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Recyclable montmorillonite-supported thiazolium ionic liquids for high-yielding and solvent-free upgrading of furfural and 5-hydroxymethylfurfural to C_{10} and C_{12} furoins

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ABSTRACT

Six Na⁺/montmorillonite (MMT) – supported thiazolium (TM) ionic liquids (ILs), MMT-[TM], which are precatalysts to N-heterocyclic carbene (NHC) catalysts, have been synthesized and employed to catalyze highly selective of furfural (FF) and 5-hydroxymethylfurfural (HMF) into C_{10} and C_{12} furoins, respectively. Among them, five supported [TM] salts carrying the electron-donating group exhibit excellent catalytic activity. Thus, supported NHC catalysts, generated in situ from activation of MMT-[TM] with Et₃N, afford C_{10} and C_{12} furoins in 97%-99% and 97%-98% yield, respectively. This condensation reaction is also carried out under solvent-free conditions, and the catalysts can be readily recycled, showing no noticeable loss in their catalytic activity over four consecutive recycles. Thus, these desired features possessed by the current catalyst system have enabled the development of the greener and more environmentally benign process for the upgrading of FF and HMF.

Keywords: Na⁺-montmorillonite, furfural (FF), self-condensation coupling, N-heterocyclic carbene (NHC), 5-hydroxymethylfurfural (HMF)

1. Introduction

With increasing depletion of nonrenewable resources and increased societal awareness of environmental protection, both the scientific community and industrial entity pay increasing attention to the research needs for sustainable energy and renewable chemicals.¹⁻⁴ Annually renewable biomass resources have emerged as the most abundant and sustainable resources to potentially meet such needs.⁵ Furaldehydes, particularly furfural (FF) and 5-hydroxymethylfurfual (HMF) are considered to be two of the most value-added biomass building blocks or platform chemicals by the U.S. Department of Energy.⁶ FF and HMF can be converted into a variety of chemicals and fuels.⁷⁻¹² However, these FF and HMF derivatives possess low carbon numbers, low energy density and high volatility, unsatisfactory as fuel additives.^{13,14} In addition, FF has been a large-scale production in industry, as well as HMF has been studied extensively as part of major efforts in developing technologically and economically feasible routes for liquid fuels, so it has more practical significance for their transformation and utilization. Therefore, upgrading of FF and HMF into higher-energy-density fuel intermediates via C-C bond formation or chain extension is of particular interest.¹⁵⁻¹⁸ However, such furaldehydes can not undergo self-aldol condensation due to lack of α -hydrogen. In this context, Dumesic and co-workers utilized cross-aldol condensation of HMF with acetone, followed by hydrodeoxygenation process to produce C_9 - C_{15} liquid alkane fuels.¹⁹

Direct coupling of FF and HMF into the corresponding C_{10} and C_{12} furoins has been made possible via benzoin-type umpolung condensation catalyzed by organic

N-heterocyclic carbene (NHC) catalysts.²⁰ For example, NHC-catalyzed direct coupling of two HMF molecules form exclusively C_{12} 5,5'-dihydroxymethyl furoin (DHMF), which has been converted into C_{10-12} linear hydrocarbons.²¹ An integrated catalytic process for conversion and upgrading of biomass feedstocks into DHMF and subsequently into $n-C_{12}H_{26}$ alkane fuel has also been developed.²² Benzoin condensation of FF has been extensively investigated,²³⁻²⁷ with the best furoin yield (>99%) achieved most recently by the NHC derived from the acetate substituted thiazolium.²⁸

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While molecular NHC catalysts are highly effective for the self-coupling of FF and HMF, they are difficult to recycle and reuse. In this context, there has been increased interest in developing recyclable, supported NHC catalysts. For example, crosslinked polymer-supported NHCs were used as recyclable organocatalysts for the benzoin condensation reaction,²⁹ but the catalytic activity and recyclability of this system were limited. Poly(4-vinylimidazolium) iodides combined with bases were found to be a more efficient and recyclable catalyst system for benzaldehyde condensation reaction,³⁰ but an analogous polymeric NHC catalyst, when employed for HMF self-coupling, gave a low yield of DHMF (18%).²² Insoluble polystyrene (PS) supported thiazolium (TM) salts, when combined with a base, produced furoin with under 67% yields in the FF coupling reaction.²³ Likewise, polymer-supported imidazolium salts, when employed for the benzoin condensation of aldehydes in the presence of a base, gave acyloin products under 77% yields.³¹ Recently, PS- and silica-supported imidazolium or benzimidazolium ionic liquids (ILs), which generate

