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# Functionalized expanded corn starch-anchored Cu(I): An efficient and recyclable catalyst for oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran

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**Abstract**

The development of new strategies for the synthesis of biomass-based non-precious metal heterogeneous catalysts has recently received great interest from chemists because of the advantages of these catalytic systems being sustainable, low cost and green. An expanded corn starch-supported CuBr catalyst (ECS-SB-CuBr) has been successfully prepared and well characterized using Fourier transform infrared spectroscopy, thermogravimetric analysis, powder X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy/energy-dispersive X-ray spectroscopy. Further, ECS-SB-CuBr was used as a heterogeneous catalyst for the selective oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-diformylfuran (DFF) and a full HMF conversion is obtained with 98% DFF yield in acetonitrile under ambient pressure of dioxygen at 50°C. The catalyst also showed good reusability, could be easily recovered through filtration and washing and was reused in at least six consecutive runs with virtually no loss of catalytic performance.

KEYWORDS

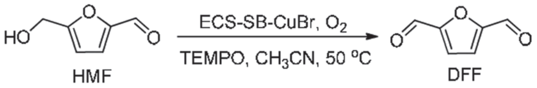
2,5-diformylfuran, 5-hydroxymethylfurfural, copper, expanded corn starch, heterogeneous catalyst

## 1 | INTRODUCTION

2,5-Diformylfuran (DFF) is a versatile compound that has various applications, including as a polymeric monomer and a promising cross-linking agent for battery separation, in pharmaceuticals, antifungal agents, furan–urea resins, heterocyclic ligands and other value added products,[1,2] which is synthesized predominantly via the oxidation of 5-hydroxymethylfurfural (HMF). However, this transformation can be accompanied by the formation of several other kinds of furan compounds like 2,5-furandicarboxylic acid, 5-formyl-2-furancarboxylic acid and 5-hydroxymethyl-2-furancarboxylic acid.[3,4] Thus, for DFF production, highly selective oxidation of HMF is important.

In several cases late transition metals like Pd,[5] Pt,[6] Ru,[7–9] Ag[10] and Au[11,12] have been used as efficient catalysts for selective oxidation of HMF to DFF. From the practical and environmental points of view, there is a strong demand for exploring efficient catalytic systems using inexpensive and nontoxic first-row transition metal (Cu, Fe, etc.)-based catalysts and nontoxic air or oxygen as the terminal oxidant. To this end, many homogeneous copper catalysts have been applied in the presence of $O_2$ and offered high DFF yield.[13,14] Ma *et al*. reported a catalyst system consisting of Cu $(NO_3)_2$ and $VOSO_4$ (1:1), which showed excellent activity for the conversion of HMF (99%) to yield DFF (99%) in acetonitrile at 80°C, 10 bar $O_2$, after 90 min.[15] Kompanets *et al.* reported Cu $(NO_3)_2$ as an efficient catalyst for the production of DFF from HMF in the presence of *N*-hydroxyphthalimide as a co-catalyst, yielding 71% DFF in acetonitrile, at 50°C, 1 bar $O_2$.[16] Tong *et al.* showed that CuI assisted by 1-hydroxybenzotriazole afforded 93% conversion of HMF, with 99% selectivity towards DFF, in dimethylsulfoxide at 130°C, 3 bar $O_2$, after 10 h reaction time.[16] Riisager and co-workers also developed homogeneous Cu-based catalytic systems bearing various organic ligands in combination with 2,2,6,6-tetramethylpiperidinooxy (TEMPO) as a highly efficient method for the aerobic oxidation of HMF to DFF using $O_2$ or air as the terminal oxidant.[17] However, these methods generally suffer from some drawbacks, e.g. high pressure of $O_2$, low product yield and the use of high-boiling-point solvents. Also, the synthesis of DFF proceeds in the presence of copper salts as homogeneous catalysts, which makes the separation and recovery of the copper catalysts very difficult. In addition, it is probable that the obtained DFF can be contaminated by copper metal in a homogeneous catalytic system. Therefore, separation from the products and recycling of the copper catalysts remains a key issue. In contrast, heterogeneous catalytic systems are beneficial for industrial applications because of the ease of handling and purification of products.

