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Copper-catalyzed oxidative methyl-esterification of 5hydroxymethylfurfural using TBHP as oxidizing and methylating reagent: A new approach for the synthesis of furan-2,5-dimethylcarboxylate

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Abstract: Catalytic conversion of 5-hydroxymethylfurfural (HMF) into furan-2,5dimethylcarboxylate (FDMC) is of great significance in the production of polyethylene furanoate (PEF), a renewable biomass-derived polymer that can replace the fossil dependent polyethylene terephthalate (PET). Herein, for the first time, we report the synthesis of FDMC from oxidative methyl-esterification of HMF using *tert*-butyl hydroperoxide (TBHP) as an oxidizing and methylating reagent catalyzed by mesoporous alumina nanospheres-embedded with CuO nanoparticles (CuO/m-Al₂O₃). The CuO/m-Al₂O₃ catalysts with different copper contents were prepared by evaporation-induced self-assembly of a structure-directing agent (Pluronic P-123). The decomposition of P-123 during calcination in air results into the formation of a mesoporous structure with highly dispersed CuO nanoparticles. The asprepared 6-CuO/m-Al₂O₃ exhibits excellent catalytic activity towards oxidative methylesterification of HMF into FDMC with 92% yield and turnover frequency (TOF) of 0.56 h⁻¹. Furthermore, oxidative methyl-esterification of a range of substrates through SP³ C-H bond functionalization has also been demonstrated using the same catalyst.

Keywords: HMF; FDMC; Biomass; Copper-catalyzed; oxidative methyl-esterification

1. Introduction

Sustainable production of fuels and chemicals from renewable biomass is highly demanding to combat the rapid depletion of fossil resources and climate change due to carbon footprint. Therefore catalytic valorization of biomass has become important and drawn considerable attention of researchers worldwide.[1–6] Among the various biomass-derived molecules, 5-hydroxymethylfurfural (HMF) is of special interest. HMF can be obtained from the acid-

catalyzed dehydration of lignocellulosic biomass and used for the production of 2,5furandicarboxylic acid (FDCA) through oxidation of its side-groups.[7–10] FDCA has been recognized as a promising replacement for petroleum-based terephthalic acid in polymer production, especially polyethylene furanoate (PEF).[11,12] PEF exhibits tensile strength, glass transition temperature, enzymatic hydrolysis and gas-impermeable properties superior to those of polyethylene terephthalate (PET).[13–15] Despite the significant potential of FDCA, there have been a lot of difficulties in its direct use for PEF production because of its quantitative isolation in high purity for polymerization, high boiling point and low solubility in various industrial solvents.[16-18] Esterification of FDCA into furan-2,5dimethylcarboxylate (FDMC) is the most promising approach to overcome the limitations associated with FDCA. FDMC possesses a low boiling point and a high solubility in most solvents and can easily be purified by low-temperature sublimation method. In addition it can be directly employed in the transesterification step with ethylene glycol to produce PEF.[11,17] Therefore, one-pot synthesis of FDMC from HMF is a cutting-edge process that is in high demand, since such process will enhance the efficiency and reduce the cost in PFE production (Figure 1).



Fig. 1. One-pot synthesis of FDMC from HMF.

Considering these points, several research groups have been actively working on the development of a facile approach for the synthesis of FDMC from HMF. For example, the pioneering work on direct synthesis of FDMC from HMF using molecular oxygen as the oxidant and sodium methoxide as a base additive in the presence of an Au/TiO₂ catalyst was reported by Christensen and co-workers.[19] Corma and co-workers developed gold supported nano ceria catalyst for oxidative esterification of HMF using molecular oxygen and eliminated the use of any base additive as Lewis acidity of the unsaturated cerium assisted in

alcohol oxidation.[20] Subsequently, various gold-based catalysts were developed for the efficient production of FDMC from HMF.[21–26] Considering the high cost of gold, Deng et. al. applied pyrolyzed Co_xO_y-N@C along with an equal amount of K-OMS-2 as the catalytic system for oxidative esterification of HMF in the presence of K₂CO₃ using 10 bar molecular oxygen and obtained the desired product FDMC in 96% yield.[27] Sun et. al. studied the effect of pyridinic nitrogen content in CoO_x-N/C towards its catalytic activity in oxidative esterification of HMF along with α -MnO₂ as a co-catalyst and concluded that pyridinic nitrogen facilitates the dehydrogenation of the hydroxyl group in HMF thereby eliminating the need of a base.[28] Recently, Sun et. al. prepared a MOF derived hollow yolk-shell Co@CN material using SiO₂ as a hard template and studied its catalytic activity in oxidative esterification of HMF. It was reported that, the SiO₂ shell prevents the aggregation of cobalt nanoparticles during pyrolysis at high temperature and its removal by NaOH etching afforded highly dispersed cobalt with a hollow yolk-shell structure.[29] Inspired by these results, several other cobalt-based catalysts have been developed for oxidative esterification of HMF affording FDMC in excellent yields.[30-33] The aforementioned processes for oxidative esterification of HMF into FDMC involve the use of molecular oxygen as a cheap and easily available oxidant. However, the requirement of high oxygen pressure is a critical drawback from the practical point of view, as it requires the specific equipments and extreme safety precautions.[34]

Herein, for the first time, we report on the synthesis of FDMC through oxidative methylesterification of HMF using *tert*-butyl hydroperoxide (TBHP) as both oxidizing as well as methylating agent catalyzed by mesoporous alumina nanospheres-embedded with CuO nanoparticles. A series of CuO/m-Al₂O₃ with varying amount of CuO was prepared by evaporation-induced self-assembly (EISA) of an structure-directing agent (P-123) in an ethanolic solution containing aluminium isopropoxide, Cu(NO₃)₂.3H₂O and nitric acid (Figure 2). Calcination of the resultant gel in air atmosphere resulted into the decomposition of P-123 affording formation of alumina nanospheres with highly ordered, hexagonally arranged mesopores embedded with CuO nanoparticles.[35–38] In comparison to the incipient wetness impregnation of conventional alumina with metal precursors, which often leads to the lowered surface area due to pore blockage, the one-pot EISA method is suitable to achieve high-quality mesopores with homogeneous dispersion of active metals.[38,39] Furthermore, the embedding of active metals in alumina framework mitigates their aggregation during the reaction and improves the catalyst recycling. Recently, Ghosh et. al.

