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Aqueous-phase selective aerobic oxidation of 5-hydroxymethylfurfural on Ru/C in the presence of base

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ABSTRACT

The aerobic oxidation of 5-hydroxymethylfurfural (HMF) was performed on an activated carbon-supported ruthenium (Ru/C) catalyst in water. The presence of Mg–Al hydrotalcite (HT, Mg/Al molar ratio = 3/1) as a base afforded higher selective oxidation of HMF to 5-formyl-2-furancarboxylic acid (FFCA) and 2,5-furandicarboxylic acid (FDCA) than with the bases MgO, Ca(OH)₂ and NaOH owing to its appropriate strength of basicity. X-ray photoelectron spectroscopy characterization confirmed that metallic Ru⁰ species were the active sites for HMF oxidation. Isotopic tracer experiments conducted with ¹⁸O₂ and ¹⁶O₂ indicated that H₂O rather than O₂ provided the oxygen atom for the oxidation of HMF to FFCA and FDCA via hydration of the formyl group. These results and kinetic studies of the oxidation of HMF and 2,5-diformylfuran (DFF) led to the proposition that the aerobic oxidation of HMF to FFCA follows a Langmuir–Hinshelwood mechanism. The oxidation involved dissociative adsorption of HMF and O₂ to form adsorbed alcoholate and atomic oxygen species followed by kinetically relevant abstraction of β-H from the alcoholate species via the atomic oxygen species to adsorbed DFF species on the Ru surface, which then underwent hydration and oxidation to FFCA under basic conditions.

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1. Introduction

In the last decade, many studies have focused on using renewable biomass to alleviate the strong worldwide dependence on fossil fuels [1]. In this context, 5-hydroxymethylfurfural (HMF) has attracted increasing interest as an important bio-platform molecule in the synthesis of a variety of value-added chemicals and intermediates [2–4]. One promising route for the transformation of HMF is aerobic oxidation leading to the formation of 2,5-diformylfuran (DFF), 5-hydroxymethyl-furan-2-carboxylic acid (HMFA), 5-formyl-2-furancar-

boxylic acid (FFCA), and 2,5-furandicarboxylic acid (FDCA) (Scheme 1), which are important intermediates as macro-cyclic ligands and monomers for polymers to replace their petroleum-derived aromatic counterparts [5–9].

A number of catalysts for the oxidation reaction have been investigated, including V and Mn-based catalysts [10–14], and catalysts containing noble metals such as Pt, Ru, and Au [15–23]. Notably, Ru catalysts are efficient for HMF oxidation. For example, high yields of DFF (92%) and FDCA (95%) were obtained on the hydrotalcite (HT)-supported Ru(OH)_x (Ru(OH)_x/HT) catalyst in *N,N*-dimethylformamide and water,

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Scheme 1. Selective aerobic oxidation of HMF to different products.

respectively [19,20,24]. However, the catalyst tends to deactivate when recycled, most likely because of the unstable HT surface and Ru leaching, especially in the presence of the acid products. Recently, we reported that carbon-supported ruthenium (Ru/C) catalyzes the oxidation of HMF to DFF with a high yield of 96% and excellent recyclability at 383 K and 2.0 MPa O_2 in toluene [23,25]. Moreover, our preliminary results showed that the products on Ru/C can be tuned; for example, from DFF to FFCA (83% yield) and FDCA (78% yield) using water as the solvent and HT as the solid base under the same conditions [23].

Based on these previous studies, it appears that HMF oxidation favors the formation of the acid products (i.e., FFCA and FDCA) in water especially under basic conditions. In this study, to better understand the underlying reaction mechanism in water and the function of the base, we report a detailed study of the aerobic oxidation of HMF on Ru/C in water with different bases, which included the representative solid bases HT, MgO , and $Ca(OH)_2$, as well as NaOH for comparison. The effect of basicity was investigated using buffer solutions with specific pH values (5–12). In addition, the reaction pathways for the oxidation of hydroxymethyl and formyl groups in HMF were determined based on kinetic and isotopic tracer studies.