In recent years, low-cost and green synthesis of supported catalysts from biomass has attracted growing interest.[18,19] In continuation of our efforts to develop green, highly efficient and practical chemical methods as well as a focus on the application of biomass-based heterogeneous catalysts in organic reactions,[20] we identified that Schiff base-functionalized expanded corn starch-supported CuBr (ECS-SB-CuBr) in the presence of TEMPO as a co-catalyst was an efficient catalyst for promoting the selective aerobic oxidation of HMF into DFF under ambient pressure of dioxygen at 50°C in acetonitrile (Scheme 1). In addition, the catalyst is stable to air and moisture and can be easily recovered and reused. To the best of our knowledge, this is the first example of catalytic aerobic oxidation of HMF to DFF catalyzed by biomass-supported CuBr using a low-cost and more sustainable method.



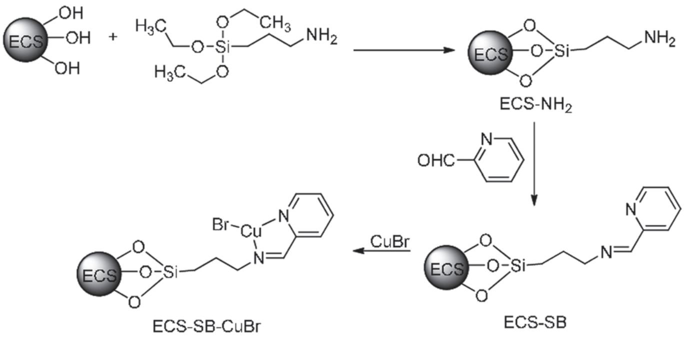
**SCHEME 1** Oxidation of HMF to DFF

## 2 | RESULTS AND DISCUSSION

### 2.1 | Preparation and characterization of ECS-SB-CuBr catalyst

As shown in Scheme 2, the general design of the ECS-SB-CuBr catalyst was first to modify expanded corn starch (ECS) using 3-aminopropyltriethoxysilane to obtain an amine-functionalized surface (ECS-$NH_2$). Then, the formation of Schiff base-modified ECS (ECS-SB) was achieved through the Schiff base condensation between ECS-$NH_2$ with 2-pyridinecarboxaldehyde. ECS-SB, which possessed bidentate nitrogen-binding sites, reacted with copper cations, and ultimately yielded the copper-incorporated heterogeneous catalyst (ECS-SB-CuBr).

ECS-SB-CuBr was characterized using various methods, such as Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), powder X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX). At first, ECS, ECS-SB and ECS-SB-CuBr were characterized using FT-IR spectroscopy (Figure 1). FT-IR spectroscopy provided useful information on the reaction of the $NH_2$ group with 2-pyridinecarboxaldehyde. Compared with ECS, the spectrum of ECS-SB contains two weak bands at 1568 and 1589 $cm^{-1}$, associated with pyridyl ring stretching vibrations.[21] In addition, the bands at



**SCHEME 2** Synthesis of ECS-SB-CuBr

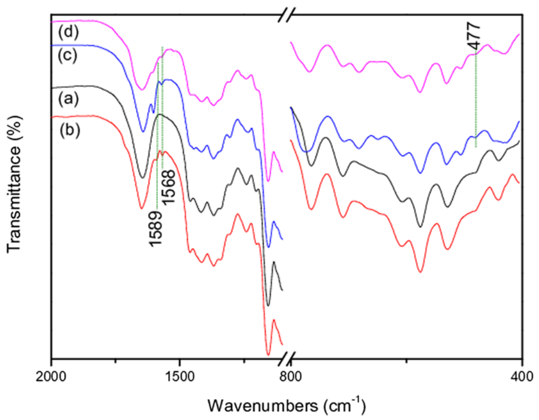


**FIGURE 1** FT-IR spectra of (a) ECS, (b) ECS-SB, (c) as-prepared ECS-SB-CuBr and (d) recovered ECS-SB-CuBr after six consecutive trials

477 cm$^{-1}$ assigned to the Cu—N bond[22] stretching vibration confirmed the interaction between nitrogen atoms in the Schiff base and copper cations, suggesting a Cu—N coordination in the as-synthesized ECS-SB-CuBr.

