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One-pot preparation of methyl levulinate from catalytic alcoholysis of cellulose in near-critical methanol

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ABSTRACT

One-pot preparation of methyl levulinate (MLA) from cellulose in near-critical methanol was studied. Acids containing SO_3H group were proven to be effective catalysts for the production of MLA from cellulose's catalytic alcoholysis. The effects of different reaction conditions, such as an initial cellulose concentration of 10–30 g/L, a temperature range from 170 to 190 °C, and a sulfuric acid concentration of 0.01–0.03 mol/L, on the production of MLA were investigated. The results showed the reaction temperature and acid concentration significantly affected the process of cellulose alcoholysis and the yield of MLA. A high yield of up to 55% MLA was achieved at 190 °C for 5 h, using 0.02 mol/L H_2SO_4 as a catalyst.

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1. Introduction

Cellulose is a renewable and alternative source for the production of chemicals and fuels. Various conversion processes from cellulose to useful chemicals, such as acid hydrolysis,[1] enzymatic hydrolysis,[2] pyrolysis,[3] and decomposition in supercritical liquid,[4] have been developed to obtain platform chemicals like ethanol, lactic acid, 5-hydroxymethylfurfural, and levulinic acid.[5] However, all these methods have some limitations such as low conversion efficiency, device corrosion, high energy consumption, and complicated processes.[5,6] Thus, there is considerable scope for the development of a novel and more effective method.

Near-critical catalytic methanol alcoholysis is a promising alternative method for the conversion of cellulose to new platform chemicals.[4,7–9] Methanol is a good solvent for the products from cellulose and lignin with relatively high molecular weight (HMW), as well as a methylating agent in chemical reactions. This allows for the conventional multi-steps process from cellulose to platform chemicals to be achieved in a facile one-pot procedure.[4,10]

Cellulose can be decomposed efficiently in supercritical methanol (350 °C), with the main products being methyl α- and β-D-glucopyranoside.[4] With the addition of acidic catalysts, a 50–60% yield of methyl-D-glucopyranoside could be obtained with a relative mild reaction condition ($\leqslant$220 °C).[8,9] There was also a low yield (<10%) of methyl levulinate (MLA) detected in the reaction. MLA is a widely used fine chemical intermediate and polymer monomer,[11] making it an ideal platform chemical from cellulose. Tominaga et al.[12] developed a mixed acid system, employing a Lewis acid and Bronsted acid to catalyze cellulose to MLA with a 75% yield. Although the yield of MLA is high, the catalytic system of mixed acids is expensive, and hard to be applied to industry. Therefore, a low-cost catalytic system needs to be explored.

In this article, the catalytic activities of several kinds of acid catalysts for the alcoholysis of cellulose to MLA in near-critical methanol were evaluated to develop an efficient and low-cost method. Kinetics on the catalytic alcoholysis of cellulose to MLA were investigated using the following reaction conditions: initial cellulose concentration of 10–30 g/L, reaction temperature range from 170 °C to 190 °C, and catalyst sulfuric acid concentration of 0.01–0.03 mol/L. The results provide insights on an efficient and low-cost approach to produce MLA from cellulose.

2. Experimental

Microcrystalline cellulose with 50 μm average particle size was obtained from Acros Organics, England. Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd, China, and were all of analytical reagent grade.

All the catalytic alcoholysis reactions of cellulose were carried out in a 316L stainless steel batch reactor with a capacity of 13.5 mL. The reactor was constructed in three parts (tube, stopper, and cap), and can be directly heated in a steel box furnace. The furnace could handle up to 12 reactors at a time. The designed maximum pressure and temperature for the batch reactor were 20 MPa and 290 °C, respectively.

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A pre-determined amount of cellulose was first added into the batch reactor, followed by 10 mL of methanol solution containing a certain amount of acid catalyst. The reactor was then sealed and put into steel box furnace for pre-selected condition. These experiments took place under the methanol saturation vapor pressure at each reaction temperature. After a pre-set reaction time period (allow extra reactor heating up time of 20 min), the reactor was removed from the furnace and immediately placed in water to quench the reaction.

An Agilent 1790 GC and an Agilent 6890 GC/5973 MSD were used in quantifying the liquid samples from the cellulose catalytic alcoholysis process. GC operation conditions were as follows: column with FFAP 30 m × 0.32 mm × 0.4 μm; Column temperature at 90 °C; Inject temperature at 200 °C; Detector temperature at 200 °C. Quantification was achieved by comparing the peak area to that of the internal standard, *n*-octanol. Reaction products were identified through comparison of individual retention time with those pure compounds' standard solutions, and further confirmed with GC–MS (Agilent 6890 GC/5973 MSD).

