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Title: Organic Radical Functionalized SBA-15 as a Heterogeneous Catalyst for Facile Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran



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#### 21 Research Highlights

22 23

24 1. TEMPO-SBA-15 was prepared via silanization of organosilane-functionalized TEMPO.

25 2. Highly selective 5-HMF oxidation to 2,5-DFF over heterogeneous TEMPO-SBA-15.

26 3. TEMPO-SBA-15 exhibited excellent recyclability without loss in catalytic activity.

27

#### 28 Abstract

29 Organic radical functionalized mesoporous silicawas prepared by theimmobilization of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) on ordered mesoporous silica (SBA-15)and 30 31 applied as a heterogeneous catalyst (TEMPO-SBA-15) for the synthesis of 2,5-diformylfuran 32 (2,5-DFF)from 5-hydroxymethylfurfural (5-HMF). A73% 2,5-DFF yield was obtained from 5-HMF oxidation under mild reaction conditions in ethyl acetate with the addition of 33 [Bis(acetoxy)iodo]benzene (BAIB) and acetic acidas co-oxidants in an oxygen-rich 34 35 environment. The presence of BAIB and oxygen facilitated the in-situ regeneration of TEMPO 36 (the hydroxylamine form) whereas acetic acid additionaided in the initial formation of 37 oxoammonium form of TEMPO, which was responsible for facile5-HMF oxidation. All reaction components were found critical in maximizing the 2,5-DFF yield. The pore size distribution and 38 39 architecture of SBA-15 played essential roles for the diffusive transport of reactants and products 40 and resulted in improved reaction selectivity. Aside from these advantages, TEMPO-SBA-41 15catalyst was easily separated and re-usedseveral times with negligibleloss in its catalytic 42 activity. The prepared heterogeneous TEMPO-SBA-15 is an efficient catalyst that offers a 43 sustainable route for 2,5-DFF production.

44

- 45 **Keywords:** 2,5-Diformylfuran, 5-Hydroxymethylfurfural, 4-Hydroxy-2,2,6,6-
- 46 Tetramethylpiperidine-1-Oxyl (TEMPO), Oxidation, Immobilization, Mesoporous Silica

#### **1. Introduction**

48	Furan derivatives are value-added chemicals that can be derived from biomass feedstocks.
49	Particularly, 2,5-diformylfuran (2,5-DFF) is a commercially important precursor for the
50	synthesis of various pharmaceuticals, fungicides, ligands of various poly-Schiff bases,
51	polymers, and cross-linking agents[1-4]. 2,5-DFF is typically synthesized by selective oxidation
52	of 5-hydroxymethylfurfural (5-HMF)[5], a dehydration product of biomass-derived hexoses [5-
53	7].
54	Many reports have been accounted for the oxidation of 5-HMF using conventional, metal
55	containinghomogeneous catalysts like Pb(OAc) <sub>4</sub> -pyridine, pyridiniumchlorochromate, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> -
56	DMSO,Co/Mn acetates,V <sub>2</sub> O <sub>5</sub> , andCu(NO <sub>3</sub> ) <sub>2</sub> /VOSO <sub>4</sub> [8-13]. Although adequate 2,5-DFF yields
57	have been reported, most of thesecatalysts are laden with toxic metals. Moreover, many of the
58	reported DFF syntheses are conducted undersevere reaction conditions ( $\geq 80^{\circ}$ C and $\geq 10$ bar) with
59	several hours of reaction time. This increases the cost of production set-up and in few cases
60	leadsto side products formation by over-oxidation, decarbonylation, and cross-polymerization of 5-
61	HMF [13].Parallel to the need of cheap, easily handled and less toxic catalytic system, a re-
62	usable oxidation catalystis also highly desirable to ease environmental and economicburdens.
63	Several heterogeneous catalytic systems likewise have been employed for the oxidation of 5-
64	HMF such asvanadyl phosphate[14], vanadyl acetylacetonate immobilized on poly(4-
65	vinylpyridine) polymer[15], Ru supported over hydrotalcite [16], porous manganese oxide [17],
66	zeolite-supported vanadium pentoxide[18] and silver impregnated manganese oxide [19].
67	Despite the remarkable developments in2,5-DFF synthesis with fair yield, nearly all these
68	systems are based on transition metal catalystsand high boiling point organic solvents which
69	hinder the facile product separation[14-19]. Moreover, the active sites in these catalysts were

transition metals, requiring higher activation energy to perform and thus these systems were
applied at higher reaction temperature.