2. Experimental

2.1. Catalyst preparation

The Ru/C catalyst containing 3 wt% Ru was prepared by the incipient wetness impregnation method [26]. In brief, activated carbon (AR, Beijing Dali Fine Chemical, Beijing, China) was added to an aqueous solution of $RuCl_3 \cdot nH_2O$ (GR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) at room temperature. The impregnated C was dried at 383 K overnight in air, and then reduced in 20% H_2/N_2 flow at 623 K for 4 h.

The HT samples were prepared by the homogeneous co-precipitation method [27]. In brief, aqueous solutions of $Mg(NO_3)_2$ (AR, Beijing Fine Chemical Co., Beijing, China) and $Al(NO_3)_3$ (AR, Beijing Yili Fine Chemical, Beijing, China) with a 3:1 molar ratio of Mg to Al were simultaneously added dropwise with solutions of Na_2CO_3 (Beijing Chemicals, Beijing, China) and NaOH (Beijing Chemicals) into 20 mL deionized water at pH 9–10, and gel-like precipitates were formed. After agitation overnight, the precipitates were filtered, dried overnight at 383 K, and then calcined in air at 673 K for 4 h. Similarly, MgO was prepared using an aqueous solution of $Mg(NO_3)_2$.

To study the effect on the products of adding HT, HT and substrate (HMF, DFF, FFCA, or FDCA) were added to 10 mL

Scheme 2. Activation of formyl group in HMF oxidation.

water in a flask and then heated at 373 K for 1 h. After filtration, HT was dried at 393 K overnight before characterization.

2.2. Catalyst characterization

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (PROFILE SPEC, Leeman) was used to estimate the Mg/Al molar ratios of the HT samples and analyze the concentrations of Mg^{2+} and Al^{3+} in the reaction solutions.

X-ray diffraction (XRD) patterns of the fresh and used HT samples were obtained on a Rigaku D/Max-2000 diffractometer from 5° to 60° using a Cu $K\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 100 mA. The scanning rate was set at $4^\circ/\text{min}$.

The ultraviolet-visible (UV-vis) diffuse reflectance spectra were recorded on a Perkin 650S UV-vis spectrophotometer operated in diffuse reflectance mode in the wave number range 200–800 nm.

The X-ray photoelectron spectra (XPS) of Ru 3p of the supported Ru catalysts were collected on an AXIS Ultra spectrometer (Kratos Analytical, Manchester, UK) using an Al anode (Al $K\alpha$, $h\nu = 1486.6 \text{ eV}$) operated at 150 W. $\alpha\text{-Al}_2O_3$ was physically mixed with the catalysts as an internal standard, and the binding energies were calibrated in reference to the Al 2p line at 74.7 eV to avoid overlap between the Ru 3d and C 1s signals.

2.3. HMF and DFF aerobic oxidation reactions

The HMF and DFF oxidation reactions were carried out in a Teflon-lined stainless steel autoclave (50 mL) with vigorous stirring at a speed of 700 rpm to avoid the mass-transfer effect. Typically, 1 mmol HMF or DFF (98%, Alfa Aesar), 0.043 g Ru/C catalyst, and 0.043 g HT were added to 10 mL water in the autoclave. The autoclave was thoroughly purged with O_2 , pressurized with O_2 to 2.0 MPa, and then heated at 383 K.

The reactants and products were analyzed by high-performance liquid chromatography (HPLC, Shimadzu LC-20A) with a UV detector and an Alltech OA-1000 organic acid column (5 mmol/L H_2SO_4 mobile phase, 0.7 mL/min flow rate, and 353 K oven temperature). The HMF and DFF oxidation activities are reported as molar conversion rates per mole of Ru per hour and selectivity on a carbon basis. To study the effect of pH, 0.1 M $HAc\text{-}NaAc$, $H_3PO_4\text{-}NaH_2PO_4$, $NaH_2PO_4\text{-}Na_2HPO_4$, and $Na_2HPO_4\text{-}Na_3PO_4$ buffers were used to maintain constant pH values of 5, 8, 10, and 12, respectively.

