



# Catalytic oxidation of biomass derived 5-hydroxymethylfurfural (HMF) over Ru<sup>III</sup>-incorporated zirconium phosphate catalyst



Fan Wang, Ziliang Yuan, Bing Liu\*, Shaohua Chen, Zehui Zhang\*

Department of Chemistry, Key Laboratory of Catalysis and Material Sciences of the State Ethnic Affairs Commission & Ministry of Education, South-Central University for Nationalities, Wuhan 430074, China

## ARTICLE INFO

### Article history:

Received 6 March 2016  
Received in revised form 19 April 2016  
Accepted 2 May 2016  
Available online 6 May 2016

### Keywords:

Oxidation reaction  
5-Hydroxymethylfurfural  
Furan chemicals  
Ruthenium catalyst  
Molecular oxygen

## ABSTRACT

In this study, a new ruthenium catalyst was used for the oxidation of biomass derived 5-hydroxymethylfurfural (HMF) under mild conditions, which was prepared by the exchange of Ru<sup>3+</sup> with H<sup>+</sup> in the structure of the zirconium phosphate (ZrP). The as-prepared ZrP–Ru catalyst showed high catalytic activity towards the oxidation of HMF, affording 100% of HMF conversion at 130 °C after 12 h under atmospheric oxygen pressure. 2,5-Furandicarboxylic acid (FDCA) and 2,5-diformylfuran (DFF) were detected to be the major oxidation products.

© 2016 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

## Introduction

The non-renewable fossil feedstocks has been used to supply chemicals and fuels to the world for a long time. However, the continuous exploitation together with ever-increasing demand will result in the drain of fossil feedstocks in one day. Thus, much more attention has been shifted to the use of renewable feedstocks for the supply chemicals and fuels [1,2]. Undoubtedly, the abundant renewable biomass can serve as a promising alternative to fossil feedstocks, as it is the only material renewable resource that can provide both chemicals and fuels [3–5].

Carbohydrates are one of the most important types of biomass feedstock. Catalytic dehydration of C6 carbohydrates can generate 5-hydroxymethylfurfural (HMF). HMF is listed as one of the top 12 important platform chemicals by the US Energy department [6], which can be used as a precursor for the synthesis of valuable chemicals, high-energy density fuel and polymer monomers [7,8]. Due to the significant importance of HMF in the link bridge between fossil feedstock and biomass resource, great effort has been devoted to the development of various methods for the synthesis of HMF from C6 carbohydrates such as fructose, glucose,

and cellulose in various catalytic systems during the past few decades [9–15].

Recently, a considerable interest has been shifted to the synthesis of HMF derivatives. Selective oxidation of HMF is one of the most pivotal transformations. As depicted in Fig. 1, the oxidation of HMF can produce several important furan chemicals including 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), and 2,5-furandicarboxylic acid (FDCA) [16–19]. These furan chemicals from the oxidation of HMF are found to be useful in modern chemistry. For example, FDCA molecular contains two carboxylic acids group in the furan ring with a similar structure of the fossil resource derived terephthalic acid, which is used for the synthesis of polymers. Thus, FDCA can serve as a substitute of terephthalic acid in the useful polymers [20]. For instance, poly(ethylene 2,5-furandicarboxylate) (PEF) has been recently prepared from renewable sources, and it showed comparable thermal stability to PET [21]. DFF can be used as a starting material for the synthesis of various poly-Schiff bases, antifungal agents, pharmaceuticals, organic conductors, furan-containing polymers and cross-linking agents of poly(vinyl alcohol) for battery separations [22–24].

In the past decades, the oxidation of HMF was carried out by the use of stoichiometric amount of tradition oxidants, which is high cost and high toxic to the environment [25,26]. With the emphasis on the sustainable chemistry at present, the oxidation of HMF is very attractive by the use of molecular oxygen as the oxidant over heterogeneous catalysts. The oxidation of HMF into DFF is

\* Corresponding authors. Tel.: +86 27 67842752; fax: +86 27 67842752.

E-mail addresses: [liubing@mail.scuec.edu.cn](mailto:liubing@mail.scuec.edu.cn) (B. Liu), [zehuizh@mail.ustc.edu.cn](mailto:zehuizh@mail.ustc.edu.cn) (Z. Zhang).

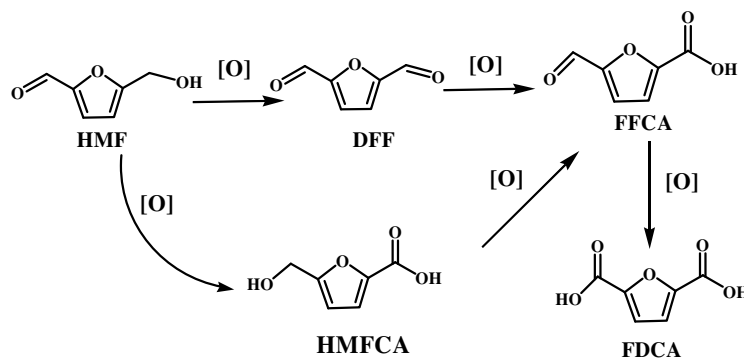


Fig. 1. Possible oxidation products from HMF.

generally performed in the organic solvents and the catalysts mainly includes in vanadium catalyst [27] and manganese oxide catalysts [28] and ruthenium catalysts [29]. As far as the oxidation of HMF into FDCA, it is generally carried out in alkaline water in the presence of noble metal catalysts [30–32]. Although good results were achieved, some catalytic systems demonstrated fatal drawbacks such as the high ratio of catalyst to substrate, and the loss of the catalytic activity.