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the corresponding NHC catalysts upon in situ activation with a base, afforded HMF and FF self-condensation products in 94% and 97% yield in THF, respectively.²⁴ Furthermore, montmorillonite (MMT) supported benzimidazolium, when activated with NaH, was found to effectively catalyze the self-coupling FF in THF producing furoin in >96% yield.²⁵ But the MMT-supported 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium precatalyst produced C₁₀ furoin in ~86% yield from the self-coupling of FF in THF at 25 °C after 5 h, and the recyclability of this catalyst system was poor, as evidenced by a large reduction in the furoin yield to only 54.1% when the recycled catalyst was used.²⁵

As can be seen from the above overview, the supported [TM] ILs gave lower yields and poor recyclability for self-condensation of FF, while the use of supported [TM] ILs for self-condensation of HMF into C_{12} furoin has not been reported. On the other hand, we recently found large electronic modulation of [TM] ILs, when converted to the discrete NHC catalysts, on their catalytic performance in the umpolung coupling of FF and HMF into C_{10} and C_{12} furoins.²⁸ Hence, we reasoned that, by supporting [TM] ILs varying electronic properties (which tune the nucleophilicity or activity of the corresponding NHC catalyst derived from in situ deprotonation with a base) onto the inexpensive MMT support, one could potentially discover highly effective MMT-supported [TM] catalyst systems that are not only highly active and efficient in achieving high yields of furoins from self-condensation of both FF and HMF, but also are recyclable and do not require use of any solvent. Accordingly, this contribution presents a full account of our study towards the above

central objective.

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2. Experimental Section

2.1 Materials and Methods

All anhydrous and oxygen-free operations were carried out in a nitrogen-filled glovebox or under nitrogen atmosphere. Na⁺/montmorillonite (MMT) with a cation exchange capacity (CEC) of 120 meq. /100g and an Aspect Ratio of 300-500 was supplied by Nanocor Company. HMF (97%) was purchased from Tianjin Heowns Biochem LLC (Tianjin, China) and used as received. FF (Aladdin Chemistry Co., Ltd.) was vacuum-distilled prior to use. Tetrahydrofuran (THF) was refluxed over metallic sodium with benzophenone and distilled under nitrogen atmosphere before use. Et₃N, KO^tBu, 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU), dimethylformamide (DMF), 4-methyl-5-hydroxyethylthiazole, 4,5-dimethylthiazole, 4-methyl-5-vinylthiazole, benzyl chloride, 2-bromoethanol, allyl bromide, and methyl iodide were purchased from Across Organics and used as received.

¹H NMR spectra were recorded on a Varian Inova 300 MHz NMR spectrometer. Fourier transform infrared (FT-IR) measurements were recorded in the range of 500-4000cm⁻¹on a Bruker TENSOR37 FT-IR spectrometer using a KBr pellet technique. Thermogravimetric analysis (TGA) was performed under air atmosphere at a heating rate of 10 °C/min from 20 to 900 °C using SDT-Q600, TA Instruments. X-ray diffraction (XRD) data were recorded on a D/MAX-2500 automated diffractometer. The *d* spacing was calculated to the Bragg equation ($n\lambda = 2d \sin\theta$).

Thiazolium (TM) bromides including 4,5-dimethyl-3-hydroxyethylthiazolium

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bromide ([HMTM]Br), 4-methyl-5-hydroxyethyl-3-allylthiazolium bromide ([AHTM]Br) and 4.5-dimethyl-3-allylthiazolium bromide ([AMTM]Br) were procedures.³² literature [TM] prepared according to the iodide, ([MVTM]I)³³ 3,4-dimethyl-5-vinylthiazolium iodide [TM] chloride, and $([BHTM]Cl)^{34}$ 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride were prepared using the literature methods.



2.2 Synthesis of 4-methyl-3,5-dihydroxyethylthiazolium bromide ([HHTM]Br)

A 100 mL three-necked round-bottom flask equipped with an oil bath and a magnetic stirring was charged with 4-methyl-5-hydroxyethylthiazole (4.30 g, 0.03 mol), 2-bromoethanol (3.72 g, 0.03 mol) and acetonitrile (15 mL). The resulting mixture was refluxed for 48 h, after which acetonitrile was removed under reduced pressure, and then 15 ml of acetone was added. The solvent was removed and the residue was washed with diethyl ether (10 mL) and dried for 24 h under vacuum to give a crude product. The crude product was recrystallized from a mixed ethanol-acetone solution, and then dried under vacuum to give the pure product (79 %

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yield) as a yellow solid.