In the oxygen isotope experiments, oxidation was carried out under the same reaction conditions described above, except that $^{18}O_2$ replaced $^{16}O_2$. The reaction solutions were filtered and

analyzed by mass spectrometry (Bruker APEX IV) using the electron spray ionization method.

3. Results and discussion

3.1. Effect of using different bases for HMF oxidation on Ru/C

As mentioned above, the major product of the aerobic oxidation of HMF on Ru/C changes from DFF in toluene to the corresponding carboxylic acids (FFCA and FDCA) in water upon addition of HT (Mg/Al = 3) as the solid base [23]. To understand the base effect, the representative solid bases HT and MgO, as well as Ca(OH)₂ and NaOH for comparison, were investigated for the oxidation of HMF in water on Ru/C.

As shown in Table 1, in the absence of base, DFF and FFCA were the major products with selectivities of 48.6% and 38.1%, respectively, with 91.0% HMF conversion at 383 K (Entry 1). Addition of HT or MgO facilitated oxidation of the formyl group of HMF (Entries 2–4), leading to a significant increase of FFCA selectivity from 38.1% (no base) to 82.8% or 63.6%, respectively, along with a decrease of DFF selectivity from 48.6% (no base) to 1.4% or 0.9% at high conversion (90%–100%). FDCA was also formed and its selectivity reached 78.2% at 100% HMF conversion at the higher temperature of 423 K in the presence of HT, corresponding to 78.2% FDCA yield. However, when the stronger bases Ca(OH)₂ and NaOH were added, selective oxidation of HMF to DFF, FFCA, and FDCA was very low, and consequently the carbon balance sharply decreased (Entries 5 and 6). For example, the carbon balance was 13.6% in the presence of NaOH. Such a low carbon balance is consistent with the facile degradation or condensation of HMF at high OH[−] concentrations in aqueous reaction solutions [25]. These results indicate that the observed efficient oxidation of HMF to FFCA and FDCA using HT as the solid base originates from its appropriate basicity.

The effect of basicity was confirmed by the control experiments performed in the buffers with tunable pH values. As shown in Table 2, with increasing pH from 5 to 12, HMF conversion monotonically increased from 14.1% to 78.1% after 20 min at 373 K and 2.0 MPa O₂. The DFF selectivity increased from 55.0% to 64.1% when the pH increased from 5 to 8, and then decreased to 20.6% at pH 10. The FFCA selectivity, how-

Table 2

Effect of OH[−] concentration on HMF oxidation.

Entry	pH ^a	Conversion (%)	Selectivity (%)			Carbon balance (%)
			DFF	FFCA	FDCA	
1	5	14.1	55.0	3.1	0.0	58.1
2	8	24.7	64.1	8.1	0.1	72.3
3	10	36.9	20.6	48.5	0.0	69.1
4	12	78.1	1.6	10.9	1.6	14.1

Reaction conditions: 373 K, O₂ 2 MPa, 0.1 mol/L HMF aqueous solution 10 mL, HMF/Ru = 80/1 (molar ratio), 20 min.

^a pH values of different buffers measured at 298 K.

ever, increased from 3.1% to 8.1% when the pH increased from 5 to 8, and then dramatically increased to 48.5% at pH 10. The DFF and FFCA selectivities were very low at pH 12 as a result of the aforementioned HMF degradation or condensation to unidentified products under strongly basic conditions, leading to the much inferior carbon balance (14% at pH 12 vs. ~70% at pH 8–10). Only a trace amount of FDCA (<2%) formed in the whole pH range (5–12).