72 In context of a metal-free catalyst, nitroxyl based radicals are being explored due to 73 their efficiency inoxidizing various types of alcohols[20-22]. In addition, these have shown less 74 toxicity and remarkable reversible redox behavior[21-24]. One of these stable organic radicals, 75 2.2.6,6-tetramethylpiperidin-1-oxyl (TEMPO) and its derivatives have been used for 5-HMF 76 oxidation in the presence of various co-oxidants[25-27]. Particularly, an earlier work 77 successfully produced 2,5-DFF under mild reaction conditions viahomogeneous TEMPO-78 catalyzed 5-HMF oxidation with co-oxidantsBis(acetoxy)iodo]benzene (BAIB) and acetic acid 79 (AcOH) [27]. Despite the satisfactory formation of 2,5-DFF, this mild homogeneous reaction 80 could not address the catalyst recyclability and high reaction selectivity due to formation of side 81 product. Thus, the TEMPO moiety immobilized on an appropriate solid supportcan provide 82 aneffective, sustainable, and metal free catalytic system. Several supported TEMPO catalyst 83 systems like on silica and ferrite surface[28], on carbon nanotubes [29] and mesoporous silica 84 [30] havebeen reported for the oxidation of alcohols. However, these catalyst systems were 85 comprised of either transition metals[28] or toxic and hazardous reagents like tert-butyl nitrite 86 (TBN)[30].Recently oxidation of 5-HMF by TEMPO supported on silica coated iron oxide nanoparticles was demonstrated [31]. But the use ofnocuous TBN and high boiling point solvent 87 toluene with hours long reaction time makes this methodology inappropriate from the viewpoint 88 89 of green and sustainable chemistry. Therefore, our continuous interest is in developing a less 90 toxic reaction system for 5-HMF oxidation in low boiling point solvents [27]. Among various support materials for catalysts, the suitability of mesoporous silica like SBA-15 has been 91 92 demonstrated in numerous studies, as the silanol groups on their surfaces are easy to

93	functionalize[32]. The stability of TEMPO can be assured by its covalent immobilization on the
94	support throughorganosilane linkers. The unique structural properties of mesoporous SBA-15 like
95	a high specific surface area due to its well-ordered porous structure, large pore volumes, and
96	narrow pore size distribution (Fig. 1B, inset), would allow a high degree of TEMPO
97	functionalization leading towards anefficient heterogeneous TEMPO catalyst.
98	Thus, herein, TEMPO-functionalized-SBA-15 (TEMPO-SBA-15)catalyst was prepared
99	through silanization of TEMPO radicals functionalized with an organosilane linker.
100	Morphological and structural properties of bare SBA-15 and its functionalized form (TEMPO-
101	SBA-15) were examined by X-ray diffraction (XRD), N2 adsorption-desorption,
102	thermogravimetric analysis (TGA), FT-IR, and scanning electron microscopy (SEM).
103	Comparisons in their characterization results were performed to confirm the successful
104	immobilization of TEMPO on SBA-15. The prepared TEMPO-SBA-15was applied as
105	heterogeneous catalyst for the oxidation of 5-HMF to 2,5-DFF under mild reaction conditions.
106	For maximum 2,5-DFF yields, effects of co-oxidantswere also determined. Lastly, the long-term
107	use of TEMPO-SBA-15 was also inspected through a series of repeated 5-HMF oxidation
108	reactions using recycled catalyst.

#### 110 2. Experimental

111 2.1.Materials

4-hydroxy-TEMPO (97%), BAIB (98%), organosilane linker (3-chloropropyl)-112 triethoxysilane (CPTES) (95%), Poly(ethyleneglycol)-block-poly(propyleneglycol)-block-113 poly(ethyleneglycol) (Pluronic<sup>®</sup>P123), silica (fumed, surface area 390 m<sup>2</sup>/g) and dry toluene 114 (99.8%) were obtained from Sigma-Aldrich (South Korea). 5-hydroxymethylfufural (5-115 HMF)(98%), tetraethylorthosilicate (TEOS) (98%), sodium hydride (NaH) (60% dispersion in 116 117 oil), and dry tetrahydrofuran (THF) (99.8%) were purchased from Acros Organics while 2,5-118 diformylfuran (2,5-DFF) (>98%) was procured from Tokyo Chemicals (Japan). Hydrochloric acid (HCl) (35-37%) was bought from Showa Chemicals whereas other solvents including 119 diethyl ether (99%) and ethyl acetate (99.8%) were obtained from Dae Jung Chemicals (South 120 121 Korea). Sodium sulfate (99%) was purchased from Junsei Chemicals. All chemicals were of reagent grade or higher, and were directly used without further purification. 122 123 124 2.2. Preparation of catalyst 125 2.2.1. Preparation of SBA-15

SBA-15 was synthesizedaccording to a modified method reported elsewhere using triblock copolymer Pluronic<sup>®</sup>P123 (Average Mol. Weight = 5800) as a structure directing
agent[33]. A 10 g sample of P123 was initially dissolved ina mixture of 325 mL of deionized
(DI) water and 60 mL of HCl (35.0-37.0 %) followed by TEOS(20.6 g) addition, with 800
rpmagitation, at 40 °C for 2h. The cloudy dispersion was then statically aged at 40 °C for 24 h and
then at 80 °C for another 24 h. The solid product was filtered off; repeatedlywashed with hot (80
°C) deionized (DI)water for the removal of residual reactants. After air-drying at room

133

temperature for 4 days, the dried powder was calcinedat 500°C (in air,5 h)with2.5 °C min<sup>-1</sup>heating rate from room temperature.