The thermal stability of catalysts is essential for retaining their activity in longer reaction times, and thermally stable catalysts are especially important for industrial applications requiring high-temperature treatment. The thermal stability of the ECS-SB-CuBr catalyst in each step of production was investigated using TGA at a heating rate of 10°C min$^{-1}$ in nitrogen over a range of 30–800°C. Materials that are thermally resistant make them ideal support materials for catalyst systems. ECS exhibited marked thermal resistance as depicted in Figure 2a (thermal degradation temperature of 259°C), demonstrating the suitability of ECS as a catalyst support. Also, thermograms corresponding to each chemical modification are presented in Figure 2. As seen, despite the chemical treatments, the catalyst still had high thermal stability (Figure 2b–d).

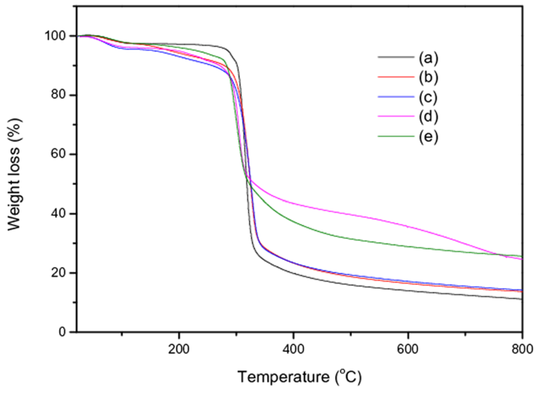


**FIGURE 2** TGA curves of (a) ECS, (b) ECS-$NH_2$, (c) ECS-SB, (d) as-prepared ECS-SB-CuBr and (e) recovered ECS-SB-CuBr after six consecutive trials

Surface morphologies of the products at each chemical modification step are presented in Figure 3. As a result of chemical treatment, each sample exhibited different morphological features, showing that modification of the support materials was achieved. Cu element was detected on the whole ECS-SB-CuBr surface (scanning area in Figure 3d) using EDX. Figure 3f shows that the distribution of Cu (red) element is uniform in the ECS-SB-CuBr catalyst.

The XRD pattern of ECS-SB-CuBr is shown in Figure 4. The broad peak at 10–30° can be attributed to starch due to its amorphous nature. Three additional peaks are clearly visible in the diffraction pattern of the ECS-SB-CuBr at $2\theta = 27.1°$, 45.0° and 53.7° corresponding to the (111), (220) and (311) lattice planes of cubic CuBr,[23] implying the presence of CuBr.

Furthermore, the electronic state of the Cu element in the catalyst was analyzed using X-ray photoelectron spectroscopy (XPS). Figure 5 shows the binding energies of Cu 2p for the as-prepared ECS-SB-CuBr catalyst. The distinct peaks at 932 and 952 eV are ascribed to Cu $2p_{3/2}{}^{+}$ and Cu $2p_{1/2}{}^{+}$,[24] respectively. The peaks at 934 and 954 eV confirm the presence of Cu(II) species,[25] probably arising from oxidation of $Cu^+$ during catalyst preparation.[26,27] The XPS atomic percentages (N, 2.3%; Cu, 1.1%) show that the atomic ratio of nitrogen to copper is about 2 in ECS-SB-CuBr, proving that one copper atom coordinates with two nitrogen atoms in the ECS-SB-CuBr catalyst.

