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Activated carbon-supported ruthenium as an efficient catalyst for selective aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran

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ABSTRACT

The aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) was performed on an activated carbon-supported ruthenium (Ru/C) catalyst. The excellent DFF yield of 95.8% was achieved at 383 K and O_2 pressure 2.0 MPa in toluene. It exhibited superior activity and DFF selectivity than other C-supported noble metals (i.e. Pt, Rh, Pd, and Au) with comparable nanoparticle size. The Ru/C catalyst was stable and can be recycled by a simple hydrothermal treatment. Moreover, the product distribution in the HMF oxidation on Ru/C can be tuned by the use of water as solvent and the addition of hydrotalcite, giving either 5-formyl-2-furancarboxylic acid or 2,5-furandicarboxylic acid as the dominant product.

Because of increasing attention to the use of biomass [1,2], 5-hydroxymethylfurfural (HMF) has been identified as one of the important biomass-based platform molecules for the sustainable production of chemicals and fuels [3,4]. HMF can be converted to a variety of useful chemicals, and one such example is 2,5-diformylfuran (DFF). Similar to HMF, DFF is a versatile intermediate and is used in the synthesis of fungicides, pharmaceuticals, and functional polymers with numerous applications [5–8].

Selective aerobic oxidation of HMF forms DFF, but the presence of the more reactive aldehyde group in HMF makes it difficult to get high yields of DFF from this reaction. To improve this selectivity, a number of homogeneous and heterogeneous catalysts have been explored to date [9–17]. Moreau et al. [9] reported that HMF was converted to DFF with 93% selectivity and 91% conversion on V_2O_5/TiO_2 with a high weight ratio of catalyst to HMF (i.e. 2:1 by weight), reflecting the low catalytic activity. By using homogeneous $VOSO_4/Cu(NO_3)_2$ catalysts in acetonitrile, Ma et al. [10] obtained a nearly quantitative yield of DFF at 353 K but suffered from a difficult catalyst recovery. Takagaki et al. [14] achieved a 92% yield of DFF with a hydrotalcite (HT)-supported $Ru(OH)_x$ catalyst ($Ru(OH)_x$/HT) in DMF. Antonyraj et al. [17] reported a ~97% DFF yield on $RuCl_3/Al_2O_3$. However, the $Ru(OH)_x$/HT and $RuCl_3/Al_2O_3$ catalysts were deactivated significantly when recycled [14,17]. A similarly high DFF yield has also been reported recently by Yang et al. [15] with MnO_2-based catalysts in dimethyl sulfoxide (DMSO). However, DMSO tends to undergo disproportionation to noxious and toxic Me_2SO_2 and Me_2S under oxidizing conditions [18,19]. Herein, we report that activated car-

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bon-supported Ru (Ru/C) acts as an efficient and recyclable heterogeneous catalyst for selective aerobic oxidation of HMF to DFF in toluene with yields as high as ~96% under mild conditions.

Ru/C was prepared by incipient wetness impregnation of activated carbon with an aqueous solution of $RuCl_3 \cdot nH_2O$, followed by evaporation and drying at 383 K in air overnight, and subsequent reduction in a flow of 20% H_2 in N_2 at 623 K for 4 h [20]. Similarly, Pt/C, Pd/C, and Rh/C were prepared for comparison [20]. The metal loadings of these catalysts were 3 wt%. In accordance with our previous report, 1 wt% Au/C was prepared by a single-step borohydride reduction [21]. HMF oxidation reactions were carried out in a Teflon-lined stainless steel autoclave (50 ml). Typically, 1 mmol HMF (98%) and 40 mg catalyst were added to 10 ml toluene in the autoclave. The reactants and products were analyzed by HPLC using a UV detector and an Alltech OA-1000 organic acid column [13]. HMF reaction activities were reported as molar HMF conversion rates per mole of dispersed metal per hour and selectivities on a carbon basis. The Ru contents in the catalysts and in the filtrate after the HMF oxidation reaction were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Profile Spec, Leeman Labs). X-ray photoelectron spectra (XPS) of Ru 3*p* were collected on an AXIS Ultra spectrometer (Kratos, Manchester, UK) using an Al anode (Al K_α, $h\nu = 1486.6$ eV) operating at 150 W.

Figure 1 shows how the oxidation activities and selectivities to DFF and 5-formyl-2-furancarboxylic acid (FFCA) vary with the HMF conversions over Ru/C at 383 K and 2.0 MPa O_2. The DFF selectivity was essentially constant at 95.8% even when the HMF conversion increased from 21.3% to 100%. The selectivity toward FFCA was always small and increased slightly from 0.7% to 1.5%. These results show that DFF selectivity is stable on Ru/C in toluene, and thus DFF was obtained in yields as high as 95.8%. Moreover, this excellent DFF yield was obtained at high activity (15.8 h^{-1}), which is much greater than ~3.8 h^{-1} observed for $Ru(OH)_x$/HT catalyst (at 393 K under flowing oxygen) [14], showing the superiority of Ru/C for catalyzing the HMF oxidation to DFF.