reported the oxidative methyl-esterification of various derivatives of benzyl alcohol, benzaldehyde and benzoic acid catalyzed by Pd/Cu₂Cl(OH)₃ using TBHP and K₂CO₃ as a base additive.[40] Here, we report the base free as well as a noble metal-free catalytic system for oxidative methyl-esterification of various derivatives of benzyl amine and toluene in addition to the substrates reported by Ghosh et. al. Furthermore, we have also demonstrated the one-pot oxidative methyl-esterification of a range of substrates involving SP³ C-H bond functionalization for the first time establishing the wide applicability of the present synthetic strategy. TBHP has been used as a multipurpose reagent in various organic transformations [40–46]. Here also it plays a crucial role, it acts as an oxidant as well as a methyl source in oxidative methyl-esterification of HMF and eliminates the need of a stoichiometric amount of base additive as the corresponding product does not lower the pH of the reaction medium.



Fig. 2. Graphical representation of CuO/m-Al₂O₃ catalyst preparation.

2. Experimental details

2.1 Catalyst preparation

A series of CuO/m-Al₂O₃ catalyst with different copper contents (2-CuO/m-Al₂O₃, 4-CuO/m-Al₂O₃, 6-CuO/m-Al₂O₃ and 8-CuO/m-Al₂O₃ containing 2, 4, 6 and 8 wt% of copper oxide respectively) have been prepared by evaporation-induced self-assembly method in conformity with a previous study with slight modifications [35]. In a general synthesis of 6-CuO/m-Al₂O₃, Pluronic P123 (4 g) was transferred into a beaker containing 40 mL of ethanol

and stirred at room temperature until it gets dissolved completely. Then, 65% nitric acid (7 mL) was added to another beaker containing aluminium isopropoxide (8 g) and ethanol (40 mL) and stirred until complete dissolution of aluminium isopropoxide. Addition of nitric acid into the mixture of aluminium isopropoxide and ethanol was exothermic hence; the beaker was placed in a cold water bath. The two solutions were mixed with continuous stirring and Cu(NO₃)₂.3H₂O (0.4 g) was added to the resulting mixture. The obtained mixture was stirred at room temperature for 48 h and then placed in an oven maintained at 60 °C for ethanol evaporation for 72 h. A blue coloured gel was obtained after ethanol evaporation which was calcined in air atmosphere using a tubular furnace at 400 °C for 4 h with a heating rate of 1 °C per min. Similarly, the other catalysts were also prepared by varying the quantity of cupric nitrate.

2.2 Procedure for oxidative methyl-esterification reaction

The liquid phase oxidative methyl-esterification of various substrates was carried out in a 15 mL glass vial equipped with a magnetic stirrer. In a general procedure, 1 mmol of the substrate was added to the reaction vial containing 3 mL of dimethyl sulfoxide (DMSO), 1 mL of distilled water and 10 mg of the catalyst. To the resulting mixture, 70% aqueous TBHP (4 mmol - 12 mmol) was added dropwise under continuous stirring. The addition of TBHP was exothermic. The reaction vial was sealed with a Teflon septum fitted aluminium cap and immersed in an oil bath maintained at 100 °C. The reaction was continued for 20 h. After the reaction, the catalyst was isolated by centrifugation and the filtrate was mixed with 100 mL of water in a 250 mL separating funnel. The organic compounds were extracted from the aqueous mixture using ethyl acetate (50 mL x 2 times). The organic portion was combined and dried over Na₂SO₄ and evaporated under vacuum using a rotator evaporator to obtain the crude product. The crude products were purified by column chromatography using silica gel (100-200 mesh) and a mixture of petroleum ether and ethyl acetate. The products were initially identified by GC-MS and finally confirmed by NMR spectroscopy.

3. Results and discussion

3.1 Catalyst characterization

Phase identification of the as-prepared catalysts was done by recording their powder XRD patterns and represented in Figure 3. The sharp diffraction peaks at 35.4° and 38.6° confirm the presence of highly crystalline CuO nanoparticles (ICDD PDF No. 80-1268). The intensity of the diffraction peaks corresponding to CuO in 8-CuO/m-Al₂O₃, 6-CuO/m-Al₂O₃ and 4-

CuO/m-Al₂O₃ reduced gradually due to the decreased copper content (Figure 3). The CuO characteristic diffraction peaks were absent in 2-CuO/m-Al₂O₃ catalyst. This could be possibly due to the small particle size of CuO or high dispersion of CuO inside the mesopores of the alumina making it unavailable for X-ray diffraction. The absences of characteristic diffraction peaks of Al₂O₃ suggest the formation of amorphous alumina [37]. Calcination at 400 °C afforded the decomposition of template P123 resulting into the formation of highly ordered hexagonal mesopores in alumina which was confirmed by recording the small-angle X-ray scattering (SAXS) pattern of 6-CuO/m-Al₂O₃ (Figure S1, ESI). The sample 6-CuO/m-Al₂O₃ shows a sharp X-ray scattering peak at 0.2° confirming the formation of mesoporous structure [37]. The combination of powder XRD and SAXS results confirm the formation of mesoporous alumina with crystalline CuO nanoparticles on its surface.



Fig. 3. XRD patterns of the as-prepared catalysts.

Elemental composition and chemical state of the elements in 6-CuO/m-Al₂O₃ was studied by XPS analysis (Figure 4). The survey spectrum (Figure 4a) shows the presence of Cu, Al and O elements in 6-CuO/m-Al₂O₃. The two peaks at 934.7 eV and 954.9 eV in Cu 2p high-resolution scan (Figure 4b) corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ suggest the presence of Cu²⁺. The strong shake-up satellite peaks at 943.9 eV, and 962.5 eV confirms the oxidation state of copper as Cu²⁺ [47]. The bivalent oxidation state of copper was further confirmed by Cu LMM spectrum (Figure S10, ESI). The Cu LMM spectrum shows a peak at 569 eV,

which corresponds to CuO species [48]. The two peaks in high-resolution Al 2p spectra (Figure 4d) indicate the presence of two different forms of aluminium in 6-CuO/m-Al₂O₃. The low binding energy peak at 74.2 eV corresponds to Al-O (Al₂O₃), whereas the higher binding energy peak at 77.3 eV can be assigned to Al-O (CuAl₂O₄) [49].