## 2.2 | Selective aerobic oxidation of HMF to DFF

We continued our investigations by using the Cu-based catalyst for selective aerobic oxidation of HMF to DFF under ambient pressure. Based on the literature,[17] in our preliminary experiment, a mixture of 1 mmol of HMF, 10 mol% of TEMPO and 10 mol% of CuCl in acetonitrile was stirred at 50 °C under ambient pressure of dioxygen for 24 h to afford DFF in 36% yield (Table 1, entry 1). To examine the activity of other copper(I) sources, $Cu_2O$, CuBr and CuI were used as catalysts. CuBr showed the best yield of DFF (98%) (Table 1, entries 2–4). Copper(II) or other metal catalysts such as $NiBr_2$ showed no catalytic activity. After the catalyst, various oxidants (air, *tert*-butyl hydroperoxide (TBHP) and $H_2O_2$) were evaluated, and from the results oxygen gas appeared to be best along with CuBr (Table 1, entries 7–9). Various solvents including HAc, EtOH, water, dichloroethane (DCE) and EtOAc and solvent-free

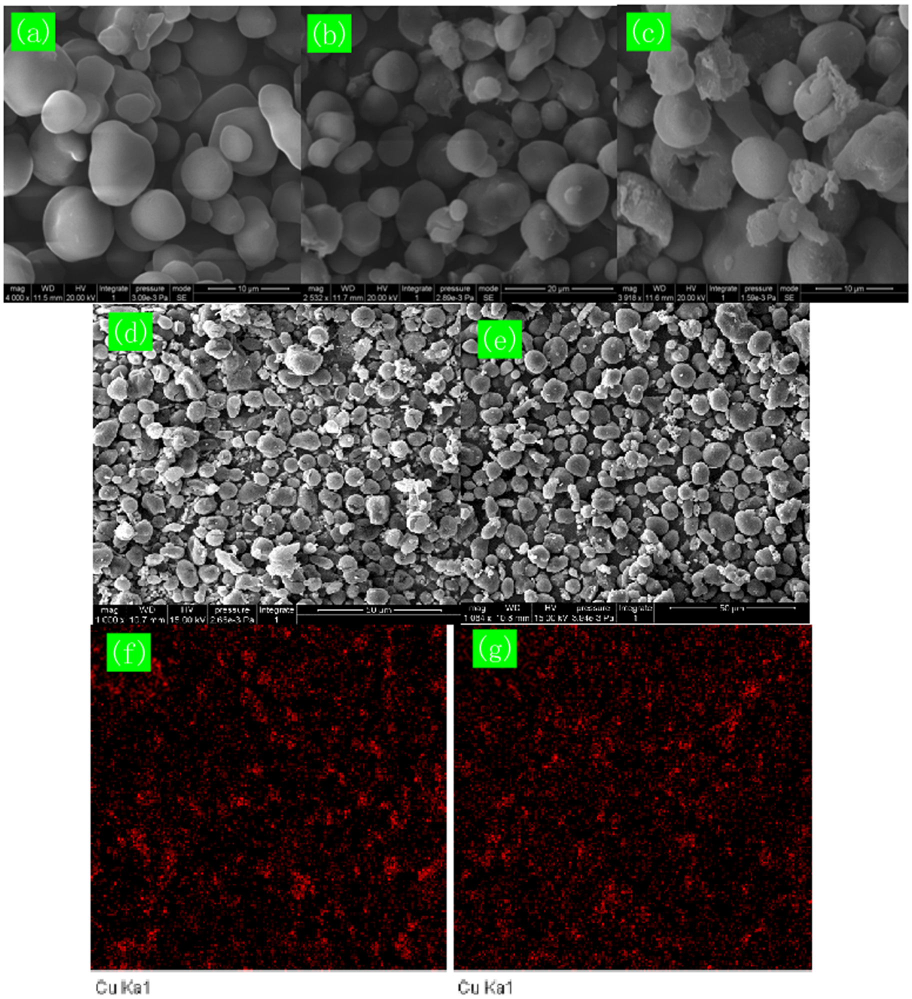


**FIGURE 3** SEM images of (a) ECS, (b) ECS-$NH_2$, (c) ECS-SB, (d) as-prepared ECS-SB-CuBr and (e) recovered ECS-SB-CuBr after six consecutive trials. EDX mapping of Cu of (f) ECS-SB-CuBr and (g) recovered ECS-SB-CuBr after six consecutive trials

