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Introduction

The valorization of renewable and abundant lignocellulosic resources for the production of sustainable fuels and chemigarnered global consensus.^{1,2} cals has 5-Hydroxymethylfurfural (HMF) is a typical cellulose-based furanocarbohydrate that can yield various high-value chemicals through oxidation, hydrogenation, and esterification.^{3,4} In particular, 2,5-furandicarboxylic acid (FDCA), obtained via selective oxidation of HMF, is among the top 12 value-added chemicals identified by the U.S. Department of Energy. In principle, FDCA has the potential to replace terephthalic acid as a crucial feedstock for the production of non-toxic and biodegradable polyesters, thereby reducing reliance on petroleum.^{5,6} The aerobic oxidation of HMF to FDCA represents a typical tandem reaction involving two possible routes and three typical intermediates (2,5-furandicarboxaldehyde (DFF), 5-hydroxymethyl-

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Solid-state synthesis of CN-encapsulated CoFe alloy catalysts for mild HMF oxidation to FDCA: insights into the kinetics and mechanism[†]

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The efficient and environmentally friendly oxidation of biomass-based HMF to FDCA under mild conditions is highly desirable yet challenging. In this study, a series of CoFe alloy catalysts encapsulated in porous carbon ($Co_xFe_y@NC$) were synthesized using a solid-state synthesis method. By adjusting the Co/ Fe ratio, an FDCA yield of 96.1% was achieved with the optimal $Co_2Fe_1@NC$ catalyst, which exhibited an impressive FDCA formation rate of 0.428 mmol_{FDCA} g_{cat}⁻¹ h⁻¹ at 100 °C and 0.5 MPa O₂, surpassing the performance of its monometallic Fe or Co counterparts. Experimental and kinetics observations demonstrated that the presence of the CoFe alloy significantly enhanced the HMF oxidation rate and shifted the rate-determining step from HMFCA oxidation to FFCA oxidation when compared to the Co@NC catalyst. Additionally, the CoFe alloy facilitated the adsorption/activation of both substrates and oxygen, synergistically working with the support material to lower the reaction energy barriers and enhance FDCA formation. This study presents a novel and environmentally friendly approach for designing efficient Cobased catalysts for complex tandem oxidation reactions.

2-furancarboxylic acid (HMFCA), and 5-formyl-2-furancarboxylic acid (FFCA)) (Scheme 1).⁷ In this process, both the OH and C=O groups in HMF need to undergo oxidation to form COOH groups, while over-oxidation of FDCA must be prevented. The key to efficiently producing FDCA lies in having an active catalyst and precise control over selectivity.

In recent decades, numerous catalysts have been investigated for the oxidation of HMF to FDCA. Initially, homogeneous catalysts (such as Co(OAc)₂/Mn(OAc)₂/HBr and CuCl₂) were employed due to their high activity.^{8,9} However, the difficulty in reusing and separating homogeneous catalysts has hindered their largescale industrial application. Heterogeneous precious metal catalysts, including Pt, Pd, Au, and Ru, have demonstrated remarkable catalytic performance, particularly Au-based catalysts with their exceptional activity and selectivity,^{10–19} but they are of



Scheme 1 Reaction routes for the aerobic oxidation of HMF to FDCA.

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Paper

limited industrial use in view of their high cost. As a result, heterogeneous non-precious metals including Fe, Cu, Mn, Co, Ce, Zr, V, and others^{20,21} have become the focal point of current research. Koley *et al.*²² achieved an FDCA yield of 82.1% using Cu-BTC as a catalyst under the conditions of 120 °C and 2 MPa O_2 for 5 h. Hayashi *et al.*²³ synthesized a range of crystalline MnO₂ catalysts and achieved 86% FDCA yield at 100 °C and 1 MPa O_2 for 24 h. Despite the significant progress in HMF oxidation, these catalytic systems suffer from low catalytic efficiency and the requirement of high temperature and high pressure for a high FDCA yield. From an economical and practical perspective, the development of a non-noble metal catalyst with mild features and high efficiency for HMF oxidation is highly desirable yet challenging.

