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Ru/$Mn_XCe_1O_Y$ catalysts with enhanced oxygen mobility and strong metal-support interaction: Exceptional performances in 5-hydroxymethylfurfural base-free aerobic oxidation

Tianyu Gao [a], Jing Chen [b], Wenhao Fang [a,*], Qiue Cao [a], Weiping Su [b], Franck Dumeignil [c]

[a] *School of Chemical Science and Technology, Key Laboratory of Medicinal Chemistry for Natural Resource – Ministry of Education, Functional Molecules Analysis and Biotransformation Key Laboratory of Universities in Yunnan Province, Yunnan University, 2 North Cuihu Road, 650091 Kunming, China*
[b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, 350002 Fuzhou, China*
[c] *Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, 59000 Lille, France*

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ABSTRACT

Mn-Ce mixed oxides-supported Ru nanoparticles (Ru/$Mn_XCe_1O_Y$) with enhanced oxygen mobility and strong metal-support interaction were prepared and applied to the aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) without addition of any base additives. Oxygen and water were used as green oxidant and solvent, respectively. The catalysts were characterized in depth by XRD, H_2-TPR, O_2-TPD, UV–Vis DRS, XPS and TEM, to reveal materials properties from bulk to surface. The influence of Mn/Ce molar ratios in support materials and reaction parameters (*i.e.*, HMF/Ru ratio, O_2 pressure, reaction temperature and time) was systematically studied and optimized. The reaction route and rate-determining step for oxidation of HMF to FDCA over the Ru/$Mn_XCe_1O_Y$ catalysts were investigated by kinetic analysis. Well-dispersed metallic Ru nanoparticles with a mean size of 4.4 nm deposited on the support were found essential to activate and oxidize the HMF molecule. The Mn/Ce molar ratio was found to affect not only conversion of HMF but also distribution of products. The Ru/$Mn_6Ce_1O_Y$ catalyst demonstrated an exceptional yield (≥99%) of FDCA, which corresponds in our conditions to one of the best productivity (5.3 $mol_{FDCA}\cdot mol_{Ru}^{-1}\cdot h^{-1}$) ever reported in literature. The superior activity of the Ru/$Mn_6Ce_1O_Y$ catalyst was mainly associated with (i) the strong metal-support interaction and (ii) the synergistic effect between manganese and cerium oxides. This catalyst showed the highest surface concentrations in Mn^{4+} and Ce^{3+} among the series, which, as a consequence, enhanced the availability and mobility of active oxygen species. This catalyst was shown resistant to deactivation during eight recycling uses thanks to a strong metal-support interaction between Ru nanoparticles and the Mn-Ce mixed oxide used as a support.

1. Introduction

Pressures for an evolving sustainable society are calling for awareness upon chemistry science and for a need to develop smart technologies to convert lignocellulosic biomass, as an abundant and environmentally sound resource, into chemicals and fuels. An effective and desirable strategy for chemical utilization of cellulose is direct conversion of the reactive platform compounds under mild conditions [1–5]. 5-Hydroxymethylfurfural (HMF) is regarded as a versatile platform molecule from plentiful cellulosic derivative C_6 carbohydrates and can be used as a precursor for the production of various value-added chemicals [6–9]. In particular, *2,5*-furandicarboxylic acid (FDCA) obtained by aerobic oxidation of HMF is a promising candidate for substituting terephthalic acid, a petroleum-based monomer, to manufacture renewable bio-based plastics instead of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [10].

Most often, aerobic oxidation of HMF to FDCA undergoes a multistep reaction pathway, as described in Scheme 1, yielding several possible intermediates as by-products, including *2,5*-diformylfuran (DFF), *5*-hydroxymethyl-*2*-furancarboxylic acid (HMFCA) and *5*-formyl-*2*-furancarboxylic acid (FFCA). Therefore, selective oxidation of HMF to FDCA largely relies on the development of highly active, selective and stable catalysts. In homogenous catalysis, metal halides such as Co/Mn/Br [11] and Co/Zn/Br [12] in the presence of acetic acid were reported, affording a moderate FDCA yield (*ca.* 60%). Nevertheless, the use of a corrosive solvent and at rather

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* Corresponding author.
E-mail address: wenhao.fang@ynu.edu.cn (W. Fang).