The yield of MLA was calculated by the following formula: MLA yield (%) = amount of the MLA (mol) produced/amount of $C_6H_{10}O_5$ units in cellulose (mol) × 100%.

3. Results and discussion

3.1. Catalytic activity of acid catalyst on alcoholysis of cellulose

Degradation of cellulose to small molecular compounds is an acid-catalyzed process.[7,8] Under a reaction temperature of 180 °C, a reaction time of 4 h, and without using catalyst, an MLA yield of only 3% was observed. The catalytic performances of various dilute inorganic and organic acids were tested. These acids included sulfuric acid (H_2SO_4), *p*-toluenesulfonic acid (PTSA), phosphoric acid (H_3PO_4), formic acid, and acetic acid, all with $[H^+]$ at 0.04 mol/L. Figure 1 shows the effect of inorganic and organic acid catalysts on MLA yield. The results suggested that H_2SO_4 and PTSA provided a significant MLA yield increase (both over 40%), while only 7% yield was achieved by using H_3PO_4 as catalyst. The reason is probably the relatively stronger acidity (pK_a) of H_2SO_4 and PTSA contributing to their higher catalytic activity.[8] On the other hand, the organic acids, such as formic acid and acetic acid were not that effective as catalysts in cellulose catalytic alcoholysis process. It has been reported that subsidiary reaction of acids esterification with methanol at high temperature was the main reason.[13]

Several types of heteropolyacids and solid acids with a concentration of 10 g/L were also examined and the results are summarized in Figure 1. From the data, we concluded that phosphomolybdic acid hydrate (PMA) and ferric trichloride ($FeCl_3$) were much more active than Fe_2O_3, CuO, and TiO_2 possibly due to good solubility of PMA and $FeCl_3$ in methanol. Amberlyst 35W (A-35W) exhibited strong catalytic activity because of the high density of the SO_3H group in its structure. The synthesis of dimethyl ether could be accelerated under acid catalysis. Heteropolyacids and solid acids were more effective at catalyzing the dimethyl ether formation due to their Lewis acidity, allowing them to easily accept the lone pair electron in the nucleophilic oxygen atom in methanol.[14] With the formation of more dimethyl ether, the reactor pressure also increased, especially when the reactor was cooled down because of decreased dimethyl ether solubility in methanol.

Based on above analysis, both sulfuric acid and *p*-toluenesulfonic acid were very good catalysts for the cellulose alcoholysis process. Sulfuric acid was inexpensive, therefore it was selected as the catalyst of cellulose alcoholysis for further study.

3.2. Kinetics study on cellulose alcoholysis to MLA

Microcrystalline cellulose is insoluble in methanol at room temperature, so mass transfer resistance has a significant impact on this solid–liquid reaction. However, production rates of MLA were similar at different initial concentrations at a reaction temperature of 170 °C and a sulfuric acid concentration of 0.02 mol/L (Fig. 2). The results suggested that cellulose was rapidly decomposed to methylated cellotriose, methylated cellobiose, and other oligosaccharides which possessed a certain degree of solubility in methanol at high temperature.[4] Figures 3 and 4 illustrate the influence of sulfuric acid concentration and reaction temperature on MLA yield, respectively. The results showed the production rate and equilibrium yield (the average of almost invariant yields) of MLA were dependent on sulfuric acid concentration and reaction temperature. As sulfuric acid concentration increased, equilibrium yield increased from 27% (0.02 mol/L) to 32% (0.03 mol/L). In addition, the equilibrium yield increased by 17% when the temperature rose from 170 °C to 180 °C, which indicated the reaction temperature had a more significant effect on the production of MLA than sulfuric acid concentration. The highest MLA yield (55%) was achieved at 190 °C for 5 h using 0.02 mol/L H_2SO_4 as the alcoholysis catalyst.

A literature survey[4,8] indicated the cellulose decomposition mechanism in near-critical methanol consists of two steps: the conversion of cellulose to methyl-glucopyranoside by methylation, followed by the degradation to MLA with the acid catalysis. To determine which step is the rate limiting step, separate glucose alcoholysis experiments were carried out at 170 °C with sulfuric acid concentration of 0.02 mol/L. The results indicated that glucose was completely consumed in near-critical methanol within the first 10 min, and the reaction product was mainly methyl-glucopyranoside. Therefore, the glucose alcoholysis process can be

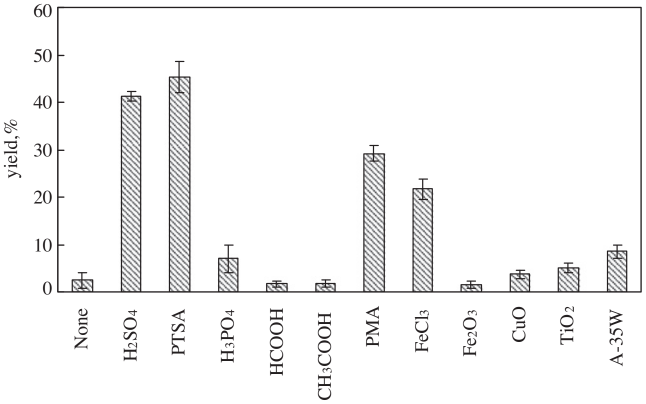

Figure 1. Effect of different acid catalysts on MLA yield.