conditions were further examined; acetonitrile was still the optimum solvent. In order to allow recycling of the copper salts, the supported ECS-SB-CuBr catalyst was employed as heterogeneous catalyst. To our delight, a complete conversion of HMF with excellent selectivity (98%) to DFF was achieved using 100 mg of ECS-SB-CuBr with 10 mol% TEMPO after 24 h of reaction at 50°C in acetonitrile (Table 1, entry 16).

The performance of the catalytic system was investigated for a series of different conditions, varying the catalyst and TEMPO dosage, reaction time and temperature (Table 2). As can be seen, the addition of ECS-$NH_2$-CuBr, CuBr or TEMPO alone did not show any conversion (Table 2, entries 1–3). The blank reaction was also carried out with only ECS, ECS-$NH_2$ and ECS-SB supports as catalysts and HPLC analysis indicated that there were no

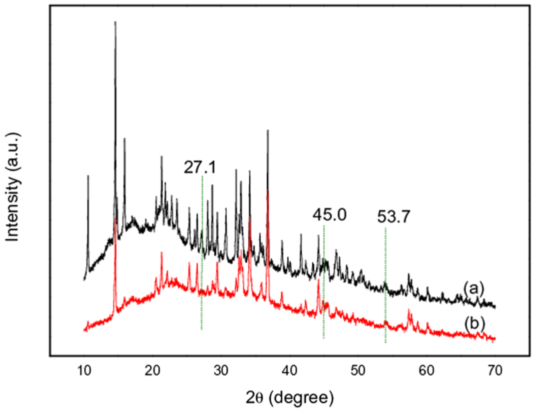


**FIGURE 4** XRD patterns of (a) as-prepared ECS-SB-CuBr and (b) recovered ECS-SB-CuBr after six consecutive trials

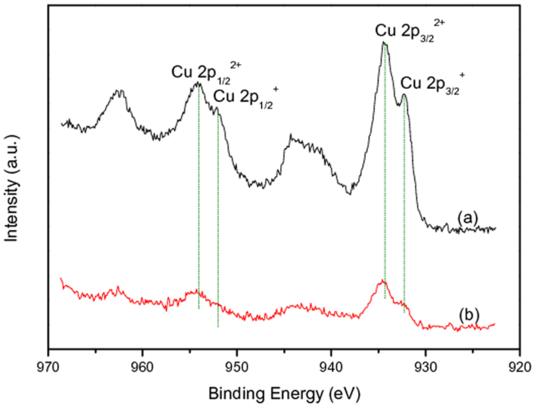


**FIGURE 5** Cu 2p XPS spectra of (a) as-prepared ECS-SB-CuBr and (b) recovered ECS-SB-CuBr after six consecutive trials

**TABLE 1** Optimization of aerobic oxidation of HMF using Cu-based catalysts[a]

| Entry | Catalyst | TEMPO (mol%) | Oxidant | Solvent | Conversion of HMF (%)[b] | Yield of DFF (%) | Selectivity (%) |
|---|---|---|---|---|---|---|---|
| 1 | CuCl | 10 | $O_2$ | $CH_3CN$ | 36 | 36 | 100 |
| 2 | CuBr | 10 | $O_2$ | $CH_3CN$ | 100 | 98 | 98 |
| 3 | $Cu_2O$ | 10 | $O_2$ | $CH_3CN$ | 22 | 20 | 91 |
| 4 | CuI | 10 | $O_2$ | $CH_3CN$ | 25 | 24 | 96 |
| 5 | $CuBr_2$ | 10 | $O_2$ | $CH_3CN$ | Trace | Trace | — |
| 6 | $NiBr_2$ | 10 | $O_2$ | $CH_3CN$ | Trace | — | — |
| 7 | CuBr | 10 | Air | $CH_3CN$ | 15 | 14 | 93 |