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136 2.2.2. Synthesis of 3-(4-oxy-TEMPO)propyl-triethoxysilane

The reactions were carried out in nitrogen  $(N_2)$  atmosphere. Sodium hydride (0.2758 g, 6.9 137 138 mmol) was suspended in dry THF (20 mL) cooledin an ice-bath. A separately prepared 4hydroxy-TEMPO (1.0 g, 5.8 mmol)solution in 5 mLdry THF was added dropwise in the 139 140 coldNaHslurry. The mixture was brought to room temperature (RT) and stirred to facilitate the 141 reaction. Aftercomplete gas evolution, the mixture was re-cooled at 0°C and CPTES (1.6615 g, 6.9 mmol) was addeddropwise. The reaction was continued at room temperature for another 48 h 142 143 (Scheme 1). The crude product was retrieved by solvent evaporation under reduced pressure. To precipitate the impurities, the oily product was dissolved in diethyl ether. The filtered diethyl 144 145 ether was dried over sodium sulfateand then re-filtered. The solvent wasremovedina 146 rotaryevaporator to obtain the pure dark oily orange 3-(4-oxy-TEMPO)propyl-147 triethoxysilane(denoted as PTES-TEMPO). 148 149 2.2.3. Preparation of TEMPO-SBA-15 catalyst 150 Calcined SBA-15 (2.0 g) was vacuum-dried for 1 h at 90°C and then suspended in 90 mLdry toluene with vigorous stirring under N2atmosphere.A solution of PTES-TEMPO (1.53 151 152 mmol) in toluene was then added dropwise in the SBA-15 suspension. The mixture was refluxed 153 at 110 °Cfor20 h with continuous stirring (Scheme 1). After which, the reaction was terminated 154 and cooled to room temperature. The product, denoted as TEMPO-SBA-15, was filtered, washed three times with toluene, and then dried in air at room temperature. 155

156

#### 157 2.3. Catalyst characterization

158	Powder low angle X-ray diffraction (XRD) patterns of SBA-15 and TEMPO-SBA-15
159	samples were acquired usingPANalyticalEMPYREAN SWAX diffractometer(40 kV,25 mA)
160	with Ni-filtered Cu-K $\alpha$ radiation ( $\lambda = 0.15406$ nm)source scanned at 20 angles from 0.3° to
161	10°. The FT-IRspectra of the samples were recorded by a Shimadzu IRPrestige-21
162	spectrophotometer equipped with DLaTGS detector using standard KBr disc method (1 wt.%
163	sample) between wavenumbers 400 and 4000 cm <sup>-1</sup> at room temperature. Thermogravimetric
164	analysis (TGA) was carried out ina SCINCO TGA (N-1000)from 35°Cto 1000°Cwith a ramping
165	rate of 5 $^{\circ}$ C min <sup>-1</sup> , supplied with 50 mLmin <sup>-1</sup> ofN <sub>2</sub> . N <sub>2</sub> adsorption-desorption isothermswere
166	obtained using a Micromeritics ASAP-2020 surface area analyzer at 195.8 °C. The sampleswere
167	outgassed(in vacuum)at 100 $^{\circ}$ C for 24 h prior to the adsorption experiments. The carbon and
168	nitrogen contents of the samples were determined by elementanalysis using Vario EL cube
169	CHNS analyzer (Elementar Corporation, Germany). The morphology of the samples was
170	observed under Hitachi S-3500N Scanning Electron Microscope (SEM) and JEOL JSM-7600F
171	Field Emission Scanning Electron Microscope(FE-SEM).
172	

173 2.4. Catalyst activity

174 2.4.1. Typical procedure for the synthesis of 2,5-DFF from 5-HMF

All experiments were carried out in two-necked round bottom flasks initially purged with
O<sub>2</sub> and then fastened with an O<sub>2</sub>-filled balloon (1 atm). The flasks were placed in a temperaturecontrolled oil bath with magnetic stirring. Typically, appropriate amounts of the reactants 5HMF, TEMPO-SBA-15, BAIB, and acetic acid (if used) were allowed to reactin ethyl
acetatesolvent (10-15 mL). The reaction mixture was magnetically stirred fora certain reaction

180	time, at a controlled temperature. After each run, the reaction mixture was filtered to separate the
181	solid catalyst. The filtrate was dried under reduced pressure, dissolved in deionized(DI) water and
182	then analyzedinhigh pressure liquid chromatography (HPLC).

