

Synthesis of 2,5-Furandicarboxylic Acid using Molecular Oxygen by a Manganese Dioxide Catalyst

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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 biopolyesters, such as polyethylene furanoate. While various homogeneous, heterogeneous, and enzymatic catalysts have been reported to date for the oxidation of HMF using O₂,^[1] effective catalytic systems are limited to supported noble metal catalysts which 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 but 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 catalyst are desired. In this work, we report a simple, efficient, and non-precious-metal-based MnO₂/NaHCO₃ system for aerobic oxidation of HMF to FDCA.^[2]

First, the oxidation of HMF to FDCA catalyzed by various metal oxides in the presence of NaHCO₃ (3 equivalents with respect to HMF) at 1 MPa O₂ was investigated. Among the catalysts tested, MnO₂ showed the highest yield of FDCA (91%). Other metal oxide catalysts were almost inactive. The effect of base addition was also investigated. Regardless of the cation, bicarbonates were the most effective. In the presence of 2–3 equivalents of NaHCO₃, FDCA was obtained in high yield whereas 5-formyl-2-

furancarboxylic acid (FFCA) and leaching of manganese species was not observed (Fig.1). The pH values of the reaction solutions with 2–3 equivalents of NaHCO₃ were in the range of 5.8–7.1 and larger than those (4.0–4.5) with 0–1.5 equivalents of NaHCO₃. These results suggest that 2–3 equivalents of NaHCO₃ are required not only to facilitate the oxidation reaction of HMF into FDCA, but also to prevent the leaching of manganese species into the reaction solution.

The used MnO₂ catalyst could be recovered from the reaction mixture by simple filtration, washing with water, and drying at 80 °C. The recovered MnO₂ catalyst could be reused without leaching of manganese species. In addition, the present MnO₂/NaHCO₃ system was applicable to the selective oxidation of other biomass-derived substrates and large-scale oxidation of HMF to FDCA.

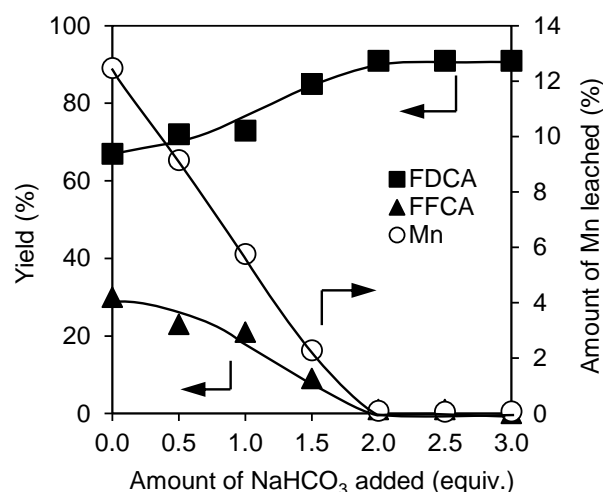


Fig.1 Yields and amounts manganese leached into the reaction solution against amounts of NaHCO₃ added. Reaction conditions: MnO₂ (0.1 g), HMF (0.2 mmol), NaHCO₃ (0.0–0.6 mmol), water (5 mL), pO₂ (1 MPa), 100 °C, 24 h.

REFERENCES

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