| 8 | CuBr | — | TBHP (1.5 equiv.) | $CH_3CN$ | 42 | 36 | 85 |
| 9 | CuBr | — | $H_2O_2$ (1.5 equiv.) | $CH_3CN$ | NR | — | — |
| 10 | CuBr | 10 | $O_2$ | AcOH | 9 | 3 | 33 |
| 11 | CuBr | 10 | $O_2$ | EtOH | 20 | 4 | 20 |
| 12 | CuBr | 10 | $O_2$ | $H_2O$ | NR | — | — |
| 13 | CuBr | 10 | $O_2$ | DCE | 31 | 29 | 94 |
| 14 | CuBr | 10 | $O_2$ | EtOAc | 33 | 30 | 91 |
| 15 | CuBr | 10 | $O_2$ | — | 84 | 77 | 92 |
| 16[c] | ECS-SB-CuBr | 10 | $O_2$ | $CH_3CN$ | 100 | 98 | 98 |

[a] Reaction conditions: HMF (1 mmol), catalyst (10 mol%), solvent (5 ml), $O_2$ (1 atm), 50°C, 24 h.
[b] NR, no reaction.
[c] ECS-SB-CuBr (100 mg).

**TABLE 2** Effects of reaction parameters on aerobic oxidation of HMF catalyzed by ECS-SB-CuBr[a]

| Entry | Catalyst | Catalyst loading (mg) | TEMPO (mol%) | *T* (°C) | Time (h) | Conversion of HMF (%)[b] | Yield of DFF (%) | Selectivity (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | — | — | 10 | 50 | 24 | NR | — | — |
| 2[c] | CuBr | — | 10 | 50 | 24 | NR | | |
| 3 | ECS-SB-CuBr | 100 | — | 50 | 24 | NR | — | — |
| 4 | ECS | 100 | 10 | 50 | 24 | NR | — | — |
| 5 | ECS-$NH_2$ | 100 | 10 | 50 | 24 | NR | — | — |
| 6 | ECS-SB | 100 | 10 | 50 | 24 | NR | — | — |
| 7 | ECS-SB-CuBr | 60 | 10 | 50 | 24 | 70 | 69 | 98 |
| 8 | ECS-SB-CuBr | 80 | 10 | 50 | 24 | 89 | 87 | 98 |
| 9 | ECS-SB-CuBr | 120 | 10 | 50 | 24 | 90 | 89 | 99 |
| 10 | ECS-SB-CuBr | 100 | 6 | 50 | 24 | 67 | 64 | 96 |
| 11 | ECS-SB-CuBr | 100 | 8 | 50 | 24 | 83 | 81 | 97 |
| 12 | ECS-SB-CuBr | 100 | 10 | 40 | 24 | 47 | 46 | 97 |
| 13 | ECS-SB-CuBr | 100 | 10 | 80 | 24 | 72 | 69 | 96 |
| 14 | ECS-SB-CuBr | 100 | 10 | 50 | 18 | 35 | 35 | 100 |
| 15 | ECS-SB-CuBr | 100 | 10 | 50 | 20 | 95 | 94 | 99 |

[a] Reaction conditions: HMF (1 mmol), $CH_3CN$ (5 ml), $O_2$ (1 atm).
[b] NR, no reaction.
[c] CuBr (10 mol%).