183

#### 184 2.5. Product analysis and quantification

Prior to HPLC analysis, samples were filtered through a syringe filter (0.2 µm Nylon). The 185 186 Waters HPLCwas equipped with Waters 2414 refractive index (RI) detector maintained at 40 °C and BioradAminex HPX-87H ion-exclusion column (300×7.8 mm) kept at 60°C.A 5 mM H<sub>2</sub>SO<sub>4</sub> 187 mobile phase was delivered at a flow rate of 0.6 mLmin<sup>-1</sup>. The HPLC retention times for reaction 188 components were observed as 14.7 min for AcOH, 14.7 min for 2,5-FDCA, 28.0 min for 5-HMF 189 190 and 32.7 min for 2,5-DFF. The concentrations of 2,5-DFF (i.e. [DFF]) and 5-HMF (i.e. [HMF]) 191 weredetermined against calibration curves of standard samples. The amount of produced 2,5-DFF 192 (W<sub>DFF</sub>)and corresponding reaction yields were calculated according to equations (1) and (2). 2,5-193 DFF selectivity was calculated according to equation S1 (Eq. S1). V is the sample volume, 194 MWis the molecular weight of 5-HMF(126.11 g/mole) or 2,5-DFF (124.09 g/mole) while W<sub>RM</sub>, W<sub>AL</sub>, and W<sub>HMF</sub> are the masses of the entire reaction mixture, aliquot for analysis and supplied 195 196 HMF, respectively. All reported data are average values of triplicate reaction runs.

197 
$$W_{DFF}(mg) = \frac{[DFF] \times V(mL) \times W_{RM}(mg)}{W_{AL}(mg)}$$
(1)

198 DFF yield(%) = 
$$\left(\frac{W_{DFF}}{W_{HMF}}\right) \left(\frac{MW_{HMF}}{MW_{DFF}}\right) \times 100$$
 (2)

199

200 2.6. Recycling of the catalyst

- After oxidation reaction, TEMPO-SBA-15was retrieved from the reaction mixture via filtration. The used catalystwaswashed with the reaction solvent to remove traces of reaction debris. Then the catalyst wasair-dried at room temperatureprior toreuse.
- 204

#### 205 3. Results and discussion

206 *3.1. Synthesisof catalyst* 

The mesoporous silica support SBA-15 was prepared throughTEOShydrolysis in the presence of the triblock co-polymer P123 (EO20PO70EO20) as the surfactant [33]. Meanwhile in a separate reaction, TEMPO was etherified with CPTES to form PTES-TEMPO. To complete the synthesis of TEMPO-SBA-15, PTES-TEMPO was used to silanize the support, in which covalent Si-O-Si bonds were formed by the reaction of silanol groups on SBA-15 with the ethoxy groups of PTES-TEMPO (Scheme 1).

214

215 *3.2. Characterization of catalyst* 

Textural properties of SBA-15 were analyzed by X-ray diffraction (XRD) pattern and N<sub>2</sub> 216 217 adsorption-desorption isotherms (Fig. 1). The bare support material (SBA-15) exhibited three well-resolved diffraction peaks at  $2\theta = 0.9^\circ$ , 1.5°, and 1.7° in the XRD pattern (Fig. 1A), which 218 219 correspond to reflection planes of(100), (110), and (200), respectively. These peaks indicate a 220 significant degree of long-range order and a well-formed two-dimensional (2-D) hexagonal 221 meso-structure of SBA-15 [34]. Afterimmobilization, the resulting TEMPO-SBA-15 exhibited all 222 of the prominent diffraction peaks at  $2\theta = 0.9^\circ$ ,  $1.5^\circ$ , and  $1.7^\circ$  (Fig. 1A) similar to SBA-15. This implies that the 2-D hexagonal meso-structure of SBA-15 does not deteriorate after the 223

immobilization of PTES-TEMPO. Thus,preparedTEMPO-SBA-15 demonstrated analogous
 reflection planes to its support material,suggesting that the periodic mesoporousstructure was
 retained [35].Furthermore, the decrease in intensity of diffraction peak corresponding to
 reflection plane of (100)confirms the successfulimmobilization of PTES-TEMPO to SBA-15
 surface.