Metal alloy nanoparticle catalysts have been extensively studied, employing various ratios of metal components to optimize catalytic surfaces. For example, Guo *et al.*²⁴ found that a nanostructured Pt–Bi alloy induced by defect engineering of N-doped carbon had an excellent reaction rate for the direct oxidation of C_5 – C_9 linear α -alcohols to the corresponding fatty acids. Bimetallic AgPd sites at the interfaces between Ag and Pd clusters have also been noted to enhance catalytic performance in the selective synthesis of FDCA from HMF at ambient temperature.¹⁴ Hutchings's group reported that having separated gold and palladium regions in NP alloys, with an Au/Pd ratio of 4:1, produced the most efficient sites for catalyzing aqueous HMF oxidation to yield FDCA.²⁵ This illustrates the critical importance of active-site structures in determining the overall catalytic performance.

Herein, we constructed a series of highly dispersed carboncoated bimetallic CoFe alloy catalysts (CoxFev@NC) using a solid-state grinding-pyrolysis strategy and investigated their catalytic performance in the HMF oxidation reaction. The optimal Co2Fe1@NC exhibited a high production rate of 0.428 $\text{mmol}_{\text{FDCA}}\ {g_{\text{cat}}}^{-1}\ h^{-1}$ and an FDCA yield of 96.1% at 100 °C and 0.5 MPa O₂, which is 1.4 and 3.7 times that of the monometallic Co and Fe catalysts, respectively. Mechanistic studies indicated that the CoFe alloy facilitated the adsorption/ activation of both substrates and oxygen, synergistically working with the support material to lower the reaction energy barriers and enhance FDCA formation. The effects of temperature, oxygen pressure, different atmospheres, catalyst dosage, and reaction time on the oxidation of HMF were thoroughly investigated. Through in situ characterization and kinetics the reaction pathways and mechanisms studies, of Co2Fe1@NC-catalyzed HMF oxidation were further elucidated.

Results and discussion

Catalyst characterization

The preparation of CoFe@NC using the solid-phase grindingpyrolysis method is illustrated in Fig. 1(a). All Co_xFe_y @NC catalysts present a sharp N₂ adsorption isotherm at relative pressures (*P*/*P*₀) of 0–0.08, indicating typical type IV characteristics. Additionally, the H1 hysteresis loop observed at *P*/*P*₀ \geq 0.4 **Dalton Transactions**



Fig. 1 (a) Schematic illustration of the synthesis of Co_xFe_y @NC. (b) N₂ adsorption–desorption isotherms, (c) XRD patterns, and XPS spectra of (d) Co 2p and (e) Fe 2p of the prepared Co_xFe_y @NC catalysts.

demonstrates the presence of micro- and mesopores (Fig. 1b). As shown in Table S1,† the specific surface area and pore volume of Co_xFe_y @NC increase with higher Fe content. Specifically, Co@NC exhibits a specific surface area of around 328 m² g⁻¹ and a pore volume of 0.126 cm³ g⁻¹, which slightly increase to 372 m² g⁻¹ and 0.141 cm³ g⁻¹, respectively, for Co₂Fe₁@NC. On the other hand, Fe@NC shows a specific surface area of approximately 510 m² g⁻¹ and a pore volume of 0.131 cm³ g⁻¹, indicating that the introduction of Fe enhances the porosity of the catalysts.