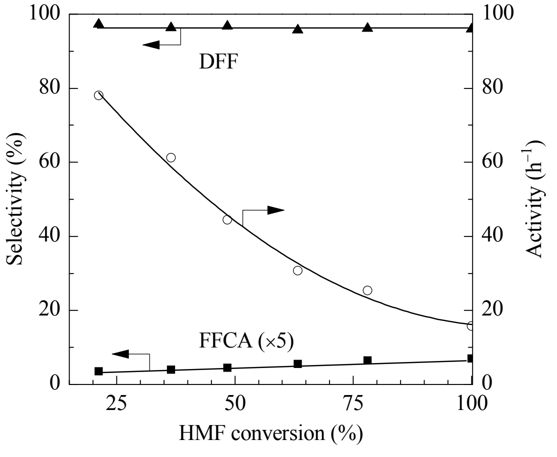

Fig. 1. Changes in the activity and selectivity for DFF and FFCA with HMF conversion over Ru/C (383 K, 2.0 MPa O_2, 1.0 mmol HMF, 40 mg Ru/C, 10 ml toluene, 0.3–7.0 h).

Table 1
Activity and product selectivity in the aerobic oxidation of HMF in toluene on carbon-supported Ru, Pt, Pd, Rh, and Au nanoparticles of comparable size.

Entry	Catalyst	Particle size (nm)	Activity (h^{-1})	Selectivity (%)	
				DFF	FFCA
1	Ru/C	1.7 (1.8)[a]	61.2	96.2	0.9
2	Pt/C	2.3	44.0	72.6	0.4
3	Pd/C	1.7	4.9	53.1	0.6
4	Rh/C	1.8	5.0	40.8	0.7
5	Au/C	3.5	28.2	32.5	1.0
6	C[b]	—	1.1%[c]	22.1	0.4

Reaction conditions: 383 K, $p(O_2) = 2.0$ MPa, 1.0 mmol HMF, 40 mg catalyst (120 mg for Au/C), 10 ml toluene, ~30% HMF conversion.

[a] The number in parenthesis is the Ru particle size for Ru/C after five reaction cycles.

[b] 0.043 g of C was used.

[c] The conversion after HMF oxidation for 30 min.

For comparison, several other noble metals, Pt, Pd, Rh, and Au, supported on C were also examined in the HMF oxidation. As shown in Table 1, characterization of these catalysts by TEM shows that the metal particles were 1.8–2.3 nm in diameter, except for Au/C (3.5 nm Au), and were similar to the size of Ru/C (1.7 nm). Pt/C was active for the HMF oxidation, but with a lower activity (44.0 h^{-1}) and DFF selectivity (72.6%) than Ru/C (61.2 h^{-1} and 96.2%) at similar HMF conversions (~30%) in the kinetic regime. Au/C was also active (28.2 h^{-1}), but it gave a DFF selectivity as low as 32.5%. Pd/C and Rh/C exhibited very low activities (4.9 and 5.0 h^{-1}) and DFF selectivities (53.1% and 40.8%) under the same reaction conditions.

The stability and recyclability of Ru/C were examined at 383 K and 2.0 MPa O_2 in the kinetic controlled regime (i.e. at ~30% HMF conversion). To recycle, the catalyst was simply washed with water. As shown in Fig. 2, the HMF oxidation activity decreased from 61.2 to 53.7 h^{-1} in the second run, and continuously to 26.0 h^{-1} in the fifth run, while the DFF selectivity remained almost unchanged. To understand this decline in activity, the filtrate after each run was measured by ICP-AES and showed no detectable leaching of Ru. The oxidation of HMF

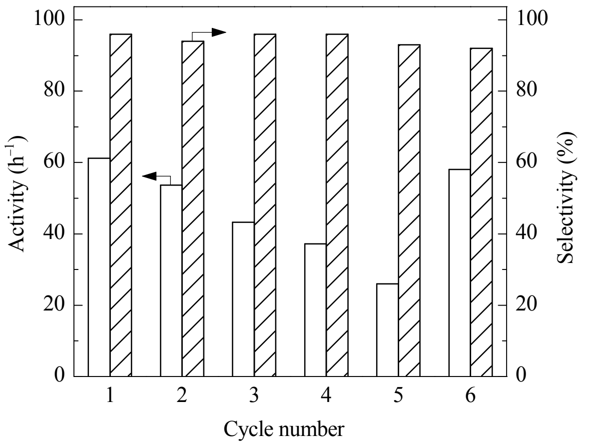

Fig. 2. Activity and DFF selectivity for the recycle examination of HMF oxidation on Ru/C at ~30% HMF conversion (383 K, 2.0 MPa O_2, 1.0 mmol HMF, 40 mg Ru/C, 10 ml toluene). Ru/C was filtered and simply washed with water for cycles 2–5, and for the 6th cycle it was treated under hydrothermal conditions at 383 K for 4 h.