Highly efficient production of hydroxymethylfurfural from fructose by solid acid catalysts under evacuation

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Abstract: A variety of solid acids and metal salts of heteropoly acid were tested for the dehydration of fructose under reduced pressure. In this reaction condition, all the catalysts showed higher yield and selectivity to 5-Hydroxymethylfurfural (HMF) than those in normal pressure. Although FePW₁₂O₄₀ showed highest rate of HMF formation, the catalyst dissolved in the reaction mixture. Among the heterogeneous catalysts, HBEA zeolite was most effective in terms of the HMF selectivity. It showed the highest HMF yield to date (99%) with no by-products formation at 100% fructose conversion.

Keywords: fructose, catalyst, renewable resources

1. INTRODUCTION

Saccharides have recently attracted much attention as biomass for substituting petroleum resources, and their conversion to useful chemicals has actively been investigated as a promising route to a sustainable, versatile carbon source [1-6]. 5-Hydroxymethylfurfural (HMF) is a key furan derivative readily accessible from renewable resources like carbohydrates, and it is a particularly suitable starting material for the preparation of further furanic monomers required for the preparation of non-petroleum-derived polymeric materials such as polyesters, polyamides and polyurethanes [2]. Although several attempts have been developed acid-catalyzed processes for the selective dehydration of fructose to HMF, to the best of our knowledge, there are no reports in the literature reporting nearly quantitative HMF yield. This is possibly because the initial product HMF suffers further hydration to levulinic acid under the reaction condition. Control of the dehydration/hydration processes should be improved to achieve the highly selective HMF formation. In this study, the effect of evacuation on the acid-catalyzed dehydration of fructose was examined using various solid acids. We developed a simple heterogeneous catalytic process to achieve highest HMF yields to date (99% HMF selectivity at 100% fructose conversion) using HBEA zeolite under reduced pressure.

2. EXPERIMENTAL

H₃PW₁₂O₄₀·28H₂O was obtained from Nippon Inorganic Color and Chemicals Co. A Fe(III) salt of PW₁₂O₄₀³⁻ was prepared by stirring aqueous solution containing H₃PW₁₂O₄₀ and FeCl₃·6H₂O followed by evaporation to dryness. The cesium salt Cs₂₋₃HₓPW₁₂O₄₀ was prepared by titrating H₃PW₁₂O₄₀ by cesium carbonate in aqueous solution. Sulfonic resins, Nafion® and Amberlyst-15® were purchased from Aldrich. HY zeolite (JRC-Z-HY4.8, SiO₂/Al₂O₃=4.8) and HBEA zeolite (JRC-Z-HB25, SiO₂/Al₂O₃= 25±5) were supplied from the Catalysis Society of Japan.

The dehydration of fructose was carried out in a 100 cm³ flask. A mixture of D-fructose (1.0 mmol) and DMSO (10 cm³) with catalyst powder (0.02 g) was stirred (800 rpm) and heated at 120 °C under reduced pressure (~60 kPa). The major product, HMF, was identified by GC-MS with DB1 capillary column. HMF yield was calculated with gas chromatography (Shimadzu GC-14B equipped with FID detector and DB1 capillary column) using n-dodecane as internal standard. The concentrations of fructose, levulinic acid, and formic acid were analyzed by HPLC equipped with a UV detector, using a Sugar-Pak Ca column and degassed water as the eluent.

3. RESULTS AND DISCUSSION

Fig. 1 shows the dehydration of fructose in the presence of a catalytic amount of FePW₁₂O₄₀ at 120 °C. When the reaction was performed for 60 min under normal pressure in a closed reactor equipped with a condenser, fructose conversion was 100% and HMF yield was 70%. The HMF yield decreased with further increase in reaction time, while the yield of the by-product, levulinic acid, increased with time, suggesting that rehydration of HMF yielded levulinic acid. A decrease in the pressure dramatically enhanced the yield and selectivity of HMF. HMF yield of 97% (97% HMF selectivity at 100% fructose conversion) was achieved after 120 min. The yield of levulinic acid (1%) was lower under reduced pressure. The decrease in the pressure increased the conversion of fructose after 5 min. From these results, the positive effect of evacuation may be explained as follows; the removal of water suppresses the rehydration of HMF to fructose (reverse reaction) and to levulinic acid (HMF degradation).

A variety of solid acids and metal salts of heteropoly acids were tested for the dehydration of fructose under

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evacuation at 120°C (Fig. 2). In this reaction condition, all the catalysts showed higher yield and selectivity to HMF than those in normal pressure. FePW$_{12}$O$_{40}$ showed highest rate of HMF formation. It should be noted that H$_3$PW$_{12}$O$_{40}$, the starting material of FePW$_{12}$O$_{40}$, also showed high HMF yield (95% after 120 min), though the catalyst showed relatively higher yield of levulinic acid (4%, the result not shown). H$_2$PW$_{12}$O$_{40}$ and FePW$_{12}$O$_{40}$ dissolved in the reaction mixture (homogeneous catalysts). Other solid catalysts did not dissolve in the mixture (heterogeneous catalysts) and hence can be easily separated from the mixture by filtering. Among the heterogeneous catalysts, HBEA zeolite was most effective in terms of the HMF selectivity; it showed 99% HMF yield and no by-products at 100% fructose conversion after 120 min.

4. CONCLUSION
In conclusion, we have presented a novel strategy for the selective dehydration of fructose to produce HMF. The reaction under reduced pressure resulted in the higher HMF selectivity than those under normal pressure. The reaction with heterogeneous HBEA catalyst under reduced pressure provides one of the greenest route to HMF reported to date in view of the following advantages. It shows the highest yield to date (99%) with no formation of by-products. The catalyst is stable and non-polluting solid that offers easy handling and ready work-up. Vacuum evaporation may be effective to remove water, which can cause the rehydration of HMF to fructose (inverse reaction) and to levulinic acid (HMF degradation).

Fig. 1 Fructose conversion (□, ■) and yields of (○, ●) HMF, (▲, △) levulinic acid, (▼) formic acid under normal pressure (closed symbols) or under evacuation (open symbols) at 120°C.

Fig. 2 HMF yield under evacuation at 120°C; (○) FePW$_{12}$O$_{40}$, (●) Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$, (■)SO$_4^{2-}$/ZrO$_2$, (+) blank, (□) HY, (▲) Nafion, (△) Amberlyst-15, (▼) HBEA.

REFERENCES