The crystal structures of various Co_xFe_y@NC catalysts were characterized using XRD (Fig. 1c). All catalysts exhibit a broad peak at 24.2-26.4°, corresponding to C (002) diffraction (JCPDS no. 75-1621). As for Co@NC, distinct peaks are observed at 44.2°, 51.5°, and 75.8°, attributed to the Co (111), (200), and (220) planes (JCPDS no. 15-0806), confirming the presence of Co NPs. In terms of Co_xFe_y@NC, distinct peaks are observed at 44.8° and 65.1°, attributed to the (110) and (200) planes of Co3Fe7 (JCPDS no. 48-1816), and distinct peaks are observed at 43.9°, 51.1°, and 77.0°, attributed to the (330), (420), and (771) planes of Co_{0.72}Fe_{0.28} (JCPDS no. 51-0740). This indicates that Fe doping leads to a mixed crystalline phase of Co3Fe7 and Co0.72Fe0.28 in bimetallic catalysts.26 Additionally, when Co/Fe is 1:2, the diffraction peaks of Co₃Fe₇ are significantly enhanced while the peak positions remain constant, whereas the diffraction peaks of Co_{0.72}Fe_{0.28} nearly disappear, and the catalytic activity is reduced. These results indicate that the alloy phase can be adjusted by varying the molar ratio of Co to Fe. Moreover, the Co, Fe loadings in

 Co_xFe_y (MORE) Were measured by inductively coupled plasma mass spectrometry (ICP-MS, Table S2[†]).

The surface structure and composition of Co_xFe_y @NC were investigated using XPS spectra (Fig. 1d, e, Fig. S1 and Table S3†).^{27,28} The Co 2p XPS spectrum reveals that Co@NC primarily exists as Co⁰, consistent with the XRD spectra. The relative content of surface Co⁰ decreases from 36.7% in Co@NC to 19.6% in Co₂Fe₁@NC, while both Co²⁺ and Co³⁺ contents increase. As for the Fe 2p XPS spectrum, the proportion of Fe²⁺ increases from 57.7% in Fe@NC to 62.9% in Co₂Fe₁@NC, while the content of Fe³⁺ decreases. This confirms the electron transport from Co to Fe.

The morphology and microstructure of the samples were examined using TEM (Fig. 2, Fig. S2 and Table S4[†]). The average nanoparticle size in Co₂Fe₁(a)NC (20.3 nm, Fig. 2a-c) was found to be similar to that in Co@NC (19.3 nm, Fig. 2g and h). This indicates that the incorporation of Fe does not affect Co dispersion but rather forms an alloy, as confirmed by the XRD results. On the other hand, Fe@NC appears as pristine carbon nanotubes with smooth surfaces (Fig. 2i and S2c[†]). HRTEM images reveal the encapsulation microstructures of Co@NC and Co₂Fe₁@NC (Fig. 2c and h), where the spacing between the outer carbon layer measures ~0.340 nm, corresponding to the (002) facet of graphite carbon. Additionally, XPS Ar ion sputtering results (Fig. S9[†]) indicate that with an increase in the etching depth, the metal content increases while the carbon content decreases, further proving that the catalyst has a core-shell structure with metal nanoparticles coated by carbon. Such a structure helps prevent the aggregation and sintering of the Co metal during calcination, thereby enhancing the stability of the catalysts.²⁹ The micro-



Fig. 2 TEM images of $Co_xFe_y@NC$ catalysts. (a–f) $Co_2Fe_1@NC$, (g–h) Co@NC, and (i) Fe@NC.

structure of Co_2Fe_1 (a) NC shows the (111) and (300) crystal planes of the Co_3Fe_7 and $Co_{0.72}Fe_{0.28}$ alloys. Fig. 2e further confirms the uniform distribution of C and N in Co_2Fe_1 (a) NC, with the Co and Fe elements precisely overlapping and coinciding with the positions of metal NPs in the high-angle annular dark-field (HAADF) image. This suggests that the observed NPs exhibit a homogeneous alloy composition consisting of Co and Fe.

Catalyst performance for HMF oxidation

Selective oxidation of HMF at 100 °C and 0.5 MPa O2 over various Co_xFe_y@NC catalysts was performed and the results are outlined in Table 1. Varying the Co/Fe ratios has a significant impact on both HMF conversion and product distribution. Notably, N-C achieves an FDCA yield of 13.7% with 99% HMF conversion in 7 h (entry 9), indicating that the absence of active metal sites limits FDCA production. The introduction of Co and Fe elevates the FDCA yields of Co@NC and Fe@NC to 46.9% and 17.7%, respectively (entries 1 and 7). In contrast, Co_xFe_y@NC demonstrates significantly enhanced activity (entries 2-6), exhibiting a volcano relationship between the FDCA yield and Co/Fe ratio. Specifically, the optimal Co₂Fe₁@NC catalyst achieves a remarkable FDCA yield of 72%. However, as the Co/Fe ratio decreases to 1:1 and 1:2, the FDCA yield decreases to 60% and 55%, respectively. Furthermore, a physical mixture of Co@NC and Fe@NC yields only 39.1% FDCA, indicating that a close interaction between Co and Fe species is crucial for achieving a strong synergistic effect in HMF oxidation.