To investigate the stability of the HT sample, it was characterized by XRD before and after the HMF oxidation reaction at 383 K. HT is composed of positively charged brucite-like layers, with trivalent cations substituting divalent cations in octahedral sites, separated by interlayer anions and water molecules. As shown in Fig. 1, the (003), (006), and (009) peaks, which are characteristic of the basal *d*(001) spacing of HT, were essentially the same before and after HMF oxidation (conversion >90%), indicating that the layered structure of HT and its basal spacing were maintained after the reaction. Analysis of the aqueous reaction solution after the reaction by ICP-AES showed that leaching of Al³⁺ ions was negligible, but Mg²⁺ ions significantly leached into the solution as a result of the reaction between HT and FFCA or FDCA. Such leaching was confirmed by the control experiments using pure aqueous solutions of HMF, DFF, FFCA, and FDCA in the absence of Ru/C under the same reaction conditions. As shown in Table 3, when heated together with HMF or DFF at 373 K, HT was stable and negligible amounts of Mg²⁺ and Al³⁺ leached into the reaction solution. However, for HT in solutions containing FFCA or FDCA, the concentrations of Mg²⁺ ions in solution were 0.016 or 0.024 mol/L, respectively, indicating that significant leaching oc-

Table 1

HMF conversion and product selectivity for HMF oxidation on Ru/C in the presence of different bases.

Entry	Base	HMF conversion (%)	Selectivity (%)			Carbon balance (%)
			DFF	FFCA	FDCA	
1	None	91.0	48.6	38.1	3.2	89.9
2	HT	100	1.4	82.8	5.4	89.6
3	HT	100 ^a	0.0	3.6	78.2	81.8
4	MgO	99.7	0.9	63.6	18.4	82.9
5	Ca(OH) ₂	95.3	5.2	25.1	7.0	37.3
6	NaOH	79.2 ^b	1.3	10.6	1.7	13.6

Reaction conditions: 383 K, O₂ 2.0 MPa, 0.1 mol/L HMF aqueous solution 10 mL, HMF/Ru = 80/1 (molar ratio), solid base 0.043 g.

^a 423 K, 0.3 g HT.

^b 333 K, 1.0 mol/L NaOH solution.

Fig. 1. XRD patterns of HT samples before and after HMF oxidation with HMF conversion of > 90%.

Table 3

ICP-AES results for leaching of HT with different substrates.

Substrate	Mg ²⁺ concentration (mol/L)	Al ³⁺ concentration (mol/L)
HMF	3.0×10^{-5}	2.3×10^{-5}
DFF	2.2×10^{-4}	1.2×10^{-4}
FFCA	0.016	2.6×10^{-5}
FDCA	0.024	3.7×10^{-5}

Reaction conditions: 373 K, air 0.1 MPa, 0.03 mol/L aqueous solution 10 mL, HT 0.043 g, 1 h.

curred. The leaching of Al³⁺ ions was negligible. These results revealed that more robust solid bases are required for the oxidation of HMF to FFCA or FDCA, such as solid bases containing divalent metal ions other than Mg²⁺ that are resistant to carboxylic acids.

In contrast to HT, the Ru/C catalyst was stable under the reaction conditions used in this work. Analysis of the filtered aqueous solution by ICP-AES after HMF oxidation (at >90% conversion) showed no detectable leaching of Ru. Characterization of Ru/C by transmission electron microscopy (TEM) (not included here) showed essentially no difference in the mean diameter of the Ru particles (~1.8 nm) and their size distributions before and after the reaction, as previously observed in toluene [25]. The Ru oxidation states before and after reaction were characterized by XPS. As shown in Fig. 2, the Ru/C catalyst mainly contained metallic Ru⁰ with a small fraction of Ru⁴⁺, and there was essentially no difference in the composition before and after the reaction (76% vs. 77% Ru⁰, and 24% vs. 23% Ru⁴⁺, respectively).

3.2. Reaction kinetics and mechanism of HMF oxidation under basic conditions

The oxidation of HMF to DFF, and the subsequent oxidation of DFF to FFCA and FDCA (Scheme 1), involves oxidation of the hydroxymethyl group of HMF and the formyl group of DFF, respectively. Recently, we have reported the mechanism for the oxidation of the hydroxymethyl group of HMF to DFF on Ru/C in toluene, which involves β -H elimination of the hydroxyme-

Fig. 2. XPS spectra of Ru 3p signals for fresh (76% Ru⁰ and 24% Ru⁴⁺) and used (77% Ru⁰ and 23% Ru⁴⁺) Ru/C catalysts. The used catalyst was filtered and dried after the HMF oxidation reaction (> 90% conversion).

