



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Facile production of 2,5-diformylfuran from base-free oxidation of 5-hydroxymethyl furfural over manganese–cobalt spinels supported ruthenium nanoparticles

Dinesh Kumar Mishra^a, Jin Ku Cho^{a,b}, Yong Jin Kim^{a,b,*}

^a Green Chemistry & Material Group, Korea Institute of Industrial Technology (KITECH), 89 Yangdaegiro-gil, Ipjang myeon, Cheonan-si 31056, Republic of Korea

^b University of Science and Technology (UST), 176 Gajeong-dong, 305-350, Yuseong-gu, Daejeon, Republic of Korea

ARTICLE INFO

Article history:

Received 25 September 2017
Received in revised form 14 November 2017
Accepted 22 November 2017
Available online xxx

Keywords:

Oxidation
HMF
DFF
MnCo₂O₄
Ruthenium

ABSTRACT

This work reports manganese–cobalt spinels (MnCo₂O₄) supported ruthenium (Ru) nanoparticles, Ru/MnCo₂O₄, efficiently catalyzed 5-hydroxymethyl furfural (HMF) oxidation to 2,5-diformylfuran (DFF) with high yield 98.3% at 130 °C and 1.0 MPa of O₂ pressure in toluene used as solvent under base-free conditions. A new class of spinels MnCo₂O₄ having multiple valence states of Mn and Co was synthesized by using simple co-precipitation method and used as support with ruthenium nanoparticles as heterogeneous catalyst. The reusability tests of catalyst Ru/MnCo₂O₄ were also carried out and was found to be recyclable up to several consecutive cycles without significance loss of original activity.

© 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Introduction

Over recent years, a considerable attention has been paid by several scientists and researchers on the utilization of biomass as the sole renewable resources to produce biofuels [1–3] and platform molecules [4–7]. Indeed, the use of biomass is being considered as an alternative for the production of fuels, fine chemicals, and is also desirable more for sustainable society point of view. Biomass derived molecules (so-called platform molecules or building blocks) [6] have multiple functionalities in their structures and can be subjected to various chemical transformations to produce high-valuable compounds [8–11]. Among them as outlined by Bozell and Petersen [6], 5-hydroxymethyl furfural (HMF) is one of the most important molecules which is obtained from hexose such as fructose (via fructose dehydration), glucose (via isomerization of glucose to fructose) [12–18], and also directly from carbohydrates up to 98% yield [8,9,19,20]. Several studies have demonstrated the synthesis of HMF from cellulose or cellulose derived carbohydrates [19,20]. The selective production of 2,5-diformylfuran (DFF) from HMF oxidation is commercially

important because DFF is known as promising precursor used in the synthesis of pharmaceuticals, fungicides, and a variety of functional polymers [21–26].

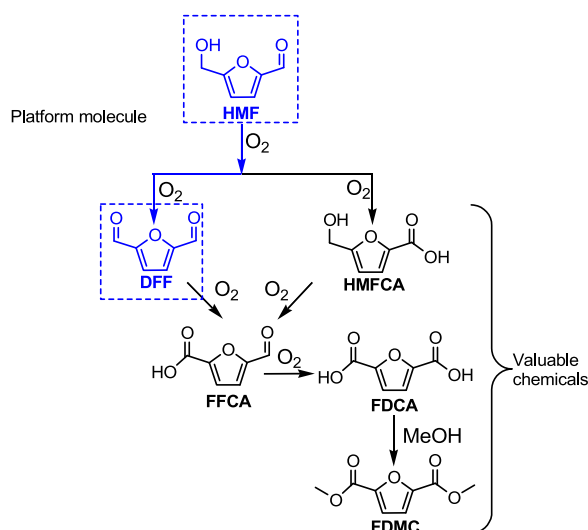
HMF is known as versatile key intermediate for the production of the dimethylfuran (DMF) as biofuel [3,27] and other important molecules such as levulinic acid (LA) [7,28], 2,5-furandicarboxylic acid (FDCA) [29–35], dihydroxymethylfuran, 5-hydroxy-4-keto-2-pentenoic acid, and DFF [9,36–38]. Undoubtedly, HMF could also be used in a broad array of industrial products and chemical manufacturing applications [21,22,26]. Despite the many exciting catalytic processes such as dehydration, hydrogenation, dehydrogenation, decarbonylation, and decarboxylation, the catalytic oxidative transformation of HMF to DFF remains a formidable challenge because it gives several by-products such as 5-hydroxymethyl-2-furancarboxylic acid (HMFA), 5-formyl-2-furancarboxylic acid (FFCA), and ultimately FDCA (Scheme 1). Therefore, the selective oxidation of HMF to DFF is an interesting approach which requires oxidation of its only primary hydroxyl group, except aldehyde group. For this purpose, a number of literatures have been found on HMF oxidation to DFF in the presence of homogeneous and heterogeneous catalysts. For example, a homogeneous catalyst system comprising Co(II)/Mn(II)/Zr(II)-Br₂ has been employed to give 61% selectivity of DFF at 99.7% HMF conversion in acetic acid used as solvent at 70 bar oxygen pressure [39]. However, the use of corrosive media and hazardous compounds makes the process circumvent. Moreover,