#### 229 <<Insert Figure 1>>

230

231 The N<sub>2</sub>adsorption-desorption isotherms obtained from bare SBA-15 exhibits the typical 232 type IV isotherm pattern having sharp capillary condensation with H1 hysteresis loop at higher 233 relative pressure (Fig. 1B). This pertains to the 2-D hexagonal symmetry of a mesoporous 234 material [36-37]. TEMPO-SBA-15 showed similar adsorption-desorption isotherm curves and 235 hysteresis loop with that of bare SBA-15.In addition, both SBA-15 and TEMPO-SBA-15 showed narrow pore size distributions(Fig. 1B, inset), indicating structural consistency of the catalyst 236 237 before and after immobilization. The bare SBA-15 showed a very high BET surface area of 883  $m^2/g$  (Table 1)and large total pore volume of 1.24 cm<sup>3</sup>/g (Table 1). The gradual decrease in BET 238 239 surface area and total pore volume upon immobilization of PTES-TEMPO confirms its 240 successful immobilization to the pore channels of SBA-15. Nonetheless, incorporation of 241 TEMPO on SBA-15 did not reduce the average pore size of the supportdue to simultaneous 242 functionalization in micro- and meso-pores which counterbalances the changes in pore size. 243 Thus, kept intact the mesoporous structure of the support material even after functionalization. 244 <<Insert Table 1>>

246	The TG analyses of the heterogeneous catalyst and SBA-15 were done to assess the
247	functionalization of TEMPO on SBA-15 and to estimate the loading of TEMPO radical (Fig. 2).
248	The first weight losses(< 2%) in bare SBA-15 and TEMPO-SBA-15 were observed below100
249	°C, due to the evaporation of surface-adsorbed moisture. Further weight loss up to 8.58% was
250	observed in TEMPO-SBA-15 from 110 to 235 °C with a sharp decrease around 156 °C, due to the
251	degradation of the3-(4-oxy-TEMPO)propyl chain on the SBA-15 surface[38]. This result
252	indicated the loss of 0.4 mmol of 3-(4-oxy-TEMPO)propyl chainper gram of the catalyst
253	material, from which, 0.3 mmol/g loading of TEMPO was estimated. Without the functional groups
254	on the bare support, such weight loss was absent in SBA-15 within the same temperature range.
255	Only 3.21% total weight loss was observed for bare SBA-15, mainly due to the condensation of
256	surface silanolsthatformssiloxane groups and releaseof watermolecules at higher temperatures (>
257	600°C)[39]. For TEMPO-SBA-15, the significant weight loss of 16.68% between 235 and 1000
258	°C is associated to the breakdown of the unreactedethoxy groups of the organosilane and
259	partially to the silanol condensation. Elementalanalysis also determined the loading of TEMPO
260	as0.3 mmol/g of TEMPO-SBA-15 (Table 1) along with 15.7 C/N ratio, which strongly
261	corroborates the TGA result.
262	< <insert 2="" figure="">&gt;</insert>

263

The successful immobilization of the TEMPOon SBA-15 was furtherconfirmed via the FT-IR spectra(Fig. 3). The IR spectrum of PTES-TEMPO (Fig. 3a) features characteristic absorption bands at 1373 and 1165 cm<sup>-1</sup> for the C–N and C–O stretching vibrations, respectively[29]. Additionally, the spectrum presents peaks in the range of 2995-2870 cm<sup>-1</sup> associated with C–H stretching vibrations. Characteristic bands of the silica frameworkswere observed both in bare

269	SBA-15 and TEMPO-SBA-15(Fig. 3b and 3c); at 3600-3200 cm <sup>-1</sup> for stretching of H-bonded
270	silanol groups, at 1085 and 806 cm <sup>-1</sup> for asymmetric and symmetric Si–O–Si stretching and at
271	964 cm <sup>-1</sup> for Si–O stretching[40]. The absorption peak at 1629 cm <sup>-1</sup> is associated with the bending
272	vibration of the adsorbed water[41]. In the heterogeneous catalyst, aC-N stretching vibration was
273	present (Fig. 3c) at 1377 cm <sup>-1</sup> , which asserts the presence of TEMPO moiety. The wide band of
274	Si-O-Si stretching(albeit it overlapped the C-O stretching) concomitant with the decrease in the
275	peak intensities of (1)O-H stretching and bending (3600-3200 cm <sup>-1</sup> and 1629 cm <sup>-1</sup> , respectively)
276	and (2)Si–O stretching (964 cm <sup>-1</sup> )are all indications of asuccessful silanization of PTES-TEMPO
277	on SBA-15.
278	< <insert 3="" figure="">&gt;</insert>
279	
280	The morphologies of bare SBA-15 and TEMPO-SBA-15were examined by SEM asshown
281	in Fig. 4. The mesoporous SBA-15 features a long-range, self-organized morphology and
282	uniform-sized particles which were preserved after PTES-TEMPO immobilization (Fig. 4a-4b
283	and 4c-4d). Both samples were composed of rod like, bean-shaped particles of approximately
284	800-1000 nm in length. The FE-SEM images of SBA-15 and TEMPO-SBA-15 (Fig. 4c and 4d,
285	respectively) (100 nm scale) also showed well-ordered arrays of mesoporous channels [42] and
286	intact morphology of SBA-15 after immobilization of TEMPO.
287	< <insert 4="" figure="">&gt;</insert>
288	
289	3.3.Homogeneous TEMPO-catalyzed 5-HMF oxidation
290	In an earlier work, homogeneous TEMPO-mediated oxidation of 5-HMF in ethyl acetate
291	afforded 2,5-DFFthrough the 'oxoammonium' mechanism [18]. Concomitant with 5-HMF

