also found that the presence of excess of alcohol was important to enhance the yield of levulinic acid ester. These results inspired us to investigate Brønsted acid-type solid acid catalysts for the conversion of sugars to ethyl levulinate and EDGP. Hence, we have here examined various solid acid catalysts; sulfated zirconia, sulfonic acid functionalised SBA-15 (SO_3H-SBA-15) and hydrogen form of microporous zeolites (beta, Y, ZSM-5 and mordenite) as catalyst for the conversion of sugars (glucose, fructose, sucrose and cellobiose) to ethyl levulinate and EDGP.

2. Experimental

2.1. Catalyst preparation

Hydrogen form of Y and ammonium form of beta, ZSM-5 and mordenite zeolites with silicon to aluminium ratios of 2.6, 12.5, 11.5 and 10.0, respectively, were purchased from Zeolyst International. To obtain the hydrogen form of the zeolites, the ammonium forms were calcined at 550 °C for 6 h in air.

Three sulfated zirconia catalysts with 3.4 wt.% SO_4^{2-} in t-ZrO_2 (3.4 SO_4^{2-}-SGN), 3.9 wt.% SO_4^{2-} in t-ZrO_2 (3.9 SO_4^{2-}-SGN) and 4.7 wt.% SO_4^{2-} in t-ZrO_2 (4.7 SO_4^{2-}-SGN) have been used for the study. All were obtained from Saint-Gobain Norpro and used directly.

The sulfonic acid functionalised SBA-15 catalysts were synthesised by following two approaches. In the first approach [10] pluronic P123 (8.0 g, Aldrich) was dissolved in concentrated hydrochloric acid (81.0 g, 37 wt.%, Sigma-Aldrich) and the mixture heated at 40 °C. An aqueous solution of sodium metasilicate nonahydrate (21.8 g, Sigma) in water (250 g) was added to the surfactant solution followed by (3-mercaptopropyl)trimethoxysilane, 3-MPTMS (1.0 g, Fluka). The reaction gel mixture was then mechanically stirred at 40 °C for 24 h, transferred into a polypropylene bottle and aged at 100 °C for 24 h. The solid product was filtered off and washed with copious amount of water and ethanol separately, where after the surfactant was removed by Soxhlet extraction with ethanol for 24 h. The extracted material was afterwards oxidised with 30 wt.% aqueous hydrogen peroxide (10.0 g per 0.3 g of catalyst) at room temperature for 24 h under argon atmosphere, filtered off and washed several times with water and ethanol. The wet material was finally suspended in 1 M sulfuric acid for 2 h, collected by filtration, washed with water and ethanol and dried at 60 °C under vacuum for several hours to obtain the final product SO_3H-SBA-15-D. The second synthesis approach was a post-synthetic grafting method in which the calcined SBA-15 was refluxed overnight with excess quantity of 3-MPTMS in anhydrous toluene under inert atmosphere [12]. The final product (SO_3H-SBA-15-PS) was obtained by following the same procedure as above.

Physico-chemical characteristics of the used catalysts are comprised in supplementary information (Table S1).

2.2. Catalytic reactions

The dehydration reactions were carried out in 15 ml ace pressure tubes. 270.2 mg of fructose or glucose or 256.7 mg of sucrose or cellobiose, 80 mg of catalyst, 30 mg of naphthalene (internal standard)

and 4 g of ethanol were charged into the ace pressure tube and heated under stirring (600 rpm) at 140 °C (oil bath temperature) for 24 h. After the reaction, the ace pressure tube was cooled to room temperature before collecting the samples. All chemicals were purchased from Sigma and used as received.

2.3. Reactant and product analysis

Aliquots of the reaction mixtures were subjected to GC-FID analysis (Agilent 6890N instrument, HP-5 capillary column 30.0 m × 320 μm × 0.25 μm) and analysis by HPLC with RI detection (Agilent 1200 series, 30 cm Aminex© HPX-87H column, 0.005 M aqueous sulfuric acid eluent, flow rate 0.6 ml/min) after filtering off the catalyst. An Agilent 6850 GC system coupled with an Agilent 5975C mass detector was used for qualitative analysis. Sugar conversions and yields of HMF and HMF-ether were determined by HPLC. Since sucrose inverts to fructose and glucose on the used acidic HPLC-column, the conversions were calculated from the monosaccharides fructose, glucose and mannose on a carbon-basis. In principle, 1 mol of sucrose can form 1 mol of fructose and 1 mol of glucose and these sugars can isomerise to mannose to some extent. The amounts of unreacted monosaccharides were calculated from their individual HPLC standards and added together to find the unreacted sucrose. HPLC standards were made from commercial samples except HMF-ether. The yield of ethyl levulinate was calculated from GC results on series of ethyl levulinate standards with naphthalene as internal standard.

3. Results and discussion

Initial experiments of dehydration of fructose to ethyl levulinate were conducted with beta-, Y-, ZSM-5- and modernite zeolite in ethanol at 140 °C. The results are presented in Table 1. The medium pore zeolites, H-ZSM-5 and H-mordenite, formed HMF and 5-(ethoxymethyl)furan-2-carbaldehyde (HMF-ether) as the main products and no ethyl levulinate under the applied reaction conditions (entries 1 and 2). The two large pore zeolites, H-Y and H-beta, yielded 8 and 7% of ethyl levulinate, respectively (entries 3 and 4). Hence, even though the H-ZSM-5 and H-mordenite zeolites have a large number of acid sites (see supplementary information, Table S1), they were apparently not able to form ethyl levulinate from fructose.

The formation of ethyl levulinate from fructose is a consecutive reaction which probably proceeds by: dehydration of fructose to give HMF followed by etherification with ethanol to form HMF-ether and rehydration of HMF-ether to form ethyl levulinate as shown in Scheme 1 [28]. Moreau et al. have reported that fructose over mordenite zeolite can dehydrate to form HMF which then rapidly diffuses out of the pores avoiding rehydration to form levulinic acid [29]. A similar effect was also observed in our study suggesting that HMF-ether was unable to get into the pores and rehydrate to form ethyl

Table 1
Catalytic conversion of fructose to ethyl levulinate over solid acid catalysts[a].

Entry	Catalyst	Fructose conversion (%)	Yield (%)		
			HMF	HMF-ether	Ethyl levulinate
1	H-ZSM-5 (11.5)	94	15	17	0
2	H-MOR (10)	92	13	42	0
3	H-Y (2.6)	93	<1	28	8
4	H-beta (12.5)	92	<1	26	7
5	SO_3H-SBA-15-D	>99	<1	11	56
6	SO_3H-SBA-15-PS	>99	<1	12	57
7	SO_3H-SBA-15-D[b]	>99	<1	32	37
8	SO_3H-SBA-15-D[c]	>99	<1	21	53

Values in the parenthesis correspond to silicon to aluminium ratios.
[a] See the Experimental section for reaction conditions.
[b] The concentration of fructose was three times higher than under the normal conditions.
[c] The results obtained after three runs by adding fresh fructose after each run.