thyl group as the rate-determining step [25]. To understand the HMF oxidation mechanism under the conditions used in this work, we investigated the effects of the reaction parameters (i.e., OH⁻ and HMF concentrations and O₂ pressure) on the reaction activities for the oxidation of HMF to DFF and the oxidation of DFF to FFCA at 353 K within the kinetically controlled regime at ~15% HMF and ~30% DFF conversion, respectively. The OH⁻ concentrations were tuned using phosphate buffer solutions.

For oxidation of HMF to DFF, the activities were almost independent of the concentration of OH⁻ in the range 5.6×10^{-6} to 6.8×10^{-4} mol/L (Fig. 3), corresponding to a variation of the pH from 8.7 to 10.8. This indicates that OH⁻ is not directly involved in the rate-determining step, which is most likely the cleavage of the C–H bond of the hydroxymethyl group of HMF, of the mechanism for the oxidation of HMF to DFF in toluene on Ru/C [25]. The activities slightly increased with increasing HMF concentration in the range 0.05–0.1 mol/L (Fig. 4), suggesting saturated adsorption of HMF in the form of the alcoholate, apparently as a result of the strong affinity of HMF for the Ru surface via its furan ring, as proposed by van Vinke and coworkers [15]. Figure 5 shows that increasing the oxygen pressure from 0.5 to 2.0 MPa led to an increase in the activity from 0.40 to 0.83 min⁻¹, from which the reaction order of O₂ was estimated to be 0.51. The half-order dependence indicates dissociative

Fig. 3. Effect of OH⁻ concentration on the oxidation of HMF to DFF. Reaction conditions: 353 K, O₂ 2.0 MPa, 0.1 mol/L HMF aqueous solution 10 mL, 3% Ru/C 0.0215 g, HMF conversion ~15%.

Fig. 4. Effect of HMF concentration on the oxidation of HMF to DFF. Reaction conditions: 353 K, O₂ 2.0 MPa, HMF aqueous solution 10 mL, 3% Ru/C 0.0215 g, OH⁻ 2.2×10^{-4} mol/L buffer, HMF conversion ~15%.

Fig. 5. Effect of O₂ pressure on the oxidation of HMF to DFF. Reaction conditions: 353 K, 0.1 mol/L HMF aqueous solution 10 mL, 3% Ru/C 0.0215 g, OH⁻ buffer 2.2×10⁻⁴ mol/L, HMF conversion ~15%.

chemisorption of O₂ and formation of adsorbed atomic O* species on the Ru surface.

Based on the kinetic results and our previous mechanistic study in toluene [25], the sequence of elementary steps for the oxidation of HMF to DFF on Ru/C in aqueous solution is proposed in Scheme 3. In this sequence, HMF and O₂ dissociatively adsorb on the Ru surface to form the alcoholate (R-CH₂O*, R hereafter denotes the furfural CHO-C₄H₂O- part of HMF), H*, and O* species. The subsequent β-H elimination of R-CH₂O* via the reaction with O* is irreversible and kinetically relevant, leading to the formation of the adsorbed DFF (R-CHO*) and hydroxyl (OH*) species. OH* can also be formed via the reaction of O* and H*. Finally, R-CHO* desorbs from the Ru surface and forms DFF.

By referring to the method reported in our previous work [25], the rate equation was derived as

$$r = \frac{M_1[R-CH_2OH][O_2]^{3/4}}{(1+M_2[O_2]^{1/2}+M_3[R-CHO]+M_4[R-CH_2OH][O_2]^{1/4}+M_5[O_2]^{-1/4}+M_6[O_2]^{1/4}+M_7)^2} \quad (1)$$

where M_1 to M_7 are the combinations of rate constants and equilibrium constants of reaction steps in Scheme 3. Based on the low conversion and observed kinetic dependence on the concentrations of HMF and O₂, the surface coverages of the R-CHO*, OH*, and H* species are likely to be much smaller than those of R-CH₂O*, O*, H₂O* and free Ru surface sites (*) under the conditions used in this work. Thus, Eq. (1) can be simplified to

$$r = \frac{M'_1[R-CH_2OH][O_2]^{3/4}}{(1+M'_2[O_2]^{1/2}+M'_3[R-CH_2OH][O_2]^{1/4})^2} \quad (2)$$