Fig. 4. XPS of 6-CuO/m-Al₂O₃ catalyst (a) survey scan, (b) Cu 2p, (c) O 1s and (d) Al 2p high-resolution scans.

Surface morphology of the as-prepared 6-CuO/m-Al₂O₃ was examined by SEM and TEM analysis. FEG-SEM images (Figure 5 a&b) reveal the formation of spherical shaped alumina with particles having sizes in the range of 100 to 200 nm which is in good agreement with the earlier report [50]. The formation of spherical shaped alumina can be attributed to the fast hydrolysis of alumina precursor, which gets attached to the outer part of the spherical micelle [51]. The low to high magnification TEM images (Figure 5 c&d) admit the formation of CuO nanoparticles on the surface of alumina nanospheres. The presence of CuO particles on alumina nanospheres was further confirmed by HRTEM analysis. The interplanar spacing

was found to be around 0.25 nm (Figure 5e) which is characteristic of the CuO (111) plane. The concentric rings in selected area electron diffraction (SAED) pattern of 6-CuO/m-Al₂O₃ (Figure 5f) suggest the polycrystalline nature of the CuO nanoparticles. Elemental mapping of 6-CuO/m-Al₂O₃ using TEM (Figure 6) shows the uniform dispersion of CuO throughout the alumina support. The elemental analysis (Figure S2, ESI) and EDS line scan profile (Figure S3, ESI) confirms the formation of 6-CuO/m-Al₂O₃ with a high purity and uniform distribution of elements throughout the sample.



Fig. 5. FEG-SEM images (a) and (b), TEM images (c) and (d), HRTEM image (e) and SAED pattern (f) of 6-CuO/m-Al₂O₃ catalyst.



Fig. 6. TEM image (a) and corresponding Cu (b), Al (c) and O (d) elemental mappings in 6-CuO/m-Al₂O₃ catalyst.

The nitrogen adsorption-desorption isotherm (Figure S4a, ESI) with hysteresis loop admits the presence of mesoporous structures in 6-CuO/m-Al₂O₃ resulting into a large BET surface area of 340 m²/g with a total pore volume of 0.76 cm³/g. The pore size distribution curve shows that the 6-CuO/m-Al₂O₃ has an average pore diameter of 4 nm (Figure S4b, ESI), which is in good agreement with the earlier report [38]. XRF spectra of 6-CuO/m-Al₂O₃ (Figure S5, ESI) display a high-intensity peak at 1.5 KeV corresponding to Al-K_a and a lowintensity peak at 8.04 KeV corresponding to Cu-K_a. The XRF quantification result reveals the 2, 4, 6 and 8 wt% loadings of CuO in 2-CuO/m-Al₂O₃, 4-CuO/m-Al₂O₃, 6-CuO/m-Al₂O₃ and 8-CuO/m-Al₂O₃ catalysts respectively (Figure S5, ESI). TGA analysis (Figure S6, ESI) shows 15 wt% loss of the material at 100 °C which is possibly due to the removal of adsorbed water molecules present in the pores of 6-CuO/m-Al₂O₃. Thus, the results obtained from various characterization techniques suggest the successful formation of a mesoporous structure with embedded CuO nanoparticles throughout the alumina nanospheres.

3.2 Catalytic activity

3.2.1 Oxidative methyl-esterification of HMF

Catalytic performance of a series of as-prepared CuO/m-Al₂O₃ catalyst containing different amounts of CuO was evaluated towards oxidative methyl-esterification of HMF using TBHP,

and the results are presented in Table 1. The TBHP was used in excess during the whole process of the reaction. Hence the reaction can be assumed to have first-order kinetics [52]. The normalized initial rates of FDMC formation were calculated to arrive at a meaning comparison between the as-prepared catalysts [53,54]. The oxidative methyl-esterification of HMF using 2-CuO/m-Al₂O₃ as a catalyst provided 50 mol L⁻¹ h⁻¹ mol_{CuO}⁻¹ normalized rate of FDMC formation with a TOF of 0.56 h⁻¹ (Table 1, entry 1). The higher normalized rate of FDMC formation and TOF was obtained when 4-CuO/m-Al₂O₃ was used as a catalyst (Table 1, entry 2). The 6-CuO/m-Al₂O₃ provided the highest normalized rate of FDMC formation (200 mol L⁻¹ h⁻¹ mol_{CuO}⁻¹) and TOF (0.56 h⁻¹). The use of 8-CuO/m-Al₂O₃ as a catalyst lowered normalized rate of FDMC formation (175 mol L⁻¹ h⁻¹ mol_{CuO}⁻¹) as well as TOF (0.56 h⁻¹). The lowered normalized rate and TOF with 8-CuO/m-Al₂O₃ catalyst could be possibly due to the formation of larger CuO nanoparticles as a result of higher percentage loading of metal on the surface of alumina nanospheres. Next, the catalytic activity is completely because of the CuO nanoparticles was confirmed when m-Al₂O₃ without any copper loading was used in the reaction (Table 1, entry 5). A blank reaction without using any catalyst showed that no FDMC was formed even after 20 h which clearly indicates very slow rate of the reaction in absence of catalyst (Table 1, entry 6). The more details for TON and TOF calculations are provided in Table S1 (ESI).