A time-course study was conducted to monitor the progression of HMF oxidation over various Co_xFe_y@NC catalysts (Fig. 3a-c). Throughout the reaction, FDCA as well as HMFCA and FFCA are detected. As for Co@NC and Co2Fe1@NC, the yields of HMFCA and FFCA exhibit an increasing and then decreasing trend, while the FDCA yield continues to rise. The Co₂Fe₁@NC catalyst demonstrates a relatively rapid rate of FDCA generation and consumption of HMFCA and FFCA, achieving the highest FDCA yield (72%) within 7 h. In contrast, Fe@NC displays a lower FDCA yield with correspondingly lower consumption rates of HMFCA and FFCA, indicating inferior catalytic performance. Subsequently, the initial production rates of FDCA were calculated for different Co_xFe_v@NC catalysts. Notably, the reaction rate (HMF) over Co₂Fe₁@NC is 3.7 times higher than that over Fe@NC and 1.4 times higher than that over Co@NC, providing evidence that the synergistic effect between Co and Fe facilitates efficient activation of the C-OH and C=O groups in HMF, HMFCA, and FFCA, resulting in enhanced FDCA production. In addition, compared to the literature reported in Table S5,† Co₂Fe₁@NC not only offers a simple preparation method but also achieves a similar FDCA yield for HMF oxidation when compared to most non-noble metal catalysts based on Co, Mn, and Fe, and even outperforms some noble metal catalysts, especially at high temperatures and under O₂ atmospheres.^{7,10,16,30–33}

 Co_2Fe_1 @NC is chosen as the optimal catalyst to assess the impact of O_2 pressure on HMF oxidation (Fig. 4a and S3a[†]). As

Table 1 Catalytic oxidation of HMF to FDCA over different catalysts^a

	$\begin{array}{c} HO \\ \bullet \\ \bullet \\ HMF \end{array} \xrightarrow{O_2} \\ step 1 \\ HMFCA \end{array} \xrightarrow{HO \\ \bullet \\ step 2 \\ FFCA \end{array} \xrightarrow{O_2 \\ step 3 \\ FFCA \\ FDCA \\ FDCA \end{array}$						
			Yield (%)				
Entry	Catalyst	Conv. (%)	FDCA	HMFCA	FFCA	DFF	Productivity (mmol $g^{-1} h^{-1}$)
1	Co@NC	100	46.9	17.4	13.2	0	0.279
2	Co ₅ Fe ₁ @NC	100	53.0	29.6	6.0	0	0.315
3	Co_3Fe_1 (a) NC	100	58.0	22.0	4.6	0	0.345
4	Co ₂ Fe ₁ @NC	100	72.0	8.3	3.6	0	0.428
5	Co_1Fe_1 (a) NC	100	60.0	16.3	22.0	0	0.357
6	Co_1Fe_2 (a) NC	100	55.0	20.0	24.0	0	0.327
7	Fe@NC	100	17.7	56.6	21.6	0	0.105
8^b	Co ₂ Fe ₁ @NC	100	96.1	0.8	1.7	0	0.109
9	N-C	99	13.7	9.2	22.3	0	0.082
10	Co@NC + Fe@NC(2:1)	100	39.1	14.5	29.7	0	0.233

^a Reaction conditions: HMF, 0.25 mmol; catalyst, 60 mg; NaHCO₃, 0.5 mmol; H₂O, 3 mL; O₂, 0.5 MPa; 100 °C, 7 h. ^b 22 h, 100 mg of Co₂Fe₁@NC.



