Highly dispersed ruthenium nanoparticles on hydroxyapatite as selective and reusable catalyst for aerobic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid under base-free conditions

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A B S T R A C T

The aerobic oxidation of bio-platform compound 5-hydroxymethylfurfural (HMF) to value-added 2,5-furandicarboxylic acid (FDCA) was studied over hydroxyapatite supported ruthenium (Ru/HAP) nanocatalyst without extra addition of soluble base. Molecular oxygen and water were used as the oxidant and solvent, respectively. Various dominant reaction parameters, including HMF/Ru molar ratio, O_2 pressure, reaction temperature and reaction time were systematically investigated. When HMF/Ru molar ratio was of 25, Ru/HAP catalyst exhibited the optimal catalytic performance, *i.e.*, total conversion of HMF and 99.6% yield of FDCA were achieved at 120 °C and 1 MPa O_2. Kinetic study revealed that the oxidation of HMF to FDCA followed a tandem pathway and the oxidation of carbonyl group in 5-formylfuran-2-carboxylic acid (FFCA) was found as the rate-determining step. Besides, well-dispersed uniformly-small metallic Ru^0 nanoparticles and the acidic-basic sites presented on HAP surface were both essential to drive this base-free oxidation process. During the kinetic-controlled range (*i.e.*, initial 1 h of reaction), the activity of the catalyst can be almost remained after five consecutive cycles; afterwards a minor decline in activity was observed mainly due to the partial oxidation of surface metallic Ru species, but the activity can be entirely recovered by a hydrogen reduction at 350 °C.

1. Introduction

Due to the depletion of fossil fuels and the associated deterioration of world environment, more and more attention has been paid to the valorization of biomass resources for sustainable production of fuels and chemicals [1,2]. Direct conversion of reactive biomass-derived platform instead of lignocellulosic biomass is regarded as a more effective and desirable strategy in the current stage of biorefinery [3]. 5-Hydroxymethylfurfural (HMF), a dehydration product of fructose and glucose is widely considered as an important and versatile bio-platform compound that can be converted into a variety of value-added chemicals [4–6]. Among those, 2,5-furandicarboxylic acid (FDCA) has received significant attention because FDCA can be used as a renewable bio-monomer in polymer industry, to potentially replace the petro-based terephthalic acid for the production of polyethylene terephthalate (PET) plastic and polybutyleneterephthalate (PBT) plastic [7]. As a furan derivate bearing a hydroxymethyl group and an aldehyde group, HMF can be oxidized to several possible products, such as 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), and final product

FDCA (Scheme 1). There is no doubt that developing selective and productive catalyst for FDCA production remains central in the oxidative valorization of HMF compound [8–10].

In homogenous catalysts, stoichiometric oxidants like $KMnO_4$ [11] and metal halides like $Co(OAc)_2/Zn(OAc)_2/NaBr$ [12] were employed for oxidation of HMF to FDCA. Acetic acid was needed as solvent for the latter system. But unfortunately only a moderate FDCA yield (*ca.* 60%) was obtained. In such a context, those homogeneous catalytic systems may generally result in problems of reactor corrosion, toxicity emission and catalyst recycling. Alternatively, heterogeneous catalytic systems for the selective oxidation of HMF to FDCA using supported noble metals (*e.g.* Au [13,14], Pt [15,16], Pd [17,18] and Ru [19,20]) as active components and molecular oxygen as oxidant were well developed. However, the addition of excessive amount of soluble bases (most often like NaOH or Na_2CO_3) was prerequisite to achieve high FDCA yield, as it was shown that alkali can facilitate alkoxide formation and C—H activation in alcohol oxidation process. As a result, further acidification and purification were needed for subsequent use of FDCA in the polymer industry, hampering the green footprint of the process. Therefore, some recent efforts have been made to perform the base-free
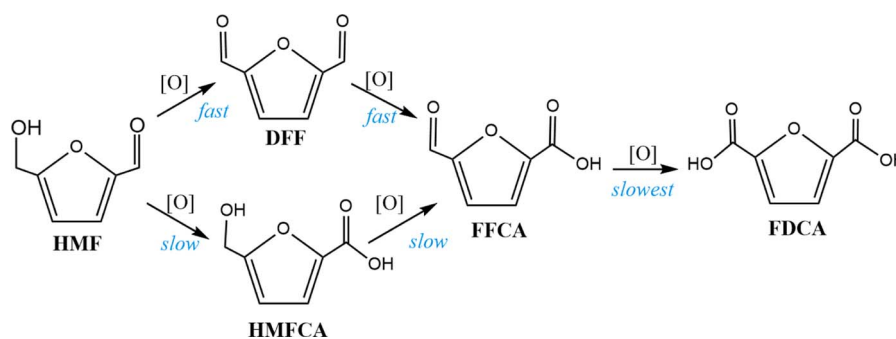
Scheme 1. Reaction pathway for the oxidation of HMF over the Ru/HAP catalyst.

aerobic oxidation of HMF to FDCA using supported noble-metal nanoparticles. And developing low-cost and novel catalyst remains still significant challenge.