Zirconium phosphate (ZrP) is reported to be a useful inorganic material with some excellent properties such as high thermal stability, and high water tolerance ability [33]. The  $H^+$  of the P–OH can be exchanged by divalent or trivalent cations to introduce new catalytic sites [34,35]. For example, the copper-exchanged ZrP catalyst can promote the oxidation of alcohols into ketones or aldehyde using  $H_2O_2$  as the oxidant [34]. As ruthenium catalysts are the effective candidates for the oxidation reactions, herein, ruthenium-incorporated ZrP catalyst was prepared in this study and used for the conversion of carbohydrates into HMF.

## Experimental

### Materials and methods

Zirconium oxychloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ , 99.0%), diammonium hydrogen ortho-phosphate [ $(NH_4)_2HPO_4$ , 98.5%], cetyltrimethylammonium bromide (CTAB, 98%) and ammonium carbonate [ $(NH_4)_2CO_3$ ] were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).  $RuCl_3 \cdot xH_2O$  (38.0–42.0 wt.% Ru) was purchased from Aladdin Chemicals Co. Ltd. (Shanghai, China). 5-Hydroxymethylfurfural (98%) was purchased from Beijing Chemical Co. Ltd. (Beijing, China). 5-Hydroxymethyl-2-furancarboxylic acid, 2,5-diformylfuran and 2,5-furandicarboxylic acid were purchased from the J&K Chemical Co. Ltd. (Beijing, China). Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA). All the chemicals were obtained commercially and used without any further purification. All the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

### Catalyst preparation

Zirconium phosphate (ZrP) was synthesized as described in our previous work [36]. Briefly, zirconium carbonate complex solution with a molar ratio of 0.1  $Zr^{4+}$ :2  $PO_4^{3-}$ :0.25 CTAB:1000  $H_2O$  was stirred at room temperature for 12 h, and then kept still at 60 °C for 48 h, followed at 80 °C for 24 h. Then the mixture was kept in an autoclave at 60 °C for 24 h. The mixture was filtrated, and washed with water until the pH was neutral. The solid was dried at 100 °C overnight and calcined at 550 °C for 6 h to get the ZrP material.

For the incorporation of ruthenium into ZrP,  $RuCl_3 \cdot xH_2O$  (50 mg, 38.0–42.0 wt.% Ru) was added to the ZrP (1 g) suspending in 20 ml of water, and then the mixture was stirred at 70 °C for 24 h. During the process, the colour of the mixture became clear gradually, and it was colourless after stirring for 24 h. The resulting Ru–ZrP catalyst was filtered and washed with deionized water several times. Finally, the resulting solid was dried in a vacuum oven overnight, and the catalyst was obtained with a grey colour, which was abbreviated as ZrP–Ru catalyst.

### Catalyst characterization

FTIR spectra were recorded on a Nicolet Nexus IR 6700 with a DTGS detector. Scans were collected in the range of wave numbers 4000–400  $cm^{-1}$  at a resolution of 4  $cm^{-1}$ . The coal/KBr disks were prepared at ratio 150 mg KBr and 1 mg sample. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al  $K\alpha$  source (1486.6 eV) at constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All binding energies (BEs) were corrected referencing to the C1s (284.6 eV) peak of the contamination carbon as an internal standard. The ruthenium content in the catalysts was quantitatively determined by inductively coupled atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure ( $P/P_0$ ) range of 0.05–0.3. The pore size distributions were derived from desorption branches of isotherms by using BJH model.

### General procedure for the oxidation of HMF

Typically, the ZrP–Ru catalyst (100 mg) and HMF (100 mg) were added to 7 ml of p-chlorotoluene. Then the reaction mixture was stirred with a magnetic stirring at 110 °C and flushed with oxygen under atmospheric oxygen pressure at a flow rate of 20 ml/min. After reaction with a certain time, the products in the reaction mixture were analyzed by HPLC.

### Determination of the products

High-performance liquid chromatography (HPLC) was used for the analysis of the furan products, which was equipped with a reversed-phase C18 column (200 × 4.6 mm) and an ultraviolet detector. The furan products were successfully separated from each other by the use of acetic acid aqueous solution (1 wt.%) and acetonitrile with the volume ratio of 15:85 as the mobile phase at a rate of 1.0 ml/min, and the column oven temperature was

Download English Version:

<https://daneshyari.com/en/article/227202>

Download Persian Version:

<https://daneshyari.com/article/227202>

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