Fig. 3 The reaction time profiles of HMF over (a) $Co_2Fe_1@NC$, (b) Fe@NC and (c) Co@NC. (d) Comparison of reaction rates over $Co_xFe_y@NC$ catalysts (reaction conditions: HMF 0.25 mmol, catalyst 60 mg, NaHCO₃ 0.5 mmol, H₂O 3 mL, 0.5 MPa O₂, 100 °C).

the O_2 pressure is increased from 0.1 to 0.8 MPa, the HMF conversion remains at 100%, whereas the FDCA yield exhibits a volcano-type trend. Notably, the peak FDCA yield of 72% is achieved at 0.5 MPa O_2 . However, the FDCA yield slightly decreases to 60.6% at 0.8 MPa O_2 , as increasing the O_2 pressure not only enhances the primary reactions but also favors side reactions such as furan ring cleavage.³⁴ Remarkably, even at a low O_2 pressure of 0.1 MPa, Co_2Fe_1 @NC still achieves an FDCA yield of 52.4%.

Subsequently, the impact of reaction temperature on product distribution is investigated (Fig. 4b and S3b[†]). HMF can achieve complete conversion within 80–110 °C, and a



Fig. 4 The influence of (a) O_2 pressure, (b) reaction temperature, (c) catalyst amount and (d) reaction time on HMF oxidation over $Co_2Fe_1@NC$ (general reaction conditions: HMF 0.25 mmol, NaHCO₃ 0.5 mmol, H₂O 3 mL; additionally for (a) 100 °C, catalyst 60 mg, 7 h; additionally for (b) 0.5 MPa O₂, catalyst 60 mg, 7 h; additionally for (c) 100 °C, 0.5 MPa O₂, 7 h; additionally for (d) 100 °C, 0.5 MPa O₂, catalyst 100 mg).

volcano relationship is noticed between the FDCA yield and temperature. Specifically, the highest FDCA yield of 72% is attained at 100 °C. However, the FDCA yield decreases to 57.7% at 110 °C, likely due to the formation of humins from HMF at higher temperatures.³⁵ Consequently, 100 °C is selected as the optimal temperature for further studies.

The impact of catalyst dosage on HMF oxidation is shown in Fig. 4c. In the absence of a catalyst, HMF conversion reaches 45% with a mere 1.2% FDCA yield. However, when the catalyst dosage is increased to 60 mg, HMF conversion reaches 100% with an FDCA yield of 72%. Further increasing the catalyst dosage to 100 mg leads to a slight increase in the FDCA yield to 76%. Subsequently, the time course of HMF oxidation under optimal conditions (0.5 MPa O_2 , 100 °C, and 100 mg of catalyst) is monitored as shown in Fig. 4d, which demonstrates a steady increase in the FDCA yield, from 76% at 7 h to 96.1% at 22 h.

The stability of the catalyst is paramount for its industrial application. The conversion of HMF remains at 100% although the yield of FDCA decreases from 72% to 52.9% (Fig. 5a). The composition, morphology and structure of the spent catalyst are found to be similar to that of the fresh one, as determined by XPS (Fig. 5c and d). XRD analysis shows that $Co_{0.72}Fe_{0.28}$ diffraction is enhanced and Co_3Fe_7 diffraction is weakened compared to the fresh catalyst, which should be accountable for the slight decline of the FDCA yield (Fig. 5b).

Study of the reaction mechanism

The oxygen activation of Co_xFe_y @NC catalysts is investigated using O₂-TPD (Fig. 6a). Oxygen species are classified into physically adsorbed oxygen (O_{2(ads)}) below 100 °C and chemically adsorbed oxygen (O⁻_{2(ads)}, O⁻_(ads)) at temperatures exceeding 100 °C.³⁶ Compared to Fe@NC, both Co@NC and Co₂Fe₁@NC exhibit stronger oxygen desorption peaks, potentially enhancing HMF oxidation.³⁷ The influence of different atmospheres on HMF oxidation is also examined (Fig. 6b). Under an N₂ atmosphere, the FDCA yield is a mere 0.6%, whereas under an air atmosphere, the yield reaches 53.1%. And under an O₂ atmosphere, the yield of FDCA is further increased to 72% as the concentration of O₂ is further increased. Thus, the oxygen concentration significantly affects the reaction rate.