products (Table 2, entries 4–6). Therefore, CuBr was the main catalytic center in the oxidation of HMF. As evident from Table 2, the HMF conversion and DFF yield increased with an increase of the catalyst amount, which can be attributed to an increase in the availability and number of catalytically active sites for the aerobic oxidation of HMF. Furthermore, an increase in the amount of ECS-SB-CuBr to 120 mg caused a decrease in the conversion of this reaction to 90% (Table 2, entry 9), which can be related to the fact that excess heterogeneous catalyst may cause an issue with reactant interaction with active sites and the mass transfer limitation leads to a decrease in DFF yield. The conversion of HMF is elevated to 67% when 6 mol% TEMPO was added (Table 2, entry 10). A further increase in the amount to 8 mol% led to HMF conversion of 83%. Decreasing the reaction temperature to 40°C slowed the reaction, affording a 46% yield of DFF (Table 2, entry 12). When the reaction was conducted at 80°C, the yield of DFF was only 69%, which was presumably due to the mass transfer resistance of oxygen from oxygen gas on the liquid surface down to liquid solution. Subsequently, the reaction was investigated at 50°C for different periods of time (Table 2, entries 14 and 15). A 94% yield of DFF was obtained even when the reaction time was reduced to 20 h. The data show that prolonging the reaction time is favorable for an increase of both HMF conversion and DFF yield. This implies that increasing the reaction time is one way to obtain high conversion and yield for low-activity catalysts.

## 2.3 | Reusability of catalyst

In a final set of experiments, we further assessed the stability and reusability of the ECS-SB-CuBr catalyst in the oxidation reaction, because it is crucial to confirm that the highly active catalyst is recyclable. As shown in Figure 6, there was no discernible loss in activity or selectivity. The results were in accordance with inductively coupled plasma experiments because only trace amounts of copper (90 ppb) were detected in the resultant solution collected by hot filtration after 1 h.

Subsequently, the FT-IR spectrum of the reused ECS-SB-CuBr catalyst was obtained, as shown in Figure 1d, which revealed that the typical absorption peak of the Cu—N bond was still present, and also the TGA curve of the reused catalyst was similar to that of the fresh one (Figure 2d,e). The surface morphology and EDX mapping image of Cu (red) element of the reused catalyst are shown in Figure 3e,g, which indicated that the recycling of the catalyst did not cause any significant change in the morphology. In addition, the XRD pattern of the reused catalyst was also similar to that of the fresh one (Figure 4a,b), which thus indicated that the present catalyst system was thermally stable. XPS analysis was further carried out to determine the composition and the surface electronic state of ECS-SB-CuBr after six recycles (Figure 5b). A similar Cu 2p band profile can be observed after ECS-SB-CuBr had been used for six catalytic cycles, which confirms the strong stability of the copper complex during the catalytic process. All these results suggested that there was no significant difference between the fresh and the reused ECS-SB-CuBr catalysts.

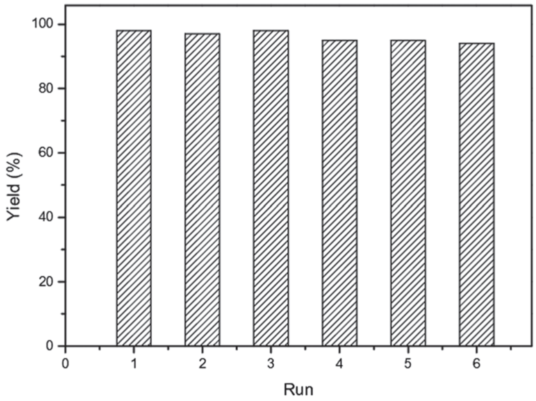


**FIGURE 6** Recycling activity of ECS-SB-CuBr in the oxidation of HMF to DFF

## 3 | CONCLUSIONS

We have successfully developed a new, low-cost and biomass-based heterogeneous catalyst, ECS-SB-CuBr, for the first time. ECS-SB-CuBr was applied as an active catalyst in oxidation of HMF to DFF. In acetonitrile, a 98% yield of DFF was obtained after 24 h with ambient pressure of dioxygen at 50°C. Furthermore, the introduced catalyst was stable and could be reused in more than six successive runs without loss of catalytic activity. To the best of our knowledge, functionalized materials supporting CuBr have not been explored as catalysts in the oxidation of HMF to DFF and hence we believe that the results of this study would make an important contribution to the existing methods for DFF synthesis.

## 4 | EXPERIMENTAL

### 4.1 | Materials and instrumentation

All chemicals were purchased from Energy Chemical Company (Shanghai, China). High-amylose corn starch was purchased from Guomin Starch Chemistry (Shanghai, China) Co. Ltd.