¹H NMR (300 MHz, D₂O): δ 4.55 (t, J = 5.1 Hz, 2H, NCH₂CH₂); 3.95 (t, J = 5.1 Hz, 2H, NCH₂); 3.80 (t, J = 6.0 Hz, 2H, CH₂OH); 3.10 (t, J = 5.7 Hz, 2H, CH₂CH₂OH); 2.46 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 157.1, 141.7, 134.8, 59.6, 58.7, 55.1, 29.5, 11.6 ppm.

2.3 Preparation of MMT-Supported [TM] via ion exchange of Na⁺/MMT with [TM]X

A typical experimental procedure, using [BHTM]Cl as an example, was described as follows. MMT (1.0 g, 120 meq. /100g) was placed in a 250 mL three-necked round-bottom flask and 100 mL of distilled water was added. The mixture was vigorously stirred under reflux and heated to 80 °C for 4 h to become a swollen MMT slurry. In a beaker, [BHTM]Cl (0.65 g, 2.4 mmol) was dissolved in 20 mL of distilled water and then poured into the three-necked round-bottom flask containing the MMT slurry. The mixture was stirred at 80 °C for 5 h. After the reaction, the mixture was cooled to room temperature, and then the solid product was filtered and washed thoroughly with distilled water to remove the excess thiazolium ionic liquid. The resulting product, MMT-[BHTM], was dried at 70 °C under vacuum overnight before analysis and use. The same procedure was employed to prepare other MMT-supported [TM] precatalysts. TGA analysis of the MMT-[TM] revealed the contents of MMT-[AHTM], MMT-[AMTM], MMT-[BHTM], MMT-[HHTM], MMT-[HMTM] and MMT-[MVTM] in the resulting MMT-[TM] precatalysts to be 0.99, 1.04, 0.88, 0.98, 0.95, and 1.05 mmol/g, respectively.

2.4 Typical procedure for the self-coupling reaction of FF into C₁₀ furoin by MMT-[TM] and base

In a typical experimental procedure, FF (0.77 g, 8.0 mmol), MMT-[BHTM] (0.2 g, 0.16 mmol [BHTM], 2 mol % relative to FF) and Et₃N (45 μ L, 0.32 mmol, 4 mol % relative to FF) were added into a 20 mL glass bottle in a glovebox. The glass bottle was sealed, taken out of the glovebox, and then the reaction mixture was placed in an oil bath at 80 °C for 3 h. After the reaction, the solid product was dissolved in dichloromethane, filtered and then dichloromethane was distilled off on a rotary evaporator. After drying under vacuum, the product was obtained as a yellow solid (99 % yield). For the recycling experiments, after the completion of the reaction, dichloromethane and 37% aqueous HCl solution (75 μ L, 0.8 mmol) was added and the catalyst was separated by filtration, then the catalyst was dried at 70 °C overnight under vacuum. The recycled MMT-[BHTM] was reused to catalyze the FF coupling reaction under the same conditions. This process was repeated several times to evaluate the recyclability of the MMT-[BHTM] catalyst.

¹H NMR (300 MHz, CDCl₃) for C₁₀ furoin: *δ* 7.63, 7.39, 7.27, 6.55, 6.42, 6.37 (m, 6H, furan ring H), 5.82 (s, 1H, CHOH), 4.23 (br s, 1H, CHOH).

2.5 Typical procedure for the self-coupling reaction of HMF into C₁₂ furoin by MMT-[TM] and base

In a typical procedure, HMF (0.126 g, 1.0 mmol), MMT-[BHTM] (0.25 g, 0.20 mmol [BHTM], 20 mol % relative to HMF) and Et_3N (55 µL, 0.40 mmol, 40 mol % relative to FF) were added into a 20 mL glass bottle in a glovebox. The glass bottle

was sealed, taken out of the glovebox, and then the reaction mixture was placed in an oil bath at 120 °C for 3 h. After the reaction, the solid product was dissolved in dichloromethane, filtered and then dichloromethane was distilled off on a rotary evaporator. After drying under vacuum, the product was obtained as a white solid (97 % yield).