Fig. 5 (a) Recycling activity of the $Co_2Fe_1@NC$ catalyst. (b) XRD patterns. (c) Co 2p and (d) Fe 2p XPS spectra of the fresh and spent catalysts (reaction conditions: HMF 0.25 mmol, $Co_2Fe_1@NC$ 60 mg, NaHCO₃ 0.5 mmol, H₂O 3 mL, O₂ 0.5 MPa, 100 °C, 7 h).



Fig. 6 (a) O_2 -TPD profiles of Co_xFe_y @NC catalysts. (b) The effect of atmosphere for HMF oxidation over the Co_2Fe_1 @NC catalyst (reaction conditions: HMF 0.25 mmol, Co_2Fe_1 @NC 60 mg, NaHCO₃ 0.5 mmol, H₂O 3 mL, pressure 0.5 MPa, 100 °C, 7 h). (c) UV-Vis spectra of the residual solutions after adsorption of FFCA over Co_xFe_y @NC catalysts. (d) HMF-adsorbed FTIR spectra over Co_xFe_y @NC catalysts.

HMF oxidation is also closely linked to the localized concentration on the catalyst surface. UV-Vis spectra (Fig. 6c) reveal that the FFCA adsorption capacity over Co2Fe1@NC surpasses that over Co@NC, which is attributable to the promotion of oxyphilic Fe species. Additionally, HMF-adsorbed FTIR spectra (Fig. 6d) indicate that peaks appear at 1633 and 1147 cm⁻¹, corresponding to the C=O and C-O-C stretching vibrations of HMF, respectively. Compared to Co@NC, the peak positions of the C=O and C-O-C functional groups on the surfaces of Fe@NC and Co2Fe1@NC show a significant redshift towards lower wavenumbers, with the most pronounced shift being observed for Co₂Fe₁@NC. Additionally, a notable reduction in the C=O aldehyde signal suggests that the planar-adsorbed HMF has been activated on Co2Fe1@NC. This suggests that Co₂Fe₁@NC exhibits robust adsorption with the furan ring and aldehyde groups of HMF, alongside parallel adsorption activation of the C–O bond, notably promoting O_2 activation of C=O groups in HMF.³⁸

To further explore the synergistic effect of Co and Fe, the oxidation kinetics of Co_xFe_y @NC catalysts are investigated for the rate-limiting step (FFCA to FDCA) (Fig. 7a and Fig. S4†). The activation energy (E_a) for FFCA oxidation over Co_2Fe_1 @NC (24.99 kJ mol⁻¹) is significantly lower than that over Co@NC (55.53 kJ mol⁻¹), while it is slightly lower than that over Fe@NC (28.99 kJ mol⁻¹). This indicates that the synergistic effect of Co and Fe reduces the energy barrier of the oxidation reaction. The influences of the FFCA concentration and oxygen pressure were investigated (Fig. 7b and Fig. S5†). It is found that the apparent rate law has a 0.12 order dependence on FFCA and a 0.05 order dependence on oxygen pressure. This



Fig. 7 (a) Arrhenius plots for FFCA oxidation over $Co_2Fe_1@NC$, Co@NC and Fe@NC. (b) Measurement of rate orders of FFCA concentration and O_2 pressure for the $Co_2Fe_1@NC$ catalyst. (c) The *k* values are calculated on the basis of the conversion rates *versus* reaction time for $Co_2Fe_1@NC$, Co@NC and Fe@NC during oxidation of HMF, HMFCA and FFCA.