* Corresponding author at: Green Chemistry & Material Group, Korea Institute of Industrial Technology (KITECH), 89 Yangdaegiro-gil, Ipjang myeon, Cheonan-si 31056, Republic of Korea.

E-mail address: yjkim@kitech.re.kr (Y.J. Kim).

<https://doi.org/10.1016/j.jiec.2017.11.040>

1226-086X/© 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.



Scheme 1. DFF and over oxidized by-products from HMF oxidation.

homogeneous catalyst systems inevitably suffer from catalyst/product separation. In another study, HMF is oxidized to DFF with 63–89% yield using Mn(III)–salen catalysts [40] wherein sodium hypochlorite (NaOCl) used as an oxidant, in a pH 11.3 phosphate buffer–CH₂Cl₂ biphasic system at room temperature, however, this catalyst was not reusable. Vanadyl–pyridine complexes (PVP) catalyzed HMF oxidation in DMSO solvent and it could give ~99.2% of DFF selectivity at ~81% conversion. While, SBA supported vanadyl–pyridine complexes (PVP) gave only ~50% conversion of HMF and 98% selectivity to DFF in 10 bar of air pressure [41]. Ma et al. reported [vanadyl sulphate, (VO₂)₂/Cu(NO₃)₂] as homogeneous catalyst system for HMF oxidation in acetonitrile, leading to a nearly quantitative synthesis of DFF at 353 K [42]. This progress demonstrated the feasibility of efficient synthesis of DFF. However, catalysts generally suffered from difficulties in separation from the product mixtures. In contrast, the use of heterogeneous catalysts has several advantages including a wide range of operating conditions (temperature, pressure), high industrial relevance, and most important factor is the ease of separation and recovery. Moreau et al. reported that a heterogeneous catalyst of mixed oxides (V₂O₅/TiO₂) with high weight ratio of catalyst to HMF (2/1) gave 85% yield of DFF in toluene at 363 K and 1.6 MPa pressure of air [43]. DFF with 86.2% yield from HMF oxidation was obtained after 12 h at 110 °C using another type of heterogeneous and reusable polyaniline-grafted vanadyl acetylacetonate [VO(acac)₂] catalyst [37]. γ -Fe₂O₃ encapsulated with Ru-exchanged hydroxyapatite (γ -Fe₂O₃@-HAP-Ru) is used as heterogeneous catalyst in aerobic oxidation of HMF to give DFF with 89.1% yield in 4-chlorotoluene [38]. Recently, Nie et al. reported that a heterogeneous catalyst, activated carbon supported ruthenium (Ru/C), which was an effective and stable catalyst in the oxidation of HMF, affording a high DFF yield (96%) at 383 K and 2.0 MPa O₂ in toluene [44]. Selective oxidation of HMF to DFF was conducted using alumina supported ruthenium catalyst which afforded 97.3% yield of DFF in toluene at 130 °C and 40 psi O₂ pressure with molar ratio of HMF/Ru = 50 [45]. Another ruthenium based catalyst, covalent triazine frameworks (CTFs) supported ruthenium catalyst gave high conversions of HMF (97.3%) and yields of DFF (72.7%) which could be obtained after only 3 h at 80 °C under 20 bar of air [46], however, HMF/Ru ratio was 40. More recently, a bimetallic catalyst, MOF-derived magnetic hollow Fe–Co nano catalyst, could deliver >99% yield of DFF at complete HMF conversion, which is quite attractive but it took long reaction time (6 h) [47].