¹H NMR (400 MHz, DMSO-*d*₆) for C₁₂ furoin (DHMF): δ 4.31 (d, *J* = 5.7 Hz, 2 H, C*H*₂OH), 4.46 (d, *J* = 5.8 Hz, 2 H, C*H*₂OH), 5.18 (t, *J* = 5.7 Hz, 1H, CH₂OH), 5.50 (t, *J* = 5.9 Hz, 1H, CH₂OH), 5.73 (d, *J* = 6.2 Hz, 1H, CHOH), 6.06 (d, *J* = 6.2 Hz, 1H, CHOH), 6.22, 6.34, 6.50, 7.50 (d, 4H, furan ring H).

3. Results and discussion

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3.1 Synthesis and Characterization of Supported Precatalysts MMT-[TM]

FT-IR analysis. As described in the Experimental section, a total of six MMT-Supported [TM] precatalyst have been synthesized via ion exchange of Na⁺/MMT with [TM]X (X = Cl, Br, I) ILs (Scheme 1). To confirm if the [TM] cations were successfully intercalated into the MMT nanogalleries or not, the resulting MMT-[TM] products were analyzed by FT-IR. As can be seen from Fig. 1, the FT-IR spectrum of Na⁺-MMT displays the peak at 3631 cm⁻¹ that can be attributed to the OH units in Na⁺-MMT. The peaks at 3431 and 1641 cm⁻¹ correspond to the –OH stretching vibration of free H₂O onto the Na⁺-MMT structure and the bands at 1044 and 917 cm⁻¹ can be collectively attributed to Si–O stretching vibrations; However, the FT-IR spectrum of MMT-[TM] exhibit the characteristic peaks at 3098 cm⁻¹, 1587 cm⁻¹ and 1457 cm⁻¹ were assigned to the =C–H, C=C and C=N stretching vibration

modes of the thiazole ring, respectively. Furthermore, the characteristic absorption bands at 2937 cm⁻¹ and 2886 cm⁻¹, attributed to the aliphatic C–H stretching vibration of methyl and methylene groups, were also observed. These results suggest that the [TM] ILs were successfully supported onto MMT.



Scheme 1. Synthesis of six MMT-[TM] precatalysts.



Fig. 1 FT-IR spectra of MMT (a), MMT-[MVTM] (b), MMT-[AMTM] (c), MMT-[AHTM] (d), MMT-[HHTM] (e), MMT-[HMTM] (f), MMT-[BHTM] (g).

XRD analysis. Power X-ray diffraction (XRD) was carried out to investigate the expansion of the MMT layers, upon intercalation of [TM] cations into the nanogallery of Na⁺/MMT. According to the Bragg's Equation: $2d \sin \theta = \lambda$ (d is the basal spacing; θ is the Bragg peak angle; and λ is the X-ray wavelength),²⁵ we calculated the basal spacings of these samples. As shown in Fig. 2, the calculated basal spacing for the MMT. MMT-[BHTM], MMT-[HMTM], MMT-[AHTM], MMT-[HHTM]. MMT-[AMTM, and MMT-[MVTM] was 12.1, 15.5, 13.3, 13.4, 13.6, 13.4, and 13.2 Å, respectively. The results showed that the basal spacing of the MMT-[TM] is clearly larger than that of MMT, especially for MMT-[BHTM], due to the presence of the larger benzyl group in [BHTM]⁺ cation. Therefore, these XRD results offered additional evidence for the [TM] ILs intercalated into the MMT interlayer spacing and showed correlation between the size of the [TM] cation and the [TM] intercalated MMT interlayer basal spacing.



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Fig. 2 XRD profiles of MMT (a), MMT-[BHTM] (b), MMT-[HMTM] (c), MMT-[AHTM] (d), MMT-[HHTM] (e), MMT-[AMTM] (f), MMT-[MVTM] (g).

 N_2 adsorption – desorption. N_2 adsorption – desorption measurements were performed to obtain more information about the catalyst. Due to the fact that the precatalysts MMT-[TM] have the similar structures, therefore, we take the N_2 adsorption – desorption isotherm of MMT and MMT-[BHTM] as an example (as shown in Fig. 3). And the curves of pore-size distribution evaluated from desorption data by utilizing the BJH model are also shown in the inset of Fig. 3. Through analysis we found that both samples showed a type IV isotherm with H_3 hysteresis, according to the IUPAC classification, which is characteristic of the micro and mesopore structure of samples with slit-like pores. BET surface area, pore volumes and pore diameters for MMT and MMT-[BHTM] were presented in Table 1. A increase in BET surface area from MMT (14.068 m²/g) to MMT-[BHTM] (15.580 m^{2}/g), that can be interpreted as being due to the pore diameters of MMT is too small (3.822 nm), leading to the organic macromolecules attached to the surface of MMT layers, and it was also indicated that the ionic liquid may be successfully intercalated to MMT layers.