292	oxidation into 2,5-DFF is the in-situ reduction of the oxoammonium form of TEMPO into
293	hydroxylamine form. As a regenerant, co-oxidant BAIBis added to oxidize hydroxylamine back
294	to TEMPO radical form and it also produces acetic acid for the initial dismutation of TEMPO
295	radical to its catalytically active oxoammoinum form [27]. Thus, 2,5-DFF production in catalytic
296	TEMPO dosage was possible in the presence of BAIB. For enhanced 2,5-DFF yield, initial
297	investigationwas performed in a homogeneous system of 5-HMF(0.5 mmol) and BAIB(0.75
298	mmol)with varied TEMPO dosages. Production of 2,5-DFF (Fig. 5) increased with the catalyst
299	dosage and the highest values were obtained at over 0.075 mmolof TEMPO. The high conversion
300	of 5-HMF at lower TEMPO dosages is the result of ligand exchange phenomenon with BAIB
301	(Fig. S4). Due to inadequate TEMPO, yield of 2,5-DFF remained less. Nonetheless, only
302	moderate 2,5-DFF yield (57.4% maximum at 0.1 mmol TEMPO dosage)was achieved in
303	homogeneous TEMPO-catalyzed system. Meanwhile, homogeneous TEMPO-catalyzed
304	reactions in oxygen-richcondition afforded much higher 2,5-DFF yields and selectivities at entire
305	range of TEMPO dosages than the system in the absence of oxygen (Fig. 5 and Fig.
306	S3).Molecular oxygen (O <sub>2</sub> ) functions similarly as BAIB by oxidizing the hydroxylamine form of
307	TEMPO catalyst to its radical formas demonstrated by Sheldon et al [43](Fig. S4).Furthermore,
308	the effect of oxygen and phenomenon of ligand exchange involving 5-HMF and BAIB were
309	validated by only 9.8% 5-HMF conversion and 5.2 % 2,5-DFF yield by the BAIB-free system
310	with oxygen supply (Fig. 7). Additionally, despite the high 2,5-DFF yield in O <sub>2</sub> -rich
311	homogeneous system, a minor amount of 2,5-furandicarboxylic acid (2,5-FDCA), an over-
312	oxidation product of 5-HMF[19], was also observed (Fig. S1).
313	< <insert 5="" figure="">&gt;</insert>

315 3.4.5-HMF oxidation in heterogeneous TEMPO-SBA-15 catalyst

316 With enhanced2,5 DFF productions in O<sub>2</sub>-rich TEMPO-catalyzed homogeneous system, 317 heterogeneous reactions were likewise performedover TEMPO-SBA-15 catalyst(Scheme 2). 318 Highest yield of 52% 2,5-DFF was achieved(Fig. 5) with heterogeneous TEMPO(at 0.075 mmol 319 of TEMPO) (Fig. S4). Unlike homogeneous system, no 2,5-FDCA was detected in 320 heterogeneous TEMPO-SBA-15 catalyst system(Fig. S2) resulting in enhanced reaction 321 selectivity by controlled conversion of 5-HMF to dialdehyde (Fig. S3). In the context of slightly 322 declined 2,5-DFF production and no 2,5-FDCA formation by TEMPO-SBA-15 (i.e. compared to 323 homogeneous TEMPO-catalyzed reaction), immobilization of TEMPO moieties into the porous 324 channels of SBA-15 played a crucial role. These results suggest the critical role of SBA-15 as 325 TEMPO support. The highly ordered and uniform porous structure of SBA-15 leads to form 326 uniform active sites of the TEMPO catalyst and also controls the spatial effects. These factors are 327 crucial for the diffusive transport of reactants to and products from active sites and, thereby 328 controlling the over-oxidation of product. 329 <<Insert Scheme 2>> 330 331 3.5.Influence of reaction temperature on TEMPO-SBA-15performance 332 The effect of reaction temperature was also investigated to attain better 2,5-DFF production. As the reaction componentshave reduced diffusive transport in heterogeneous 333 334 catalyst systems, heating the reaction could increase their kinetic mobility and improve their 335 contact frequency with active sites of catalyst. This effect became modestly observablewhen the temperature was slightly raised to  $40^{\circ}$ C as the maximum 2,5-DFF yield improved to 63% (Fig. 6) 336 from 52% (at room temperature) with complete 5-HMF conversion (Table S1) in 60 337