- (1) $R-CH_2OH + 2* \rightleftharpoons R-CH_2O* + H*$
- (2) $O_2 + 2* \rightleftharpoons 2O*$
- (3) $R-CH_2O* + O* \rightarrow R-CHO* + OH*$
- (4) $H* + O* \rightleftharpoons OH* + *$
- (5) $OH* + OH* \rightleftharpoons H_2O* + O*$
- (6) $R-CHO* \rightleftharpoons R-CHO + *$
- (7) $H_2O* \rightleftharpoons H_2O + *$

Scheme 3. Proposed reaction pathway for the oxidation of aqueous HMF to DFF.

where M'_1 to M'_3 are the combinations of M_1 to M_7 . After fitting to the experimental data in Figs. 3–5, the rate equation of the HMF oxidation was determined to be

$$r = \frac{22[R-CH_2OH][O_2]^{3/4}}{(1 + 0.041[O_2]^{1/2} + 9.1[R-CH_2OH][O_2]^{1/4})^2} \quad (3)$$

Figure 6 compares the calculated HMF oxidation activities from Eq. (3) with the experimental activities for a wide range of HMF concentrations (0.05–0.1 mol/L), O₂ pressures (0.5–2.0 MPa), and hydroxide concentrations (5.6×10⁻⁶–6.8×10⁻⁴ mol/L). The good agreement between the calculated and experimental data demonstrates that Eq. (3) well describes the observed experimental kinetic results, which indicates that the proposed elementary steps in Scheme 3 reflect the mechanism of HMF oxidation on Ru/C under the basic conditions in this work.

Differing from the oxidation of the hydroxymethyl group of HMF to DFF, which involves the elimination of two hydrogen atoms, the oxidation of the formyl group of DFF to FFCA and FDCA requires the insertion of one and two oxygen atoms, respectively. The inserted oxygen atom(s) may be provided by either O₂ or H₂O. To investigate the oxygen source, HMF oxidation was carried out at 373 K using ¹⁶O₂ and ¹⁸O₂. After complete conversion of HMF to FDCA in the buffer solution, analysis of the products by mass spectroscopy showed that the most intense peak appeared at $m/z = 177$ irrespective of the use of ¹⁶O₂ or ¹⁸O₂, as shown in Fig. 5. This peak corresponds to the sodium adduct of FDCA, i.e., [C₄H₂O(COO)₂]²⁻ Na⁺, revealing that all the oxygen atoms in FDCA are ¹⁶O. If the oxygen source was O₂, the peaks of [C₄H₂O(COO)₂]²⁻ Na⁺ produced in ¹⁸O₂ should be at $m/z = 179, 181, 183$, and 185, corresponding to one, two, three, and four ¹⁸O atoms, respectively, but these peaks are much weaker than the peak at $m/z = 177$ (Fig. 7(b)). Thus, we tentatively propose that the oxygen atoms for the oxidation of the formyl group come from H₂O rather than O₂, as observed in glycerol and HMF oxidation on Au catalysts [28,29]. This proposition agrees with our previous results [25]. For HMF oxidation in toluene, DFF is a stable product with over 96% selectivity. Oxidation of the formyl group does not occur until H₂O is used as solvent, indicating the involvement of water in the activation of the formyl group.

Figures 8–10 show the effects of the reaction parameters (i.e., OH⁻ and HMF concentrations and O₂ pressure) on DFF

Fig. 6. Parity plot for the measured activities from Figs. 3–5 and the calculated activities from Eq. (3).

