Aerobic Oxidation of 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid by Manganese Dioxide

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Abstract: A simple non-precious metal catalyst system based on cost-effective and ubiquitously available MnO_2, $NaHCO_3$, and molecular oxygen was used to convert 5-hydroxymethylfurfural to 2,5-difurandicarboxylic acid as a bioplastics precursor. This reaction system exhibited a high FDCA yield (> 90%). The MnO_2 catalyst could be recovered by simple filtration and reused several times. The present system was applicable to the aerobic oxidation of other biomass-derived substrates and the gram-scale oxidation of HMF to FDCA, in which 2.36 g (86% yield) of the analytically pure FDCA could be isolated. Furthermore, the kinetic analysis was performed and the reaction mechanism was revealed.

Keywords: Manganese dioxide, 2,5-Furandicarboxylic acid, 5-hydroxymethyl furfural.

1. Introduction

2,5-Furandicarboxylic acid (FDCA), which is obtained by the oxidation of 5-hydroxymethyl furfural (HMF), has attracted much attention as a raw material of bio-polyesters such as polyethylene furanoate. While various homogeneous, heterogeneous, and enzymatic catalysts have been reported to date for the oxidation of HMF using O_2,[1,2] effective catalyst systems are limited to supported noble metal catalysts. In addition, they typically require 2−4 equivalents of strong base with respect to HMF to obtain high FDCA yield and are susceptible to leaching during the reaction. Non-precious metal catalyst systems are promising candidates; however, they have disadvantages such as low yield and selectivity for FDCA, harsh reaction condition requirements, the use of specific oxidants and corrosive promoters (e.g., bromide), and poor recyclability. Therefore, the developments of cost-effective and ubiquitously available non-precious metal catalysts are desired. Herein, we report a simple, efficient, and non-precious-metal-based $MnO_2/NaHCO_3$ system for aerobic oxidation of HMF to FDCA.[3]

2. Experimental

Metal oxides, bases, and reagents were purchased and used as received. The catalytic oxidation of various substrates was conducted in a 13 mL autoclave reactor with a Teflon vessel containing a magnetic stirring bar. A typical procedure for the catalytic oxidation of HMF was as follows. HMF (0.2 mmol), catalyst (0.1 g), base (0.6 mmol), water (5 mL), and O_2 (1 MPa) were put into an autoclave reactor. The reaction solution was heated at 100 °C for 24 h. After the reaction was completed, the catalyst was separated by filtration and the filtrate was diluted 10 times with water and analyzed by HPLC. The recovered catalyst was washed with water (25 mL), dried at 80 °C, and reused. Conversion (%) = converted HMF (mol)/initial HMF (mol) × 100. Yield (%) = products (mol)/initial HMF (mol) × 100. The leaching amounts of manganese species were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

3. Results and discussion

The oxidation of HMF to FDCA was performed using various metal oxides in the presence of $NaHCO_3$ (3 equivalents with respect to HMF) at 1 MPa O_2 (Table 1). Among these catalysts, MnO_2 showed the highest yield of FDCA (91%). Other metal oxide catalysts were almost inactive. The effect of bases (3 equivalents with respect to HMF) on the MnO_2-catalyzed oxidation of HMF into FDCA was investigated. Regardless of the cation, bicarbonates were the most effective, and the FDCA yields exceeded 90%. MnO_2 with strong bases such as hydroxides, carbonates, and phosphate gave lower FDCA yields (14−60%) than those with bicarbonates, whereas the HMF conversion was over 99% in each reaction. These results suggested that the presence of bicarbonates would be important not only to achieve high FDCA yields but also to avoid HMF non-productive degradation.

To investigate the effect of base concentration on the oxidation of HMF to FDCA, the reactions were carried out using different amounts of $NaHCO_3$. In the presence of 2–3 equivalents of $NaHCO_3$, FDCA was obtained in high yield without the formation of 5-formyl-2-furancarboxlic acid (FFCA) and leaching of manganese species. These results suggested that 2–3 equivalents of $NaHCO_3$ are required not only to facilitate the oxidation of HMF into FDCA but also to prevent the leaching of manganese species into the reaction solution. The recovered MnO_2 catalyst could be reused without significant loss of its catalytic activity and selectivity. In addition, the present $MnO_2/NaHCO_3$ system was applicable to the selective oxidation of other biomass-derived substrates and large-scale oxidation of HMF to FDCA.

In order to investigate the present reaction mechanism for the MnO_2-catalyzed oxidation of HMF, the reactivity of MnO_2 was evaluated through the oxidation of HMF under O_2 and Ar atmospheres. HMF was converted into oxygenated products even under Ar atmosphere. In addition, the reaction rate under Ar atmosphere was almost the same as that under O_2 atmosphere. Such phenomena are also observed for aerobic oxidation with manganese oxide-based catalysts and are explained by substrate oxidation with oxygen supplied from the solid (Mars-van Krevelen mechanism).

Table 1. Effect of catalysts on the oxidation of HMF to FDCA in the presence of $NaHCO_3$.[a]

Catalyst	Conv. (%)	Yield (%)			
		FDCA	HMFCA	DFF	FFCA
MnO_2	≥99	91	–	–	–
$SrMnO_3$	≥99	58	1	–	16
Mn_2O_3	58	5	12	1	34
Mn_3O_4	17	1	1	–	–
MnO	22	–	2	1	2
Fe_2O_3	16	–	1	0	1
Fe_3O_4	40	–	1	0	1
FeO	22	–	–	–	–
Co_3O_4	17	1	1	1	–
CoO	21	–	1	2	2
NiO	19	–	1	2	1
CuO	19	1	1	1	1
Cu_2O	22	–	2	1	2

[a] Reaction conditions: Catalyst (0.1 g), HMF (0.2 mmol), $NaHCO_3$ (0.6 mmol), water (5 mL), pO_2 (1 MPa), 100 °C, 24 h.

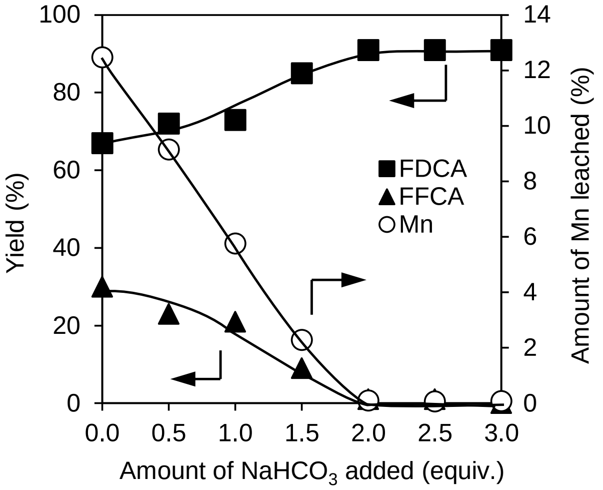

Fig.1 Yields and amounts manganese leached into the reaction solution against amounts of $NaHCO_3$ added. Reaction conditions: MnO_2 (0.1 g), HMF (0.2 mmol), $NaHCO_3$ (0.0–0.6 mmol), water (5 mL), pO_2 (1 MPa), 100 °C, 24 h.

4. Conclusions

We have successfully developed a simple and effective $MnO_2/NaHCO_3$ system for aerobic oxidation of HMF to FDCA. This reaction system can be applied to the aerobic oxidation of other biomass-derived substrates and large-scale oxidation of HMF to FDCA. Additionally, it is presumed that this reaction system proceed via Mars−Van Krevelen mechanism.

References

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