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Fig. 3 N_2 adsorption – desorption isotherms: (a) MMT ; (b) MMT-[BHTM]. (NOTE: The position of the MMT isotherm is shifted.)

Table 1. Pore structure parameters of MMT and MMT-[BHTM] derived from the N₂ adsorption – desorption isotherms.

| Sample | $S_{BET} (m^2/g)$ | $V_p (cm^3/g)$ | Pore diameter (nm) |
|------------|-------------------|----------------|--------------------|
| MMT | 14.068 | 0.05566 | 3.822 |
| MMT-[BHTM] | 15.580 | 0.07529 | 3.825 |

Elemental analysis (EA) results. The loading amount of ionic liquids on Na⁺-MMT was determined by means of elemental analysis. As can be seen from the Table 2, there is not have the elemental of C, H and N in the Na⁺-MMT, indicating that the [TM] cations were successfully intercalated into the nanogalleries of MMT. Furthermore, through the N%, we can calculated the loading amount of ionic liquids on MMT. The loading amount of ionic liquids on MMT. The loading amount of ionic liquids on MMT ranges from 0.88 to 1.03 mmol/g (By EA method). The loading amount of ionic liquids on MMT was also

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determined by TGA analysis. The corresponding results are summarized in Table 2. And the loading amount of ILs measured by TGA is in good agreement with the calculated one from the EA results. These values were used to calculate the loading of catalyst for the self-coupling reactions of furfural and HMF.^{24,25}

| Precatalysts | N (wt%) | C (wt%) | H (wt%) | Amount of IL (mmol/g) ^a | Amount of IL (mmol/g) ^b |
|--------------------|------------|------------|------------|------------------------------------|---------------------------------------|
| MMT | 0 | 0 | 0 | 0 | 0 |
| MMT-[BHTM] | 1.23 | 13.71 | 1.42 | 0.88 | 0.88 |
| MMT-[BHTM]-recycle | 1.19 | 13.26 | 1.37 | 0.85 | - |
| MMT-[HHTM] | 1.37 | 9.39 | 1.38 | 0.97 | 0.98 |
| MMT-[AHTM] | 1.38 | 10.64 | 1.39 | 0.99 | 0.99 |
| MMT-[HMTM] | 1.33 | 7.98 | 1.14 | 0.95 | 0.95 |
| MMT-[AMTM] | 1.45 | 9.94 | 1.24 | 1.02 | 1.04 |
| MMT-[MVTM] | 1.47 | 8.82 | 1.05 | 1.03 | 1.05 |

Table 2. EA and TGA methods for the loading amount of different ionic liquids on MMT.

^a The loading amount of ILs on Na⁺-MMT (C) was calculated according to the following expressiom: C = the percentage of nitrogen $\times 1 \text{ g} \times 10^3$ /nitrogen atomic weight. ^b Calculated by TGA method (see Fig. 4).

ICP analysis. ICP was carried out to investigate the composition of the prepared catalysts. As shown in Table 3, we can note that the prepared catalyst contains five metal elements (Na, Mg, Al, Si and Fe). Through the comparison of the MMT and MMT-[BHTM], we found that the content of all the five elements present a drastic decrease, that can be interpreted as being due to the intercalated of the ionic liquid, which lead to the decrease of the relative contents. However, the decrease in the content of sodium was the most obvious, for the ionic liquids via ion exchange of Na⁺ onto the MMT layer. In addition, though the EA (Table 2) and ICP (Table 3) analysis of the MMT-[BHTM] and MMT-[BHTM]-recycle, we found that the N% have a

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slight decrease and the Na% have a slight increase, so we envisioned that, some leaching problems of prepared catalysts are present in the reactions.

| Sample | Na (%) | Mg (%) | Al (%) | Si (%) | Fe (%) |
|--------------------|--------|--------|--------|--------|--------|
| MMT | 3.21 | 1.65 | 12.35 | 29.65 | 3.99 |
| MMT-[BHTM] | 1.46 | 1.34 | 10.03 | 23.98 | 3.23 |
| MMT-[BHTM]-recycle | 1.54 | 1.34 | 10.01 | 23.97 | 3.21 |

Table 3. The metal content of MMT and MMT-[BHTM].