Even though various metal oxides and its corresponding other metal supported systems have been synthesized and used as heterogeneous catalysts [48]. Moreover, we also reported firstly manganese–cobalt spinels supported ruthenium nanoparticles, Ru/MnCo₂O₄, catalyzed HMF oxidation to give FDCA with 99.1% yield at complete conversion of HMF in aqueous phase [49]. During the course of studying HMF oxidation, product selectivity was found to very depend on the use of solvent. These results led us to investigate a variety of recyclable solvents with moderate boiling points in HMF oxidation to DFF catalyzed by Ru/MnCo₂O₄. Interestingly, switching solvent from water to toluene afforded exclusive formation of DFF with 98.3% from HMF oxidation under mild conditions. Moreover, the recyclability tests of Ru/MnCo₂O₄ catalyst in HMF oxidation to DFF are carried out up to four successive runs and catalyst was found to be recyclable without considerable loss of its original activity.

Experimental

(1) Materials

All chemical reagents were used as received without any further purification. Commercially available manganese(II) acetate tetrahydrate (CH₃COO)₂Mn·4H₂O, cobalt(II) acetate tetrahydrate (CH₃COO)₂Co·4H₂O, ammonium sulphate (NH₄)₂SO₄, and ammonium bicarbonate (NH₄HCO₃) were purchased from Sigma Aldrich Company. During the preparation of support used and its corresponding ruthenium catalyst, deionized water was used. Ruthenium (III) chloride hydrate (RuCl₃·nH₂O) was purchased from DAEJUNG Chemicals & Metal Co., LTD, Korea. Sodium borohydride (NaBH₄) used as reducing agent was purchased from Sigma Aldrich Company. Solvents such as toluene, DMSO, DFF, acetonitrile, methanol, ethanol, benzotrifluoride, and 1,4-dioxane are used as such as received. Oxygen (O₂) cylinder was supplied by Gaskor. Ltd. from Korea.

(2) Synthesis of manganese–cobalt spinels support material

A new class of manganese–cobalt spinels, MnCo₂O₄, was synthesized using simple co-precipitation method [49]. In this method, (CH₃COO)₂Mn·4H₂O (8 g, 32.6 mmol) and (CH₃COO)₂Co·4H₂O (16.3 g, 65.3 mmol) were dissolved in water (400 mL) and allowed to homogenize by vigorous stirring for 30 min. Separately, ammonium sulphate (50 g) was dissolved in water (400 mL). These solutions were mixed slowly and stirred for 4 h. An aqueous solution of excess amount of ammonium bicarbonate (~50 g) was added slowly to the above mixture and stirred for 6 h. The light pink precipitate was obtained and collected by filtration. The pink precipitate was washed thoroughly with distilled water, and absolute ethanol, and dried at 60 °C for 12 h under vacuum. The obtained pink carbonate precursor MnCo₂CO₃ (Pink precipitates can be seen in Fig. S1) was calcined in a furnace at 425 °C (2 °C min⁻¹) in dry synthetic air for 8 h and kept for an additional 8 h followed by cooling naturally to room temperature (RT). The black MnCo₂O₄ was obtained (Fig. S1).

Synthesis of cobalt–manganese spinels supported ruthenium nanoparticles catalyst

Manganese–cobalt spinels supported ruthenium nanoparticles catalyst, Ru/MnCo₂O₄, was prepared by using simple impregnation–reduction method as reported in the literatures [50]. To support Ru (1.8% by weight) on manganese–cobalt spinels, 4.5 g of manganese–cobalt spinels (MnCo₂O₄) and 20 mL aqueous solution of RuCl₃·nH₂O (0.19 g) were kept together in a two neck 100 mL round bottom flask, which was submerged in cooling bath.

Download English Version:

<https://daneshyari.com/en/article/6666990>

Download Persian Version:

<https://daneshyari.com/article/6666990>

[Daneshyari.com](https://daneshyari.com)