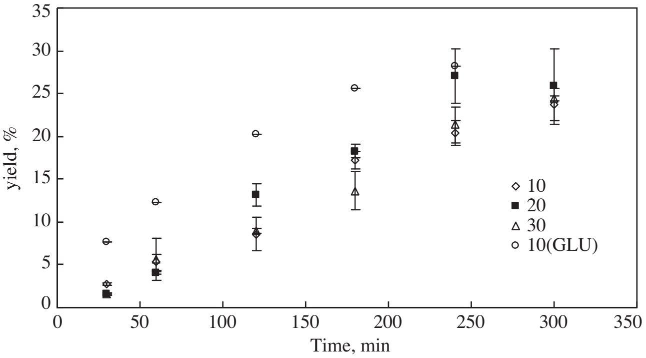

Figure 2. Effect of initial microcrystalline cellulose concentration (g/L) on MLA yield.

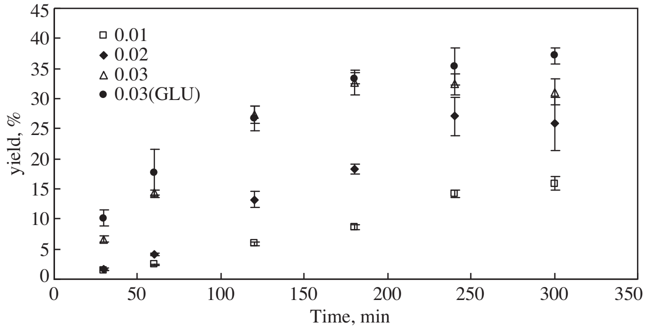

Figure 3. Effect of sulfuric acid concentration (mol/L) on MLA yield with 20 g/L cellulose at 170 °C.

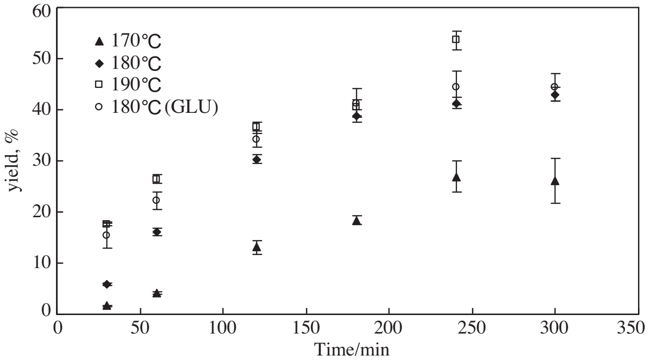

Figure 4. Effect of temperature on MLA yield at 0.02 mol/L H_2SO_4 and 20 g/L cellulose.

regarded as alcoholysis of methyl-glucopyranoside. Compared to glucose alcoholysis, MLA formation from cellulose is much slower under the same reaction conditions of initial feed concentration (Fig. 2) and reaction temperature (Fig. 4), which is mainly attributed to the shorter decomposition pathway of glucose alcoholysis. However, the production rates of MLA were almost identical from either cellulose alcoholysis (equilibrium yield of 43%) or glucose alcoholysis (equilibrium yield of 44%) under the same sulfuric acid concentration and the same reaction temperature. This phenomenon indicated that sulfuric acid could accelerate the alcoholysis process of cellulose to methyl-glucopyranoside more significantly than methyl-glucopyranoside alcoholysis to MLA, and also improve the reaction selectivity to methyl-glucopyranoside.

4. Conclusion

Acid catalysts are essential for the cellulose alcoholysis process. Various acids including inorganic acids, organic acid, and solid acids were evaluated for their catalytic activities. Sulfuric acid was determined to be the best catalyst overall with good catalytic activity for the cellulose alcoholysis process. The highest MLA yield of 55% was achieved using 0.02 mol/L H_2SO_4 as a catalyst at 190 °C for 5 h. The results of the kinetic study on cellulose alcoholysis to MLA suggested that reaction temperature had a great influence on cellulose catalytic alcoholysis and the MLA formation rate. Sulfuric acid concentration variations had greater impact on formation of methyl-glucopyranoside. The results provide insights on an efficient and low-cost approach to produce MLA from cellulose.

Acknowledgments

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