TGA analysis. TGA was performed on the prepared MMT-[TM] to characterize their thermal stability and contents of the intercalated [TM] cations. From Fig. 4, one can note that the weight loss rate of MMT-[TM] was much larger than that of MMT, further indicating that the [TM] cations were successfully intercalated into the nanogalleries of MMT (Owing to the fact that MMT-[HHTM] and MMT-[AHTM] as well as MMT-[MVTM] and MMT-[AMTM] have the similar weight loss curve, so we just draw one of them in the Fig. 4). More importantly, through the weight loss of the samples, we can calculated that the contents of the intercalated [TM] cations in the resulting MMT-TM precatalysts²⁵ MMT-[AHTM], MMT-[AMTM], MMT-[BHTM], MMT-[HHTM], MMT-[HMTM], and MMT-[MVTM] to be 0.99, 1.04, 0.88, 0.98, 0.95, and 1.05 mmol/g, respectively.

The loading amount of ionic liquids on MMT was calculated according to the following equations:

C (mmol/g) =
$$\frac{\frac{1 - \frac{W_1}{W_2}}{M_1 - M_2} \times 1000$$

C: loading amount of ionic liquids on MMT, W1: residual amount of MMT-[TM], W2:

residual amount of MMT, M₁: relative molecular mass of ionic liquids, M₂: relative molecular mass of NaX (X: Cl, Br, I).



Fig. 4 TGA curves of MMT (a), MMT-[BHTM] (b), MMT-[HMTM] (c), MMT-[AHTM] (d), MMT-[HHTM] (e), MMT-[AMTM] (f), MMT-[MVTM] (g).

3.2 Catalytic activity of MMT-[TM] for coupling reaction of FF to C₁₀ furoin

As the above analyses showed six MMT-[TM] precatalysts have been successfully prepared, next we investigated their catalytic performances for the self-coupling reaction of FF into C_{10} furoin. We envisioned that, following the established protocol,²⁵ activation of such precatalysts with a suitable base should generate the corresponding neutral NHC catalyst *in situ*, which catalyzes the self-coupling reaction; the NHC catalyst can then be readily recycled through its reaction with HCl reforming the [TM]Cl precatalyst (Scheme 2).^{24,25} To this end, we varied MMT-[TM] precatalyst structure (six total) and examined effects of reaction

conditions (including catalyst loading, solvent, time, and temperature) on their catalytic performances, the results of which are summarized in Table 4.

| Entry | Pre-catalyst (mol %) | Base (mol %) | Temperature (°C) | Time (h) | Solvent | Yield (%) ^b |
|-------|----------------------|------------------------|---------------------|-------------|---------|---------------------------|
| 1 | | E4 NL 2 | 20 | 2 | | 0 |
| 1 | MMT, 0.2 g | $El_3N, 2$ | 80 | 3 | - | 0 |
| 2 | MMT-[BHTM], 0.6 | Et_3N , 1.2 | 80 | 3 | - | 18 |
| 3 | MMT-[BHTM], 1.2 | Et ₃ N, 2.4 | 80 | 3 | - | 70 |
| 4 | MMT-[BHTM], 1.2 | Et ₃ N, 4.8 | 80 | 3 | - | 75 |
| 5 | MMT-[BHTM], 2 | Et ₃ N, 4 | 80 | 3 | - | 99 |
| 6 | MMT-[BHTM], 2 | Et ₃ N, 4 | 100 | 3 | - | 98 |
| 7 | MMT-[BHTM], 10 | NaH, 10 | 25 | 5 | THF | 86 ^c |
| 8 | MMT-[BHTM], 2 | Et ₃ N, 4 | 60 | 3 | - | 94 |
| 9 | MMT-[BHTM], 2 | Et ₃ N, 4 | 80 | 1 | - | 94 |
| 10 | MMT-[BHTM], 2 | Et ₃ N, 4 | 80 | 3 | THF | 85 |
| 11 | MMT-[BHTM], 2 | Et ₃ N, 4 | 80 | 3 | DMF | 91 |
| 12 | MMT-[BHTM], 2 | DBU, 4 | 80 | 3 | - | 64 |
| 13 | MMT-[BHTM], 2 | KO ^t Bu, 4 | 80 | 3 | - | 82 |
| 14 | MMT-[HHTM], 2 | Et ₃ N, 4 | 80 | 3 | - | 98 |
| 15 | MMT-[HHTM], 2 | Et ₃ N, 4 | 80 | 1 | - | 94 |
| 16 | MMT-[AHTM], 2 | Et ₃ N, 4 | 80 | 3 | - | 97 |
| 17 | MMT-[HMTM], 2 | Et ₃ N, 4 | 80 | 3 | - | 98 |
| 18 | MMT-[AMTM], 2 | Et ₃ N, 4 | 80 | 3 | - | 97 |
| 19 | MMT-[MVTM], 1.2 | Et ₃ N, 2.4 | 80 | 3 | - | 60 |
| 20 | MMT-[MVTM], 2 | Et ₃ N, 4 | 80 | 3 | - | 80 |
| 21 | [BHTM]Cl, 1 | Et ₃ N, 2 | 80 | 3 | - | 99 |
| 22 | [HHTM]Br, 1 | Et ₃ N, 2 | 80 | 3 | - | 97 |
| 23 | [AHTM]Br, 1 | Et ₃ N, 2 | 80 | 3 | - | 96 |
| 24 | [HMTM]Br, 1 | Et ₃ N, 2 | 80 | 3 | - | 97 |
| 25 | [AMTM]Br, 1 | Et ₃ N, 2 | 80 | 3 | - | 97 |
| 26 | [MVTM]I, 1 | Et ₃ N, 2 | 80 | 3 | - | 82 |