Table	1.	Catalytic	performance	of	the	as-prepared	catalysts	towards	oxidative	methyl-
esterifi	cat	ion of HM	F. ^a							

Entry	Catalyst	CuO	FDMC formation	DMC formationNormalized rate d		TOF
		loading ^b	rate ^c	$(mol L^{-1} h^{-1} mol_{CuO}^{-1})$	yield ^e	(h ⁻¹)
		(wt %)	$(mol L^{-1} h^{-1} g_{cat}^{-1})$		(%)	
1	2-CuO/m-Al ₂ O ₃	2	0.005	50	12	0.20
2	4-CuO/m-Al ₂ O ₃	4	0.075	150	52	0.47
3	6-CuO/m-Al ₂ O ₃	6	0.15	200	92	0.56
4	8-CuO/m-Al ₂ O ₃	8	0.175	175	93	0.42
5	m-Al ₂ O ₃	-	-	-	-	-
6	Blank	-	-	-	-	-

^{*a*} Reaction conditions: HMF, 1 mmol; catalyst, 0.1 g; TBHP, 20 mmol; solvent, DMSO: Water 3:1 mL; temperature, 100 °C; time, 20 h; rpm, 800. ^{*b*} Estimated from XRF analysis. ^{*c*} Initial rates calculated as an average value between 1 and 2 h reaction time with a FDMC yield of ~ 10%. ^{*d*} rates normalized to the molar concentration of CuO. ^{*e*} Determined from GC.

effect of catalyst loading on oxidative methyl-esterification of HMF The was comprehensively studied by varying the quantity of 6-CuO/m-Al₂O₃ from 13 to 33 g L⁻¹ (Figure 6a). Increasing the catalyst loading from 13 to 26 g L⁻¹ increased the formation rate and molar yield of FDMC due to the increased number of active sites in the reaction. Further increasing the loading of 6-CuO/m-Al₂O₃ to 33 g L⁻¹ further increases the initial rate of formation of FDMC however, the molar yield of FDMC remained constant. This indicates that the number of active sites was sufficient to obtain the maximum molar yield of FDMC. Additionally, the initial rate of FDMC formation was plotted against the loading of 6-CuO/m-Al₂O₃ (Figure 6b). The initial rate of FDMC formation was found to be directly proportional to the loading of the catalyst due to the proportional increase in the number of active sites. The linear relationship between 6-CuO/m-Al₂O₃ loading and rate of formation of FDMC suggests the absence of mass transfer resistance. Next the effect of various solvents on oxidative methyl-esterification of HMF was studied (Figure S9, ESI). The mixture of DMSO and water in 3:1 ratio provided the maximum yield of the desired product. The oxidative methyl-esterification of HMF was carried out at different agitation speeds ranging from 600 to 1000 rpm. The molar yield of FDMC was found to be constant at different agitation speeds (Figure 7a). This indicates that the rate of external diffusion was higher as compared to the rate of formation of FDMC. Therefore, all further reactions were carried out at an agitation speed of 800 rpm.



Fig. 6. Effect of 6-CuO/m-Al₂O₃ loading on oxidative methyl-esterification of HMF.

Reaction conditions: HMF, 1 mmol; 6-CuO/m-Al₂O₃, 13 to 26 g L⁻¹; TBHP, 20 mmol; DMSO:H₂O, 3:1mL; temperature, 100 °C; time, 20 h; rpm, 800. Initial rates calculated as an average value between 1 and 2 h reaction time with an FDMC yield of ~ 10%.

The effect of reaction temperature on oxidative methyl-esterification of HMF was studied. As the temperature increases from 353 to 383 K, the initial rate of FDMC formation also increases (Figure 7c). This indicates that the reaction was intrinsically kinetically controlled. Although the rate of reaction was found to increase with an increase in temperature, the molar yield of FDMC was found to be almost constant at reaction temperatures of 373 and 383 K (Figure 7b). Therefore, 373 K was considered as the optimum temperature for oxidative methyl-esterification of HMF. The Arrhenius plot was obtained to calculate the apparent activation energy (E_a) by plotting ln (initial rates) versus reciprocal of temperatures in the range of 353 to 383 K (Figure 7d) [55]. The apparent activation energy (E_a) was calculated from the slop of the plot was found to be 6.8 kcal/mol.



Fig. 7. Effect of reaction temperature on oxidative methyl-esterification of HMF.

Reaction conditions: HMF, 1 mmol; 6-CuO/m-Al₂O₃, 26 g L⁻¹; TBHP, 20 mmol; DMSO:H₂O, 3:1mL; temperature, 353 - 383 K; time, 20 h; rpm, 800. Initial rates calculated as an average value between 1 and 2 h reaction time with a FDMC yield of ~ 10%.

3.2.2 Oxidative methyl-esterification of various biomass-derived molecules

To establish the high efficiency and general applicability of the present synthetic methodology in biomass valorization, various furanic compounds derived from biomass were successfully converted into the corresponding methyl-esters using optimized reaction conditions and presented in Table 2. A higher yield of FDMC (96%) was obtained when 2,5-furandicarboxylic acid was used as the starting material (Table 2, entry 3). Oxidative methyl-esterification of 2,5-dimethylfuran and 2-methylfuran involving SP³ C-H bond functionalization also afforded the good yield of the corresponding products (Table 2, entry 4 and 5). The optimized quantity of TBHP for oxidative methyl-esterification of HMF, 2,5-DFF, FDCA, 2,5-DMF, 2-MF, 2-furoic acid, furfuryl alcohol and furfural is 8 mmol, 8 mmol, 6 mmol, 12 mmol, 6 mmol, 4 mmol, 4 mmol and 4 mmol, respectively.

Entry	Substrate	Product	Yield ^b (%)	-
1	HO H		92	
2	н С Н	0,0-	91	
3	но он		96	
4	` ↓ °≻		78	
5	_O		73	
6	O OH		82	
7	O OH		77	
8	C H		80	

Table 2. Oxidative methyl-esterification of various biomass-derived furanic compounds.^a

^{*a*} Reaction conditions: Substrate, 1 mmol; 6-CuO/m-Al₂O₃, 8 mol%; TBHP, 4-12 mmol; DMSO:H₂O, 3:1 mL; temperature, 100 °C; time, 20 h. ^{*b*} GC-MS yields.