Fig. 7. Mass spectra of the major products of HMF oxidation using $^{16}\text{O}_2$ (a) and $^{18}\text{O}_2$ (b).

oxidation to FFCA. The activity increased from 0.42 to 0.95 min^{-1} when increasing the OH^- concentration from 5.6×10^{-6} to 6.8×10^{-4} mol/L, and accordingly the reaction order was estimated to be about 0.2 for OH^- . The activities remained almost constant when the DFF concentration was varied in a wide range from 0.06–0.25 mol/L (Fig. 9). The zero-order dependence on DFF concentration indicates saturated adsorption of DFF on the Ru surface, similar to the aforementioned adsorption of HMF (Fig. 4), reflecting the strong interaction of DFF with the Ru surface via the π -electrons of the furan ring. When the O_2 pressure was increased from 0.5 to 3.0 MPa, the activity increased from 0.52 to 0.85 min^{-1} (Fig. 10), indicating a fractional O_2 reaction order of 0.3 and dissociative adsorption of O_2 to O^* on the Ru surface.

The sequence of elementary steps for the oxidation of DFF to FFCA on Ru/C in aqueous solution that is consistent with the kinetic and isotopic results is proposed in Scheme 4. DFF (R-CHO) was adsorbed and activated by adsorbed water to form R-CH(OH) O^* alcoholate species. Subsequent β -H elimination of R-CH(OH) O^* with the adsorbed O^* species (to adsorbed FFCA (R-COOH *) species), similar to HMF oxidation to DFF, is assumed to be the rate-determining step. R-COOH * then reacted with OH^- and desorbed to form its salt.

The rate equation was derived as

$$r = \frac{N_1[\text{R-CHO}][\text{O}_2]^{3/4}}{(1+N_2[\text{O}_2]^{1/2} + \frac{N_3[\text{R-COO}^*]}{[\text{OH}^-]} + N_4[\text{R-CHO}][\text{O}_2]^{1/4} + N_5[\text{O}_2]^{-1/4} + N_6[\text{O}_2]^{1/4} + N_7)^2}$$

$$\begin{array}{ccccccc} * & \text{O}^* & \text{R-CHO}^* & \text{R-CH}_2\text{O}^* & \text{H}^* & \text{OH}^* & \text{H}_2\text{O}^* \end{array} \quad (4)$$

As discussed above, the coverages of OH^* and H^* are negligible compared with those of $*$, O^* , H_2O^* , R-CH(OH)O^* , and R-COOH^* . Thus, Eq. (4) can be simplified as

Fig. 9. Effect of DFF concentration on DFF oxidation to FFCA. Reaction conditions: 353 K, O_2 2.0 MPa, DFF aqueous solution 10 mL, 3% Ru/C 0.0215 g, OH^- buffer 0.22 mmol/L, DFF conversion $\sim 15\%$.

Fig. 8. Effect of OH^- concentration on DFF oxidation to FFCA. Reaction conditions: 353 K, 2.0 MPa O_2 , 10 mL 0.025 mol/L DFF aqueous solution, 3% Ru/C 0.0215 g, and $\sim 15\%$ DFF conversion.

Fig. 10. Effect of O_2 pressure on DFF oxidation to FFCA. Reaction conditions: 353 K, 0.025 mol/L DFF aqueous solution 10 mL, 3% Ru/C 0.0215 g, OH^- buffer 0.22 mmol/L, DFF conversion $\sim 15\%$.

- (1) $R-CHO + * + H_2O^* \rightleftharpoons R-CH(OH)O^* + H^*$
- (2) $O_2 + 2* \rightleftharpoons 2O^*$
- (3) $R-CH(OH)O^* + O^* \rightarrow R-COOH^* + OH^*$
- (4) $H^* + O^* \rightleftharpoons OH^* + *$
- (5) $OH^* + OH^* \rightleftharpoons O^* + H_2O^*$
- (6) $R-COOH^* + OH^- \rightleftharpoons R-COO^- + H_2O + *$
- (7) $H_2O^* \rightleftharpoons H_2O + *$

Scheme 4. Proposed reaction pathways for aqueous DFF oxidation to FFCA.