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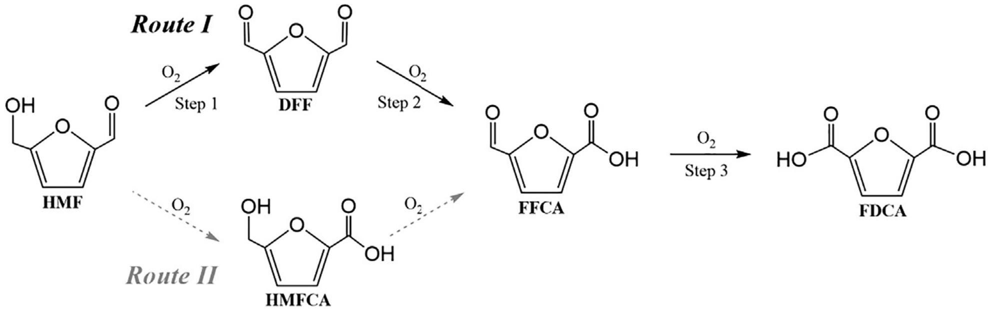

Scheme 1. Reaction pathway of aerobic oxidation of HMF to FDCA over the Ru/Mn$_X$Ce$_1$O$_Y$ (Mn/Ce $\geq$ 4) catalyst.

high pressures of oxidant made those catalytic processes less green and competitive. Alternatively, supported noble-metal nanoparticles were widely developed as heterogeneous catalysts for the aerobic oxidation of HMF to FDCA [13]. Typically, Au [14,15], Pd [16,17], Pt [18,19] and Ru [20,21] nanocatalysts were reported. However, excessive amount of soluble base additives (*i.e.*, hydroxide or carbonate of alkali metals) must be added to achieve high yield of FDCA, as it was well known that alkali could facilitate alkoxide formation and C—H activation in alcohol oxidation. In addition, the base is important for preventing the metal leaching with formation of carboxylate instead of free acid. Moreover, the transformation of —CHO to —COOH can smoothly proceed in the absence of a base [22]. As a result, the obtained FDCA in the form of a salt cannot be directly used in subsequent polymer industry. Indeed, the extra acidification and purification would lead to higher application cost and lower green process.

Therefore, aerobic oxidation of HMF to FDCA in water in the absence of a soluble base is really an ideal route although the base-free catalytic systems usually need relatively harsher conditions. Developing low-cost and efficient catalysts remains still significantly challenging. Recent advances have been achieved on various supported monometallic Au [23–27], Pd [28], Pt [29,30], Ru [31–34], and bimetallic Au-Pd [35,36], Pt-Pd [37] catalysts. It can be concluded that the properties of support materials, in combination with noble metal nanoparticles, played an important role in realizing the base-free oxidation of HMF through different mechanisms. Solid bases such as hydrotalcite (HT) [23,24,28,37], hydroxyapatite (HAP) [34] and layered double hydroxide (LDH) [36] were frequently employed as supports. The tunable basic sites not only may act to cleave the O—H bond in the HMF molecule to form metal-alkoxide intermediate but also could promote oxidation of —CHO group to —COOH group. In particular, Wilson et al. elucidated that synergistic effects between moderate strength base sites within alkali-free hydrotalcites and high gold surface concentrations can afford highly selective and entirely heterogeneous catalysts for aqueous phase cascade oxidation of aldehyde and alcohol like HMF [24]. Surface functionalized carbon was also a favorable support material. In Pt/CNTs [29] and Au-Pd/CNTs [35] catalysts, the carbonyl/quinone and phenol groups on CNTs surfaces may facilitate adsorption of HMF and intermediates, but not of FDCA, which was believed to be important for explaining the high catalytic activity of the as-designed catalysts. In Au/C catalyst [27] the basic carbon supports with positive charges resulted in a higher adsorption and local concentration of hydroxyl ions, which acted as cocatalysts for gold and enhanced gold-catalyzed dehydrogenation. Besides, metal oxide-carbon composites were also reported as good supports for base-free oxidation of HMF to FDCA [25,30]. Au/HT-AC [25] and Pt/C-O-Mg [30] catalysts showed excellent activity and stability probably due to the creation of new, strong and stable basic sites.