3.2.3 Oxidative methyl-esterification of various homocyclic aromatic compounds

To further extend the substrate scope, we explored the oxidative methyl-esterification of various homocyclic aromatic compounds using the present synthetic system. As shown in Scheme 1, various derivatives of benzaldehyde, benzyl alcohol, benzylamine, benzoic acid and toluene successfully undergo oxidative methyl-esterification reaction in the presence of 4 mmol, 6 mmol, 6 mmol, 4 mmol and 6 mmol of TBHP respectively providing good to excellent yields of the corresponding products.



Scheme 1. Oxidative methyl-esterification of various substrates.^a

^{*a*} Reaction conditions: Substrate, 1 mmol; 6-CuO/m-Al₂O₃, 8 mol%; TBHP, 4-6 mmol; DMSO:H₂O, 3:1 mL; temperature, 100 °C; time, 20 h; rpm, 800. ^{*b*} isolated yields.

3.3 Mechanistic investigation and tentative reaction mechanism

To understand the reaction mechanism involved in oxidative methyl-esterification of HMF, some controlled experiments were carried out as presented in Scheme 2. The reaction produced 84% of 1-methoxy-2,2,6,6-tetramethylpiperidine and only 8% of the desired product FDMC when 1 mmol of radical (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) was introduced in the reaction under optimized conditions (Scheme 2b). This finding

confirms the formation of methyl radical in the reaction which on successively coupling with TEMPO radical afforded the 1-methoxy-2,2,6,6-tetramethylpiperidine in major amount. Next to figure out whether the methyl radical comes from the TBHP or DMSO, we carried out the reaction using water as the only solvent instead of using DMSO and water mixture. An 87% yield of FDMC was obtained when water alone was used as a solvent for the reaction, confirming the generation of methyl radical from TBHP (Scheme 2c).



Scheme 2: Control experiments and the effect of radical inhibitor.

On the basis of the results obtained from the controlled experiments and earlier reports, a tentative reaction mechanism is proposed in Scheme 3 [40,43]. Initially, the reaction of TBHP and Cu(II) generates a *tert*-butoxyl radical and Cu(III) species in the mixture. The Cu(III) species on further reaction with an another molecule of TBHP get reduced to Cu(II) and simultaneously generates a *tert*-butylperoxyl radical (Step I, Scheme 3) [56]. In the next step, *tert*-butoxyl radical gets converted into acetone and simultaneously generated a methyl radical. The substrate, HMF or 2,5-dimethylfuran gets oxidized to FDCA in presence of the oxidant TBHP. Subsequently, the reaction of 2,5-furandicarboxylic with *tert*-butoxyl or *tert*-butylperoxyl radicals generates acyloxyl radical intermediate (Step II, Scheme 3). Finally, the successive coupling of the acyloxyl radical with methyl radicals results in the formation of the desired product FDMC (Step III, Scheme 3).



Scheme 3. The tentative reaction mechanism for the oxidative methyl-esterification of HMF.

3.4 Catalyst stability and reusability

The reusability of 6-CuO/m-Al₂O₃ in oxidative methyl-esterification of HMF was studied and the results are shown in Figure 8. During the recycling study, the catalyst was separated from the reaction mixture by centrifugation at 10000 rpm for 10 min and washed with water and then with ethanol by centrifugation and redispersion. The isolated catalyst was then dried overnight in a vacuum oven at 100 °C and then used for the next catalytic run. The conversion of HMF remained 100% during the recycling. However, the Yield of FDMC decreased slightly from 92% to 85% similarly the TOF was also decreased from 0.56 h⁻¹ to 0.51 h⁻¹ after 4 consecutive runs (Figure 8). This slight decrease in yield, as well as TOF, can be attributed to the slight loss of catalyst during recycling study. The stability of the catalyst was examined by recording the XRD of 6-CuO/m-Al₂O₃ after recycling for 4 times. The reused 6-CuO/m-Al₂O₃ shows the diffraction peaks similar to the fresh catalyst (Figure S7, ESI). Furthermore, the SEM images of the recycled catalyst (Figure S8, ESI) shows no change in the morphology of the catalyst. The XRD and SEM analysis suggest the high stability of the 6-CuO/m-Al₂O₃ catalyst.



Fig. 8. Reusability of 6-CuO/m-Al₂O₃ catalyst in oxidative methyl-esterification of HMF.

4. Conclusions

We have demonstrated for the first time the one-pot synthesis of FDMC from oxidative methyl-esterification of HMF using TBHP as an oxidizing and methylating agent in the presence of a 6-CuO/m-Al₂O₃ catalyst. The mesoporous alumina-nanospheres embedded with CuO nanoparticles were prepared from evaporation-induced self-assembly of a structuredirecting agent in ethanolic solution. The as-prepared catalyst exhibited excellent catalytic activity in oxidative methyl-esterification of HMF, providing 92% yield of FDMC. The apparent activation energy (E_a) for oxidative methyl-esterification of HMF was calculated from the Arrhenius plot was found to be 6.8 kcal/mol. We have also demonstrated the oxidative methyl-esterification of a range of substrates through SP³ C-H bond functionalization using the same catalyst. The mechanistic investigation revealed the reaction proceeds through the radical mechanism, and the methyl group in the product comes from TBHP indicating its dual role in the reaction. Besides the biomass-derived molecules, oxidative methyl-esterification of various derivatives of benzaldehyde, benzyl alcohol, benzylamine, benzoic acid and toluene also provided good to the excellent yield of the corresponding esters. Thus the wide applicability of the present protocol has been established in oxidative methyl-esterification reaction.