338	min.Additionally, oxidation of 5-HMF followed consecutive conversion into two intermediate
339	states; first by rapid ligand exchange with BAIB (Fig. S4 (a)) and then, reaction with
340	oxoammonium salt ( <sup>+</sup> N=O) form of TEMPO radical moiety (Fig S4 (b)). The formation of 2,5-
341	DFF occurred simultaneously with the reduction of oxoammonium salt to hydroxylamine form.
342	Therefore, the production of 2,5-DFF was lagging behind as compared to the quick consumption
343	of 5-HMF. As a consequence, high 5-HMF conversion with low 2,5-DFF selectivity was
344	observed in initial stages of the reaction at low reaction temperature. While the rate of 2,5-DFF
345	formation increased with reaction temperature, the declines in 2,5-DFF yields were observed
346	under prolonged reaction periods at all temperatures. This is attributable to eventual degradation
347	of 2,5-DFF to other undetected compounds [11]. Though the maximum 2,5-DFF formation
348	(57%) at 50 °C was quickly reached within 30-45 min, the reduced 2,5-DFF selectivity (Table S1)
349	might have been due to the additional occurrence of 5-HMF degradationat elevated temperatures
350	[44].
351	In a previous work, the uninhibited exposure of homogeneous TEMPO to the substrate
352	resulted in the higher propensity of the reaction components to degradation. Increase in
353	temperature beyond ambient condition was detrimental to selective 2,5-DFF production [27]. In
354	the current study, however, the insulating effect of SBA-15 on TEMPO was beneficial as it
355	rendered TEMPO-SBA-15to perform more efficiently in a wider temperature range. From the
356	results, reaction at 40°C for 60 min was most appropriate to enhance 2,5-DFF yield with minimal
357	degradation of reaction components.
358	< <insert 6="" figure="">&gt;</insert>

359

3.6.Acetic acid addition for enhanced TEMPO-SBA-15 performance 360

361 To initiate 5-HMF oxidation, the TEMPO radicals immobilized on SBA-15 must be 362 dismutated to its oxoammonium form in the presence of acetic acid (AcOH) [20] (Fig. S4). 363 Previous work identified the dual role of BAIB as TEMPO regenerant and as AcOH source (via ligand exchange), which was needed to 'jump-start' the oxidation reaction by formation of 364 oxoammonium. However, participation of BAIB in ligand exchange reaction with 5-HMF to 365 366 form AcOH was only minor, prompting the necessity of external AcOH addition [27]. Results 367 (Fig. 7 and Table S2) confirmed that addition of small amount of AcOH (0.05 mmol) remarkably 368 increased the 2,5-DFF yields of both homogeneous (78%) and heterogeneous TEMPO-catalyzed 369 systems (73%).

#### 370 <<Insert Figure 7>>

371

372 The small difference in 2,5-DFF yields between the homogeneous and heterogeneous 373 systems further affirms the benefit of using SBA-15 as the support material for TEMPO. The 374 catalyst support SBA-15 exerted minimum effect on the TEMPO due to uniform distribution of 375 active sites in its mesoporous structure. Moreover, the suitableorganosilane linker (CPTES) aids 376 to TEMPO moiety with its propyl chain by providing enough spaceto react by lessening any 377 steric hindrance in the vicinity. Thus, TEMPO-SBA-15closely mimicked the behavior of the 378 homogeneous catalyst system [45] in terms of 2,5-DFF yield. A similar heterogeneous catalyst 379 TEMPO-Silica using silica (fumed) (TEMPO loading 0.1 mmol/g) was compared for 5-HMF 380 oxidation resulting into 42 % 2,5-DFF yield (Fig. 7) with complete 5-HMF conversion (Table 381 S2). The possible reason could be the lesser exposure to active sites due to aggregation of silica 382 particles and the decreased diffusive transport of reaction components unlike in the TEMPO-SBA-15. 383