In supported catalysts the properties of support materials and the interactions between active components and support play a critical role in determining the final catalytic performances of the catalysts. Natural or synthetic acidic-basic minerals such as hydrotalcite (HT) [21–29] and hydroxyapatite (HAP) [30,31] have been successfully employed as catalyst supports for the base-free oxidation of liquid alcohols, especially HT and its derivatives are recently studied for HMF oxidation [23,26–29]. Particularly HAP with the general formula $Ca_{10}(PO_4)_6(OH)_2$ is the most stable calcium phosphate salt bearing both acidic and basic sites in a single crystal lattice. The tunable Ca/P ratio in HAP material is commonly used as an index for the (non-)stoichiometry composition and strongly affects the acidic-basic properties [32–34]. This makes HAP really attractive to be exploited as an alternative catalyst support for HMF oxidation under base-free conditions. Previously there was only one report showing that HAP encapsulated iron oxide with surface modification by ruthenium (γ-Fe$_2$O$_3$@HAP-Ru) could oxidize HMF, but the major product was 2,5-diformylfuran (DFF) with a yield of 89% [35].

On the other hand, ruthenium is less expensive than other noble metals, even though Pd [27,28], Au [29,36,37] and Pt [38,39] have been largely reported for HMF oxidation. In the point view of low-cost effectiveness, ruthenium catalysts are certainly worth of exploring and the so-far reported catalyst candidates are limited. Liu's group reported that an activated carbon supported ruthenium (Ru/C) catalyst in the presence of HT as a solid base afforded a FDCA selectivity of 78.2% [19]. Moreover, the yield of FDCA was enhanced up to 97.3% by the 5 wt% Ru/C catalyst but only in the presence of Mg(OH)$_2$ as base additive [40]. In the meantime, commercial Ru/C catalyst [41] and Ru clusters supported on covalent triazine frameworks (Ru/CTFs) [42] were reported as stable catalysts for the oxidation of HMF under base-free conditions. But those catalysts did not exhibit excellent catalytic activity, as the yield of FDCA was of 88% and 78%, respectively. Very recently, MnCo$_2$O$_4$ spinel supported ruthenium (Ru/MnCo$_2$O$_4$) catalyst was reported to afford an enhanced FDCA yield (99%) due to both Lewis and Brønsted acidic sites on the catalyst surface [43]. Nevertheless, the high Ru loading (4 wt%) of catalyst and the high pressure (2.4 MPa air) of oxidant were required to achieve the high FDCA yield.

Herein we report highly dispersed and small (*ca.* 1.8 nm) ruthenium nanoparticles loaded on the cheap and easily available commercial hydroxyapatite as highly selective and stable heterogeneous catalyst for the aerobic oxidation of HMF to FDCA under base-free conditions. To the best of our knowledge, there has been no report so far on the use of HAP supported Ru nanoparticles (1.5 wt% Ru/HAP) as catalyst in HMF oxidation. The acidic and basic properties of HAP, the morphology and valence state of Ru nanoparticles were carefully characterized. The influence of various reaction parameters (such as HMF/Ru molar ratio, O$_2$ pressure and reaction temperature) and kinetic study were investigated, allowing discussing the plausible reaction mechanism for

the oxidative conversion of HMF to FDCA over the Ru/HAP catalyst. Besides, the catalyst stability and reusability were also studied.

2. Experimental

2.1. Materials and reagents

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ 34–40% Ca), RuCl$_3$·xH$_2$O ($\geq$ 38% on Ru basis) and NaBH$_4$ (> 98%) were purchased from Alfa Aesar. Polyvinylpyrrolidone (PVP, > 98%, MW = 10,000) was purchased from Tokyo Chemical Industry Co. Ltd. 5-Hydroxymethylfurfural (HMF, 98%), 2,5-diformylfuran (DFF, 98%), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA, 98%), 5-formylfuran-2-carboxylic acid (FFCA, 98%) and 2,5-furandicarboxylic acid (FDCA, 98%) were purchased from Ark Pharm. All the chemicals were used as received without further purification or treatment.

2.2. Catalyst preparation

RuCl$_3$·xH$_2$O precursor was dispersed in a polyvinylpyrrolidone aqueous solution (PVP/Ru = 1.2/1, in wt.) under stirring and then a freshly made NaBH$_4$ solution (NaBH$_4$/Ru = 5/1, in mol.) was added dropwise to yield Ru nano-colloidal. Hydroxyapatite water-suspension was added and the mixture was stirred for 2 h under room temperature. The solid was recovered by filtration and washed with hot deionized water (90 °C) to remove PVP and with excessive deionized water to remove Na$^+$ and Cl$^-$ ions. The Ru/HAP catalyst was finally dried at 60 °C under vacuum for 12 h. In this work, the theoretical Ru loadings of Ru/HAP catalyst was 1.5 wt%.

2.3. Catalytic reaction

HMF (2 mmol) and catalyst (HMF/Ru = 25, in mol.) were added into a batch-type Teflon-lined stainless-steel autoclave (50 mL) with 20 mL deionized water as solvent. After the introduction of O$_2$ (1 MPa), the reactor was placed in an oil bath pre-heated at 120 °C with magnetic stirring at 600 rpm. After 24 h, the reactor was transferred to ice-bath. Then the catalyst was separated by centrifugation (8000 rmp for 10 min) and washed by deionized water three times followed by drying at 60 °C under vacuum for 12 h before its next use.

The liquid sample was analyzed on an Agilent 1260 Infinity high-performance liquid chromatography (HPLC) with a photodiode array detector (DAD) and a Shodex SH-1011 sugar column (8 mm × 300 mm × 6 μm) using H$_2$SO$_4$ solution (5 mM) as mobile phase. The quantification was carried out using the external standard method. HMF, DFF, HMFCA, FFCA and FDCA were calibrated by using its standard at different concentrations at the specific wavelength (260 nm for HMFCA and FDCA, 285 nm for HMF, and 290 nm for DFF and FFCA). The conversion of HMF and the selectivity of each product were defined as the molar percentage of HMF converted and the molar percentage of each product formed in HMF converted, thus the yield of