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References:

- R.A. Sheldon, Green and sustainable manufacture of chemicals from biomass: state of the art, Green Chem. 16 (2014) 950–963. doi:10.1039/C3GC41935E.
- Y. Zhu, C. Romain, C.K. Williams, Sustainable polymers from renewable resources, Nature. 540 (2016) 354–362. doi:10.1038/nature21001.
- [3] D. Bonincontro, A. Lolli, A. Storione, A. Gasparotto, B. Berti, S. Zacchini, et al., Pt and Pt/Sn carbonyl clusters as precursors for the synthesis of supported metal catalysts for the base-free oxidation of HMF, Appl. Catal. A Gen. 588 (2019) 117279. doi:10.1016/j.apcata.2019.117279.
- [4] J. Zhao, X. Chen, Y. Du, Y. Yang, J.-M. Lee, Vanadium-embedded mesoporous carbon microspheres as effective catalysts for selective aerobic oxidation of 5hydroxymethyl-2-furfural into 2, 5-diformylfuran, Appl. Catal. A Gen. 568 (2018) 16– 22. doi:10.1016/j.apcata.2018.09.015.
- [5] S.S.R. Gupta, M.L. Kantam, Selective hydrogenation of levulinic acid into γ-valerolactone over Cu/Ni hydrotalcite-derived catalyst, Catal. Today. 309 (2018) 189–194. doi:10.1016/j.cattod.2017.08.007.
- [6] S.S.R. Gupta, M.L. Kantam, Catalytic conversion of furfuryl alcohol or levulinic acid into alkyl levulinates using a sulfonic acid-functionalized hafnium-based MOF, Catal. Commun. 124 (2019) 62–66. doi:10.1016/j.catcom.2019.03.003.
- [7] X. Han, L. Geng, Y. Guo, R. Jia, X. Liu, Y. Zhang, et al., Base-free aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over a Pt/C–O–Mg catalyst, Green Chem. 18 (2016) 1597–1604. doi:10.1039/C5GC02114F.

- [8] X. Wan, C. Zhou, J. Chen, W. Deng, Q. Zhang, Y. Yang, et al., Base-Free Aerobic Oxidation of 5-Hydroxymethyl-furfural to 2,5-Furandicarboxylic Acid in Water Catalyzed by Functionalized Carbon Nanotube-Supported Au–Pd Alloy Nanoparticles, ACS Catal. 4 (2014) 2175–2185. doi:10.1021/cs5003096.
- [9] X. Han, C. Li, Y. Guo, X. Liu, Y. Zhang, Y. Wang, N-doped carbon supported Pt catalyst for base-free oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid, Appl. Catal. A Gen. 526 (2016) 1–8. doi:10.1016/j.apcata.2016.07.011.
- [10] S. Xu, P. Zhou, Z. Zhang, C. Yang, B. Zhang, K. Deng, et al., Selective Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid Using O 2 and a Photocatalyst of Co-thioporphyrazine Bonded to g-C 3 N 4, J. Am. Chem. Soc. 139 (2017) 14775–14782. doi:10.1021/jacs.7b08861.
- [11] A.F. Sousa, C. Vilela, A.C. Fonseca, M. Matos, C.S.R. Freire, G.-J.M. Gruter, et al., Biobased polyesters and other polymers from 2,5-furandicarboxylic acid: a tribute to furan excellency, Polym. Chem. 6 (2015) 5961–5983. doi:10.1039/C5PY00686D.
- [12] M.A. Hillmyer, The promise of plastics from plants, Science (80-.). 358 (2017) 868– 870. doi:10.1126/science.aao6711.
- S.K. Burgess, J.E. Leisen, B.E. Kraftschik, C.R. Mubarak, R.M. Kriegel, W.J. Koros, Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate), Macromolecules. 47 (2014) 1383–1391. doi:10.1021/ma5000199.
- [14] J. Zhu, J. Cai, W. Xie, P.-H. Chen, M. Gazzano, M. Scandola, et al., Poly(butylene 2,5-furan dicarboxylate), a Biobased Alternative to PBT: Synthesis, Physical Properties, and Crystal Structure, Macromolecules. 46 (2013) 796–804. doi:10.1021/ma3023298.
- [15] S. Weinberger, K. Haernvall, D. Scaini, G. Ghazaryan, M.T. Zumstein, M. Sander, et al., Enzymatic surface hydrolysis of poly(ethylene furanoate) thin films of various crystallinities, Green Chem. 19 (2017) 5381–5384. doi:10.1039/C7GC02905E.
- [16] X. Kong, Y. Zhu, Z. Fang, J.A. Kozinski, I.S. Butler, L. Xu, et al., Catalytic conversion of 5-hydroxymethylfurfural to some value-added derivatives, Green Chem. 20 (2018) 3657–3682. doi:10.1039/C8GC00234G.

- [17] C.F. Araujo, M.M. Nolasco, P.J.A. Ribeiro-Claro, S. Rudić, A.J.D. Silvestre, P.D. Vaz, et al., Inside PEF: Chain Conformation and Dynamics in Crystalline and Amorphous Domains, Macromolecules. 51 (2018) 3515–3526. doi:10.1021/acs.macromol.8b00192.
- [18] G. Yi, S.P. Teong, Y. Zhang, Base-free conversion of 5-hydroxymethylfurfural to 2,5furandicarboxylic acid over a Ru/C catalyst, Green Chem. 18 (2016) 979–983. doi:10.1039/C5GC01584G.
- [19] E. Taarning, I.S. Nielsen, K. Egeblad, R. Madsen, C.H. Christensen, Chemicals from Renewables: Aerobic Oxidation of Furfural and Hydroxymethylfurfural over Gold Catalysts, ChemSusChem. 1 (2008) 75–78. doi:10.1002/cssc.200700033.
- [20] O. Casanova, S. Iborra, A. Corma, Biomass into chemicals: One pot-base free oxidative esterification of 5-hydroxymethyl-2-furfural into 2,5-dimethylfuroate with gold on nanoparticulated ceria, J. Catal. 265 (2009) 109–116. doi:10.1016/j.jcat.2009.04.019.
- [21] M. Kim, Y. Su, T. Aoshima, A. Fukuoka, E.J.M. Hensen, K. Nakajima, Effective Strategy for High-Yield Furan Dicarboxylate Production for Biobased Polyester Applications, ACS Catal. 9 (2019) 4277–4285. doi:10.1021/acscatal.9b00450.
- [22] J. Du, H. Fang, H. Qu, J. Zhang, X. Duan, Y. Yuan, Fabrication of supported Au-CuO nanohybrids by reduction-oxidation strategy for efficient oxidative esterification of 5hydroxymethyl-2-furfural into dimethyl furan-2,5-dicarboxylate, Appl. Catal. A Gen. 567 (2018) 80–89. doi:10.1016/j.apcata.2018.09.004.
- [23] D.K. Mishra, J.K. Cho, Y. Yi, H.J. Lee, Y.J. Kim, Hydroxyapatite supported gold nanocatalyst for base-free oxidative esterification of 5-hydroxymethyl-2-furfural to 2,5-furan dimethylcarboxylate with air as oxidant, J. Ind. Eng. Chem. 70 (2019) 338– 345. doi:10.1016/j.jiec.2018.10.034.
- [24] A. Buonerba, S. Impemba, A.D. Litta, C. Capacchione, S. Milione, A. Grassi, Aerobic Oxidation and Oxidative Esterification of 5-Hydroxymethylfurfural by Gold Nanoparticles Supported on Nanoporous Polymer Host Matrix, ChemSusChem. 11 (2018) 3139–3149. doi:10.1002/cssc.201801560.
- [25] A. Cho, S. Byun, J.H. Cho, B.M. Kim, AuPd-Fe 3 O 4 Nanoparticle-Catalyzed