FT-IR spectra were recorded with a Nicolet 380 FT-IR instrument. TGA and differential thermal analyses were carried out with a TG 209F1 thermal analyzer under nitrogen atmosphere at a heating rate of 10 °C $\text{min}^{-1}$. SEM/EDX was conducted using a Quanta 200. Powder XRD patterns of ECS-SB-CuBr were recorded with a Rigaku D/Max 2400 X-ray diffractometer using Cu $K_\alpha$ ($\lambda$ = 0.15406 nm) radiation. XPS spectra were recorded with a Kratos Axis Ultra DLD spectrometer, and the binding energy was calibrated using the C 1s peak. $^1H$ NMR and $^{13}C$ NMR spectra were recorded with Bruker DRX-600 instruments.

## 4.2 | Synthesis of catalyst

### 4.2.1 | Synthesis of ECS-supported imine ligand (ECS-SB)

ECS and ECS-$NH_2$ were synthesized using our previously reported procedure.[28] ECS-SB was prepared via a modified method reported by Xiao and co-workers.[22] 2-Pyridinecarboxaldehyde (1.3338 g, 12 mmol) was added to a mixture of 3-aminopropyl-functionalized ECS (2.4445 g) in super-dry ethanol (60 ml) in a 100 ml round-bottomed flask. The reaction mixture was stirred under reflux for 24 h, and then filtered. The resulting solid was washed with toluene and then further washed with ethanol to remove any unreacted aldehyde. It was dried in a freeze-dryer overnight to furnish the corresponding ECS-SB material.

### 4.2.2 | Synthesis of ECS-SB-CuBr

ECS-SB (2 g) was suspended in absolute ethanol (20 ml). Then, copper bromide (1.92 g, 13 mmol) in absolute ethanol was added and the mixture was kept under refluxing condition for 24 h. The reaction mixture was cooled to room temperature. Finally, the resulting material, ECS-SB-CuBr, was filtered out, washed thoroughly with ethanol and acetonitrile and freeze-dried.

## 4.3 | General procedure for oxidation of HMF to DFF

The experiments were carried out in test tubes equipped with a balloon containing pure $O_2$ when using $O_2$ as the oxidant. In a general procedure, HMF (125 mg, 1 mmol), ECS-SB-CuBr (100 mg), TEMPO (17 mg, 0.1 mmol) and acetonitrile (5 ml) were added to a 10 ml test tube. The reaction mixture was stirred magnetically for 24 h. After completion of the reaction, the mixture was cooled to room temperature and filtered, and the remaining solid was washed with acetonitrile to separate the catalyst. Then, the recovered catalyst was dried and used in several runs in the same manner as described for the first run. Samples were collected and analyzed via HPLC.

## 4.4 | Product analysis

HMF and DFF were analyzed with HPLC (Agilent 1200) using a reversed-phase C18 column (250 × 4.6 mm) at 25°C with a detection wavelength of 280 nm. The mobile phase was acetonitrile and 0.1 wt% acetic acid aqueous solution (65:35 v/v) at 0.5 ml $\text{min}^{-1}$. The HMF conversion and DFF yield were expressed as mol% in terms of the total amount of HMF. The amounts of HMF and DFF in the samples were calculated by interpolation from calibration curves. Calibration curves for the observed products were constructed by injecting known concentrations of commercial reference products.

## 4.5 | Product isolation

DFF was purified by flash column chromatography on silica gel (eluent was petroleum ether–EtOAc, 7:3), where a colorless band was collected and the solvent removed *in vacuo* resulting in a white crystalline compound. $^1H$ NMR (600 MHz, $CDCl_3$, $\delta$, ppm): 7.35 (s, 2H), 9.80 (s, 2H); $^{13}C$ NMR (150 MHz, $CDCl_3$, $\delta$, ppm): 119.35 (2C), 154.19 (2C), 179.20 (2C).

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