384	
385	3.7.Stability and Recycling of TEMPO-SBA-15
386	
387	The stability of TEMPO-SBA-15 was examined by repeated use of the catalyst in the same
388	reaction conditions. Recovered TEMPO-SBA-15 had similar catalytic performance with that of a
389	fresh catalyst even after several recycling runs (Fig. 8e). The 2,5-DFF yields were maintained
390	above 71% with minimal variation between each cycle. After five consecutive cycles, TEMPO-
391	SBA-15 did not reveal anynoteworthy form of chemical and structural deterioration as evidenced
392	by FT-IR and SEM analyses, respectively (Fig. 8a-8d). Recycling tests confirm the potential of
393	TEMPO-SBA-15 for long term repeated use as a catalyst for5-HMF oxidation to 2,5-DFF.
394	<insert 8="" figure="">&gt;</insert>
395	
396	4. Conclusion
397	The TEMPOcatalyst with organosilane linkerwas successfully immobilizedon SBA-15
398	support via silanization as confirmed by various characterization techniques. This metal-free
399	heterogeneous catalyst presented promising results by providing high 2,5-DFF yield in short
400	reaction time at ambient reaction conditions as compared to previously reported reaction systems.
401	The mesoporous SBA-15proved suitable as support of TEMPO; there was minimal reduction in
402	2,5-DFF yields and low propensity of the products and substrates forunwanted product
403	formation. Thus, heterogeneous TEMPO-SBA-15 catalyst provides an effective route for 2,5-
404	DFFproduction, with reliable catalytic activity for repeated and long-term use.
405	
406	5. Acknowledgements

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478		1677.

480	Figure	captions
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481

482	Fig. 1	(a) Small angle powder	r XRD patterns and (b) N	12 adsorption-desorptio	on isotherms and
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- 483 pore size distribution curves (inset) of SBA-15 and TEMPO-SBA-15.
- 484
- 485 Fig. 2 Thermogravimetric curves of SBA-15 and TEMPO-SBA-15.

486

487 Fig. 3 FT-IR spectra of (a) PTES-TEMPO, (b) SBA-15, and (c) TEMPO-SBA-15.

488

Fig. 4 SEM and FE-SEM images of (a), (c) SBA-15 and (b), (d) TEMPO-SBA-15 at different
magnifications.

491

- 492 Fig. 5 Comparison of homogeneous and heterogeneous TEMPO catalysts under oxygen and no-
- 493 oxygen atmosphere. Reaction conditions: 5-HMF (0.5 mmol), BAIB (0.75 mmol), ethyl acetate
- 494 (8 mL), RT, 1 h.

495

- 496 Fig. 6 Reaction profile of 5-HMF oxidation using TEMPO-SBA-15 as catalyst at different
- 497 temperatures. Reaction conditions: 5-HMF (0.5 mmol), TEMPO-SBA-15 (0.075 mmol
- 498 TEMPO), BAIB (0.75 mmol), ethyl acetate (8 mL), O<sub>2</sub>.

- 500 Fig. 7 Comparison of different reaction systems for the oxidation of 5-HMF using
- 501 homogeneous and heterogeneous TEMPO catalyst. Reaction conditions: 5-HMF (0.5 mmol),

- 502 TEMPO (0.075 mmol), BAIB (0.75 mmol, if used), AcOH (0.05 mmol, if used), ethyl acetate (8
  503 mL), O<sub>2</sub>(if used), 1 h.
- 504
- 505 Fig. 8 Recycling results of TEMPO-SBA-15 catalyst. (a) SEM image and (b) FT-IR spectrum
- of fresh catalyst, (c) SEM image and (d) FT-IR spectrum of used catalyst, and (e) 2,5-DFF yields
- 507 in 5-HMF oxidation over five recycling runs. Reaction conditions: 5-HMF (0.5 mmol), TEMPO-
- 508 SBA-15 (0.075 mmol TEMPO), BAIB (0.75 mmol), AcOH (0.05 mmol), ethyl acetate (8 mL),
- 509  $O_2$ , 40 °C, 1 h.
- 510
- 511 Scheme 1Synthesis of TEMPO-SBA-15 catalyst.
- 512 Scheme 2Oxidation of 5-HMF to 2,5-DFF over TEMPO-SBA-15 catalyst.
- 513 Table 1
- 514 Textural properties and TEMPO content of the SBA-15 and TEMPO-SBA-15 catalyst

Sample	Surface area (m²/g)ª	Pore volume (cm³/g) <sup>b</sup>	Pore size (nm) <sup>c</sup>	TEMPO content (mmol/g) <sup>d</sup>
SBA-15	883	1.24	5.6	-
TEMPO-SBA-15	526	0.72	5.5	0.3

- 515 <sup>a</sup> Calculated by the BET equation
- <sup>b</sup>Single point pore volume calculated at a relative pressure P/P<sup>o</sup> of 0.99
- 517 <sup>c</sup> Adsorption average pore diameter
- <sup>d</sup> Determined by elemental analysis, C/N ratio = 15.7



Figure 1



519



521



Figure 4







525

Figure 7











529

528

Scheme 1