$$r = \frac{N_1[R-CHO][O_2]^{3/4}}{(1 + N_2[O_2]^{1/2} + N_3[R-CHO][O_2]^{1/4} + \frac{N_4[R-CHO]}{[OH^-]})^2} \quad (5)$$

Fitting Eq. (5) to the experimental data in Figs. 8–10 using non-linear regression gives

$$r = \frac{680[R-CHO][O_2]^{3/4}}{(1 + 0.85[O_2]^{1/2} + 130[R-CHO][O_2]^{1/4} + \frac{0.00074[R-CHO]}{[OH^-]})^2} \quad (6)$$

Figure 11 compares the calculated DFF oxidation activities from Eq. (6) with the experimental activities for a wide range of DFF concentrations (0.006–0.025 mol/L), O_2 pressures (0.5–3.0 MPa), and hydroxide concentrations (5.6×10^{-6} – 6.8×10^{-4} mol/L). The good agreement between the calculated and experimental data demonstrates that Eq. (6) well describes the observed experimental kinetic results, which indicates that the proposed elementary steps in Scheme 4 reflect the mechanism of DFF oxidation on Ru/C under the basic conditions in this work.

4. Conclusions

Aqueous-phase aerobic oxidation of HMF forms FFCA and FDCA on Ru/C in the presence of base. Compared with the bases MgO, $Ca(OH)_2$, and NaOH, the use of HT leads to superior

Fig. 11. Parity plot of the measured activities from Figs. 8–10 and the calculated activities from Eq. (6).

selective oxidation to FFCA and FDCA with higher carbon balance, as a result of its appropriate basicity. XPS characterization and isotope tracer experiments show that the predominant species on Ru/C is metallic Ru^0 (the active sites) and water is the oxygen source for the oxidation of the formyl group, respectively. Kinetic studies of the aerobic oxidation of HMF and DFF suggest that HMF oxidation to FFCA follows a Langmuir-Hinshelwood mechanism involving dissociative adsorption of HMF and O_2 to form the adsorbed alcoholate and atomic oxygen species on Ru/C, and subsequent kinetically relevant abstraction of β -H from the alcoholate species via the atomic oxygen species on the Ru surface. The base reacts with adsorbed FFCA, facilitating its desorption and the recovery of the active Ru surface.

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Graphical Abstract

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Aqueous-phase selective aerobic oxidation of 5-hydroxymethylfurfural on Ru/C in the presence of base

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Aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 5-formyl-2-furancarboxylic acid on Ru/C with base in water follows a Langmuir-Hinshelwood mechanism, involving kinetically relevant β -H abstraction from alcoholate species, which are formed from dissociative adsorption of HMF and O_2 on the Ru surface by atomic oxygen.

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碱性条件下Ru/C催化5-羟甲基糠醛选择氧化反应

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摘要: 以活性炭负载金属钌(Ru/C)为催化剂, 在碱性水溶液中研究了5-羟甲基糠醛(HMF)选择氧化反应. 与MgO, Ca(OH)₂和NaOH相比, 加入具有合适碱强度的镁铝水滑石有利于生成5-乙酰基-2-呋喃甲酸(FFCA)或2,5-呋喃二甲酸(FDCA). X射线光电子能谱实验表明金属态的钌是活性催化中心. 同位素示踪结果则表明水而非氧气提供了5-乙酰基-2-呋喃甲酸及2,5-呋喃二甲酸等羧酸产物的氧源. 根据这些结果, 并结合HMF和2,5-呋喃二甲醛氧化的动力学研究, 我们提出HMF选择性氧化制备FFCA遵循Langmuir-Hinshelwood反应机理. 其中, HMF在金属Ru表面饱和解离吸附, 在解离吸附的氧原子的协助下发生β-脱氢生成2,5-呋喃二甲醛(DFF)吸附物种. 该DFF物种进一步发生水合与氧化形成FFCA产物.

关键词: 5-羟甲基糠醛; 氧化反应; 2,5-呋喃二甲醛; 5-乙酰基-2-呋喃甲酸; 镁铝水滑石; 钌基催化剂; 反应机理

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