Synthesis of Furan-2,5-dimethylcarboxylate from 5-Hydroxymethylfurfural under Mild Conditions, ChemSusChem. 12 (2019) 2310–2317. doi:10.1002/cssc.201900454.

- [26] F. Menegazzo, M. Signoretto, D. Marchese, F. Pinna, M. Manzoli, Structure–activity relationships of Au/ZrO2 catalysts for 5-hydroxymethylfurfural oxidative esterification: Effects of zirconia sulphation on gold dispersion, position and shape, J. Catal. 326 (2015) 1–8. doi:10.1016/j.jcat.2015.03.006.
- [27] J. Deng, H.-J. Song, M.-S. Cui, Y.-P. Du, Y. Fu, Aerobic Oxidation of Hydroxymethylfurfural and Furfural by Using Heterogeneous Co x O y -N@C Catalysts, ChemSusChem. 7 (2014) 3334–3340. doi:10.1002/cssc.201402843.
- [28] Y. Sun, H. Ma, X. Jia, J. Ma, Y. Luo, J. Gao, et al., A High-Performance Base-Metal Approach for the Oxidative Esterification of 5-Hydroxymethylfurfural, ChemCatChem. 8 (2016) 2907–2911. doi:10.1002/cctc.201600484.
- [29] K. Sun, S. Chen, Z. Li, G. Lu, C. Cai, Synthesis of a ZIF-derived hollow yolk-shell Co@CN catalyst for the oxidative esterification of 5-hydroxymethylfurfural, Green Chem. 21 (2019) 1602–1608. doi:10.1039/C8GC03868F.
- [30] H. Zhou, S. Hong, H. Zhang, Y. Chen, H. Xu, X. Wang, et al., Toward biomass-based single-atom catalysts and plastics: Highly active single-atom Co on N-doped carbon for oxidative esterification of primary alcohols, Appl. Catal. B Environ. 256 (2019) 117767. doi:10.1016/j.apcatb.2019.117767.
- [31] A. Salazar, P. Hünemörder, J. Rabeah, A. Quade, R. V. Jagadeesh, E. Mejia, Synergetic Bimetallic Oxidative Esterification of 5-Hydroxymethylfurfural under Mild Conditions, ACS Sustain. Chem. Eng. (2019) acssuschemeng.9b00914. doi:10.1021/acssuschemeng.9b00914.
- [32] K.S. Kozlov, L. V. Romashov, V.P. Ananikov, A tunable precious metal-free system for selective oxidative esterification of biobased 5-(hydroxymethyl)furfural, Green Chem. 21 (2019) 3464–3468. doi:10.1039/C9GC00840C.
- [33] F. Li, X.-L. Li, C. Li, J. Shi, Y. Fu, Aerobic oxidative esterification of 5hydroxymethylfurfural to dimethyl furan-2,5-dicarboxylate by using homogeneous and heterogeneous PdCoBi/C catalysts under atmospheric oxygen, Green Chem. 20 (2018) 3050–3058. doi:10.1039/C8GC01393D.

- [34] Handbook of Compressed Gases, Springer US, Boston, MA, 1999. doi:10.1007/978-1-4615-5285-7.
- [35] Z. Zhang, Y. Zhu, H. Asakura, B. Zhang, J. Zhang, M. Zhou, et al., Thermally stable single atom Pt/m-Al2O3 for selective hydrogenation and CO oxidation, Nat. Commun. 8 (2017) 16100. doi:10.1038/ncomms16100.
- [36] S.M. Morris, P.F. Fulvio, M. Jaroniec, Ordered Mesoporous Alumina-Supported Metal Oxides, J. Am. Chem. Soc. 130 (2008) 15210–15216. doi:10.1021/ja806429q.
- [37] Q. Yuan, A.-X. Yin, C. Luo, L.-D. Sun, Y.-W. Zhang, W.-T. Duan, et al., Facile Synthesis for Ordered Mesoporous γ-Aluminas with High Thermal Stability, J. Am. Chem. Soc. 130 (2008) 3465–3472. doi:10.1021/ja0764308.
- [38] W. Cai, J. Yu, C. Anand, A. Vinu, M. Jaroniec, Facile Synthesis of Ordered Mesoporous Alumina and Alumina-Supported Metal Oxides with Tailored Adsorption and Framework Properties, Chem. Mater. 23 (2011) 1147–1157. doi:10.1021/cm102512v.
- [39] L.-B. Sun, W.-H. Tian, X.-Q. Liu, Magnesia-Incorporated Mesoporous Alumina with Crystalline Frameworks: A Solid Strong Base Derived from Direct Synthesis, J. Phys. Chem. C. 113 (2009) 19172–19178. doi:10.1021/jp907224f.
- [40] T. Ghosh, P. Chandra, A. Mohammad, S.M. Mobin, Benign approach for methylesterification of oxygenated organic compounds using TBHP as methylating and oxidizing agent, Appl. Catal. B Environ. 226 (2018) 278–288. doi:10.1016/j.apcatb.2017.12.056.
- [41] S. Wang, Z. Zhang, B. Liu, Catalytic Conversion of Fructose and 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid over a Recyclable Fe 3 O 4 – CoO x Magnetite Nanocatalyst, ACS Sustain. Chem. Eng. 3 (2015) 406–412. doi:10.1021/sc500702q.
- [42] F.A. Kucherov, L. V. Romashov, K.I. Galkin, V.P. Ananikov, Chemical Transformations of Biomass-Derived C6-Furanic Platform Chemicals for Sustainable Energy Research, Materials Science, and Synthetic Building Blocks, ACS Sustain. Chem. Eng. 6 (2018) 8064–8092. doi:10.1021/acssuschemeng.8b00971.
- [43] Y. Zhu, H. Yan, L. Lu, D. Liu, G. Rong, J. Mao, Copper-Catalyzed Methyl

