

New Strategy for Selective Production of Furan 2,5-dicarboxylic Acid from Concentrated HMF Solutions with CeO₂-supported Au Catalyst

Kiyotaka Nakajima,^{a,b,*} Minjune Kim,^a Yaqiong Su,^c Atsushi Fukuoka,^a Emiel J. M. Hensen^c

^a*Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo 001-0021, Japan.*

^b*Advanced Low Carbon Technology Research and Development Program (ALCA), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi 332-0012, Japan.*

^c*Inorganic Materials Chemistry, Schuit Institute of Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.*

*Corresponding author: nakajima@cat.hokudai.ac.jp

Abstract: Aerobic oxidation of a HMF-acetal with a CeO₂-supported Au catalyst and Na₂CO₃ in water gives a 90-95% yield toward furan 2,5-dicarboxylic acid (FDCA), an increasingly important commodity chemical for the biorenewables industry, from concentrated HMF-acetal solutions (10-20 wt%) without humin formation. The high stability of the acetal moiety suppresses thermal decomposition and self-polymerization of HMF in concentrated solutions. Kinetic studies supported by density functional theory calculations identify two crucial steps in the reaction mechanism, i.e., the partial hydrolysis of the acetal into 5-formyl-2-furan carboxylic acid involving OH⁻ and Lewis acid sites on CeO₂, and subsequent oxidative dehydrogenation of the in situ generated hemiacetal involving Au nanoparticles.

Keywords: HMF, acetal functionality, Au/CeO₂.

1. Introduction

Depletion of fossil fuel reservoir has requested sustainable resources represented by lignocellulosic biomass for energy and chemical production. Recently, there has been a strong interest on FDCA, which is considered as a promising building block for the production of biomass-derived polyesters. FDCA can be produced by aerobic oxidation of 5-(hydroxymethyl)furfural (HMF) in the presence of supported metal catalysts.¹⁻² Thermal instability of HMF frequently limits its potential application in chemical industry, because HMF is readily decomposed into an insoluble polymer so-called humin by thermal treatment at high temperature.³ It is desirable to convert HMF to a variety of useful compounds including FDCA from a concentrated solution and at high temperature within a short reaction time. Here, we report an efficient reaction system for aerobic oxidation of HMF and its derivative to FDCA with a CeO₂-supported Au catalyst under pressurized O₂ atmosphere.

2. Experimental

A CeO₂-supported Au catalyst was synthesized by precipitation-immobilization method reported in the literature.² NaOH was added to an aqueous solution (350 mL) containing HAuCl₄ (350 mg) to adjust the pH of the solution at 10. CeO₂ (4.01 g, JRC-CEO2 a reference catalyst supplied from Catalyst Society of Japan) was dispersed in deionized water (50 mL), and the mixture was added to the solution. After adjustment of its pH at 10 again and subsequent stirring for 18 h, white solid was collected by centrifugation and washed repeatedly with deionized water until no white precipitation was formed in the filtrate by addition of an aqueous AgNO₃ solution. The catalyst denoted as Au/CeO₂ was dried at 353 K for 3 h and used for HMF oxidation to FDCA.

HMF oxidation was carried out in a teflon-lined stainless steel autoclave. The mixture of HMF or its derivative (10-100 mg), Au/CeO₂ (10-100 mg, substrate/catalyst=1), Na₂CO₃, and deionized water (1.0 mL) was stirred with O₂ (0.5 MPa) at 130 °C for 15 h. The reaction mixture was diluted with deionized water to dissolve solid products completely and analyzed by high-performance liquid chromatography.

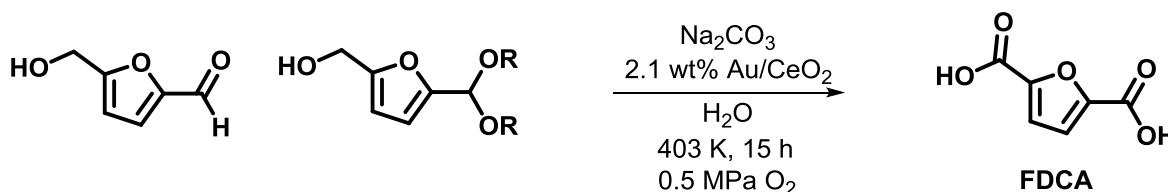
3. Results and discussion

FDCA formation was conducted with a dilute HMF (1 wt%) solution (Table 1). As reported in the literature, Au/CeO₂ gave high FDCA yield (91%) with complete HMF conversion. In order to increase in FDCA productivity, we conducted FDCA formation from a 10wt% HMF solution. Despite high FDCA yield obtained in the former reaction, FDCA yield reached maximum at 28% with complete HMF conversion. This large difference in FDCA yield is explained by humin formation.

In order to confirm deposition of insoluble humin on catalyst surface, the spent Au/CeO₂ catalysts were isolated from reaction mixture by centrifugation, washed with deionized water several time to remove weakly adsorbed organic compounds, and then dried at 80 °C for several hours. While no apparent change was observed in the former reaction, catalyst weight was significantly increased in the latter reaction (ca. 25%). This means that the formation of various by-products including solid humin deposited on catalyst surface is more preferable than HMF oxidation to FDCA in a high concentration HMF solution.

We also conducted FDCA formation from a HMF derivative using a 10 wt% concentration solution, and obtained a high FDCA yield (95%) with complete conversion under the same reaction conditions. In this reaction system, the amount of humin deposited on catalyst surface was estimated to be less than 0.4%. The decrease in humin formation is clearly attributed to the introduction of acetal functionality in HMF, which suppresses a lot of side reactions initiated by formyl group.

Table 1. FDCA formation from HMF and its acetal with Au/CeO₂ catalyst



Entry	Substrate	Concentration	Conversion /%	Base additive	FDCA yield /%
1		1 wt%	> 99.9	2 eq.	93
		10 wt%	> 99.9	2 eq.	28
2		1 wt%	> 99.9	2 eq.	95
		10 wt%	> 99.9	2 eq.	94

4. Conclusions

Introduction of acetal functionality in HMF is proposed as an approach to prevent undesired decomposition and self-polymerization, and to achieve efficient downstream conversion of the resultant the HMF acetal. We have demonstrated that FDCA can be obtained in high yield from concentrated solutions of the HMF acetal by aerobic oxidation in the presence of a Au/CeO₂ catalyst. The present results represent a significant advance over the current state of the art, overcoming an inherent limitation of the oxidation of HMF to an important monomer for biopolymer production.

References

1. N. K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, *Green. Chem.* 13 (2011) 824.
2. O. Casanova, S. Iborra, A. Corma, *J. Catal.* 265 (2009) 109.
3. P. Chambel, M. B. Oliveira, P. B. Andrade, J. O. Fernandes, R. M. Seabra, M. A. Ferreira, *Food Chem.* 63 (1998) 473.