suggests that both FFCA and oxygen adsorption are not the primary rate-limiting steps of the reaction, and the rate-determining step is most probably correlated with the activation of C=O bonds in surface-bound FFCA (Fig. 7c and Fig. S6-8[†]). Subsequently, the rate constants (k) of Co_2Fe_1 @NC, Co@NC, and Fe@NC are calculated based on time profiles during the oxidation of HMF, HMFCA, and FFCA. The results reveal that HMF has the highest k-value (6.03 h^{-1}), while HMFCA and FFCA to FDCA have lower k-values (0.63 h^{-1} and 0.59 h^{-1} , respectively) with respect to Co2Fe1@NC. In contrast, the k-value of HMF and HMFCA reaches 4.21 h^{-1} and 0.48 h^{-1} , respectively, with the Co@NC catalyst, which are inferior to those of Co₂Fe₁(a)NC. Nevertheless, the k-value of FFCA with Co@NC (0.79 h^{-1}) is higher than that of Co₂Fe₁@NC. This indicates that the Co sites exhibit enhanced catalytic activity for the conversion of HMF to HMFCA and FFCA to FDCA. The k-values of HMF, HMFCA and FFCA reach 1.63 h^{-1} , 0.28 h^{-1} and 0.26 h⁻¹, respectively, with Fe@NC, which are inferior values to those of Co₂Fe₁@NC. This further supports the observation that the lowest oxidation rate of the C=O group in FFCA serves as the rate-limiting step of the reaction.³³

Radical-trapping scavengers were employed to identify the active oxygen species and gain deeper insight into the mechanism of HMF oxidation. Compared with 2-PrOH, AgNO₃ and KI, the addition of DMPO and P-BQ significantly inhibits HMF oxidation and FDCA generation (Fig. 8a).³⁹ Additionally, EPR analysis (Fig. 8b) shows the observation of a quadruple signal in a 1:1:1:1 ratio, corresponding to DMPO-'O₂⁻ adducts, confirming that 'O₂⁻ radicals are the active species responsible for HMF oxidation.^{40,41}



Fig. 8 (a) The influence of various scavengers on the oxidation of HMF. (b) EPR spectra of the DMPO- $^{-}O_2^{-}$ adducts (reaction conditions: HMF 0.25 mmol, catalyst 60 mg, NaHCO₃ 0.5 mmol, scavenger 0.25 mmol, H₂O 3 mL, O₂ 0.5 MPa, 100 °C, 7 h).



Fig. 9 Schematic reaction mechanism of HMF oxidation to FDCA over the $\text{Co}_2\text{Fe}_1\text{@NC}$ catalyst.

Based on the above characterization studies and controlled experiments, a plausible catalytic mechanism for HMF oxidation is proposed (Fig. 9). Initially, HMF is absorbed on the NC-encapsulated CoFe alloy (Co₂Fe₁@NC) and its aldehyde group undergoes hydration to form geminal diols in the presence of a base. Molecular O₂ is activated and converted into O_2^- radicals on the Co₂Fe₁@NC surface.^{32,42} Then HMF is dehydrogenated to HMFCA, leaving two hydrogen atoms on the catalyst surface, which are then oxidized to water by active O_2^- radicals. Subsequently, the C–OH bond in HMFCA is activated and oxidized to form FFCA. Finally, the aldehyde in FFCA undergoes a similar oxidation process to HMF oxidation, ultimately yielding FDCA.

Conclusion

In summary, Co_xFe_y @NC alloy catalysts were synthesized using a solid-state method. By optimizing the Co/Fe ratio, the optimum Co_2Fe_1 @NC catalyst exhibited outstanding performance in terms of FDCA yield (96.1%) and reaction rate (k =6.03 h⁻¹) for HMF oxidation to FDCA at 100 °C and 0.5 MPa O₂, surpassing the performance of monometallic Co and Fe catalysts. The catalyst also demonstrated good stability when recycled five times. This superior performance can be attributed to the close interaction between Co and Fe, which significantly accelerated the HMF oxidation rate and shifted the rate-determining step, facilitating reactant activation and reducing reaction energy barriers. The simple, effective, and solid-state synthesis technique employed in this study presents a promising approach for the development of cost-effective HMF oxidation catalysts, particularly for large-scale applications.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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