Esterification Reactions via C–C Bond Cleavage, J. Org. Chem. 78 (2013) 9898–9905. doi:10.1021/jo4016387.

- [44] P.S. Samudrala, A. V. Nakhate, S.S.R. Gupta, K.B. Rasal, G.P. Deshmukh, C.R. Gadipelly, et al., Oxidative coupling of carboxylic acids or benzaldehydes with DMF using hydrotalicite-derived oxide catalysts, Appl. Catal. B Environ. (2017). doi:10.1016/j.apcatb.2017.12.058.
- [45] S.S.R. Gupta, A.V. Nakhate, K.B. Rasal, G.P. Deshmukh, L.K. Mannepalli, Oxidative amidation of benzaldehydes and benzylamines with: N -substituted formamides over a Co/Al hydrotalcite-derived catalyst, New J. Chem. 41 (2017). doi:10.1039/c7nj03123h.
- [46] S.S.R. Gupta, A.V. Nakhate, G.P. Deshmukh, S. Periasamy, P.S. Samudrala, S.K. Bhargava, et al., Direct Synthesis of Amides from Oxidative Coupling of Benzyl Alcohols or Benzylamines with N-Substituted Formamides Using a Cu-Fe-Based Heterogeneous Catalyst, ChemistrySelect. 3 (2018). doi:10.1002/slct.201801297.
- [47] P. Jiang, D. Prendergast, F. Borondics, S. Porsgaard, L. Giovanetti, E. Pach, et al., Experimental and theoretical investigation of the electronic structure of Cu 2 O and CuO thin films on Cu(110) using x-ray photoelectron and absorption spectroscopy, J. Chem. Phys. 138 (2013) 024704. doi:10.1063/1.4773583.
- [48] D.S. Kozak, R.A. Sergiienko, E. Shibata, A. Iizuka, T. Nakamura, Non-electrolytic synthesis of copper oxide/carbon nanocomposite by surface plasma in superdehydrated ethanol, Sci. Rep. 6 (2016) 21178. doi:10.1038/srep21178.
- [49] S. Thirumalairajan, V.R. Mastelaro, C.A. Escanhoela, In-Depth Understanding of the Relation between CuAlO 2 Particle Size and Morphology for Ozone Gas Sensor Detection at a Nanoscale Level, ACS Appl. Mater. Interfaces. 6 (2014) 21739–21749. doi:10.1021/am507158z.
- [50] H. Maruoka, T. Kimura, The rational synthesis of aerosol-assisted alumina powders having uniform mesopores and highly accessible surfaces, New J. Chem. 43 (2019) 7269–7274. doi:10.1039/C9NJ01319A.
- [51] A. Mitra, D. Jana, G. De, Synthesis of Equimolar Pd–Ru Alloy Nanoparticles Incorporated Mesoporous Alumina Films: A High Performance Reusable Film

Catalyst, Ind. Eng. Chem. Res. 52 (2013) 15817–15823. doi:10.1021/ie401854t.

- [52] D. Waffel, B. Alkan, Q. Fu, Y. Chen, S. Schmidt, C. Schulz, et al., Towards Mechanistic Understanding of Liquid-Phase Cinnamyl Alcohol Oxidation with tert -Butyl Hydroperoxide over Noble-Metal-Free LaCo 1– x Fe x O 3 Perovskites, Chempluschem. 84 (2019) 1155–1163. doi:10.1002/cplu.201900429.
- [53] W.-S. Lee, Z. Wang, W. Zheng, D.G. Vlachos, A. Bhan, Vapor phase hydrodeoxygenation of furfural to 2-methylfuran on molybdenum carbide catalysts, Catal. Sci. Technol. 4 (2014) 2340. doi:10.1039/c4cy00286e.
- [54] C.-J. Chen, J.W. Harris, A. Bhan, Kinetics of Ethylene Epoxidation on a Promoted Ag/α-Al 2 O 3 Catalyst-The Effects of Product and Chloride Co-Feeds on Rates and Selectivity, Chem. - A Eur. J. 24 (2018) 12405–12415. doi:10.1002/chem.201801356.
- [55] K.C. Badgujar, B.M. Bhanage, Enhanced Biocatalytic Activity of Lipase Immobilized on Biodegradable Copolymer of Chitosan and Polyvinyl Alcohol Support for Synthesis of Propionate Ester: Kinetic Approach, Ind. Eng. Chem. Res. 53 (2014) 18806–18815. doi:10.1021/ie501304e.
- [56] N. Khatun, S.K. Santra, A. Banerjee, B.K. Patel, Nano CuO Catalyzed Cross Dehydrogenative Coupling (CDC) of Aldehydes to Anhydrides, European J. Org. Chem. 2015 (2015) 1309–1313. doi:10.1002/ejoc.201403508.

Graphical Abstract:



Highlights:

- Mesoporous alumina nanospheres-embedded with CuO nanoparticles.
- A new approach for synthesis of FDMC from HMF using TBHP.
- TBHP acts as an oxidizing and methylating reagent.
- Oxidative methyl-esterification involving SP³ C-H bond functionalization.

Declaration of interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.