Cerium oxide and ceria-containing materials have received much attention either as catalysts or structural and electronic promoters for heterogeneous catalysts [38]. Typically, MnO$_X$-CeO$_2$ mixed oxides showed promising catalytic applications in various oxidation processes in environmental and sustainable chemistry, such as complete oxidation of formaldehyde [39] and toluene [40,41], wet oxidation of waste water containing phenol [42,43], oxidation of ammonia [44] and diesel soot [45]. As a matter of fact, mixed oxides of transition metal and rare earth usually demonstrated a large number of surface and bulk oxygen vacancies and showed enhanced oxygen storage capacities. Thus, tunable redox properties can be attained by those mixed oxides. Recently, MnO$_X$-CeO$_2$ composite was reported to catalyze aerobic oxidation of HMF to FDCA [46]. Total conversion of HMF and 91% yield of FDCA was obtained at a relatively high O$_2$ pressure (20 bar), and moreover, it is noteworthy that the presence of a homogeneous base (KHCO$_3$/HMF = 4) was needed. It was previously reported that Pd/MnCeO$_Y$ catalyst could drive base-free aerobic oxidation of benzyl alcohol to benzaldehyde [47]. It can thus be speculated that base-free aerobic oxidation of more complicated alcohol/aldehyde compounds like HMF may be realized over manganese-cerium mixed oxides-supported noble metal catalysts.

Despite supported Au, Pd and Pt catalysts have been well developed in the literature for base-free aerobic oxidation of HMF to FDCA, the rather high price of those metals has to be taken into account for scale-up trials and industrialization processes. In contrast, the Ru price is about 4% that of Au and Pt per gram. As the least expensive noble metal, Ru is undoubtedly worth exploring and studying, and very limited catalyst candidates have been reported up to date. Ru clusters supported on covalent triazine frameworks (Ru/CTFs) [31] and Ru nanoparticles loaded on spinel MnCo$_2$O$_4$ (Ru/MnCo$_2$O$_4$) [33] exhibited very stable catalytic performances during recycling tests due to the strong metal-support interaction. However, Ru/CTFs catalyst afforded 78% yield of FDCA at high pressure of air (20 bar). Moreover, synthesizing CTFs required a series of expensive monomers together with molten ZnCl$_2$ Lewis acid at 400–600 °C. Note that the formation of byproducts may lead to extra problems and higher cost due to the need of further separation and purification of the as-obtained reaction mixture. While the Ru/MnCo$_2$O$_4$ catalyst showed an enhanced FDCA yield (99.1%) due to the co-presence of Lewis and Brønsted acidic sites on the catalyst surface, a high pressure of air (24 bar) were required to achieve this high FDCA yield. Ru/C catalyst [32] exhibited a 88% yield of FDCA at 120 °C under near ambient O$_2$ pressure, while Ru/HAP catalyst [34] demonstrated 99.9% yield of FDCA at 120 °C under 10 bar O$_2$. However, those catalysts were subjected to some deactivation mainly due to impurities and/or oxidation of the Ru species.

In the present work, Mn-Ce mixed oxides-supported well-dispersed Ru nanoparticles were prepared and applied as heterogeneous catalysts to aerobic oxidation of HMF to FDCA under base-free conditions. To the best of our knowledge, the Ru/Mn$_X$Ce$_1$O$_Y$ catalytic system has not been reported so far for the oxidation of HMF. In supported catalysts, the properties of the materials used