Table 4. Experimental Results of FF Coupling Reaction Catalyzed by MMT-[TM] and Base ^a

^a Furfural (0.768 g 8.00 mmol), nitrogen atmosphere. ^b Determined by ¹H NMR. ^c Data point taken from literature.²⁵



Scheme 2. Activation, catalysis, and recycling involved in the self-condensation coupling reaction of FF and HMF by the MMT-[TM]/Base catalyst system.

A control run using MMT alone showed no activity for the coupling reaction of FF under the current conditions (entry 1, Table 4), thus confirming that MMT functions only a catalyst support. We first focused on the MMT-[BHTM] system and optimized its catalytic performance (entries 2-13, Table 4). Under the same set of conditions (2 mol% precatalyst loading, 4 mol% Et₃N, 80 °C, 3 h), the highest furoin yield of 99% was obtained in the absence of solvent (entry 5), which outperformed the reactions in THF (85%, entry 10) and DMF (91%, entry 11). Next, using the same solvent-free conditions (80 °C, 3 h), the relative amount of precatalyst MMT-[BHTM] and base (Et₃N) was varied for the coupling reaction. When the mole ratio (relative to furfural, mol%) of MMT-[BHTM] and Et₃N was 0.6:1.2, 1.2:2.4, and 1.2:4.8, furoin was achieved in 18 %, 70%, and 75 % yield, respectively (entries 2-4, Table 4). Excitingly, when the mole ratio was changed to 2:4, essentially quantitative yield (99%) of C₁₀ furion was achieved (entry 5, Table 4). Through temperature variations from 60 °C to 100 °C, we found the reaction carried out at 80 °C gave the best furoin

yield (entry 5 vs. 6 and 8, Table 4). Shortening the reaction time from 3 h to 1 h noticeably decreased the yield to 94% (entry 9, Table 4). Other common bases used to NHC generate the catalyst for coupling reactions, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and KO^tBu,^{25,28} also worked to certain extent, but they were much inferior to Et_3N (64% by DBU, entry 12; 82% by KO^tBu, entry 13, Table 4). Overall, the optimal reaction conditions for achieving the highest furoin yield (99%) from the FF self-coupling reaction were identified as follows: 2 mol % pre-catalyst, 4 mol % Et₃N, 80 °C, 3 h, no solvent. The current system also outperformed considerably the previously reported system consisting of 10 mol% MMT-[BHTM], 10 mol% NaH, THF, 25 °C, 5 h, which gave a furoin yield of 86 % (entry 7, Table 4).²⁵

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Having established the optimal FF coupling reaction conditions for MMT-[BHTM], next we examined other five precatalysts intercalated into the nanogalleries of MMT, including MMT-[AHTM], MMT-[AMTM], MMT-[HHTM], MMT-[HMTM], and MMT-[MVTM]. Under the above optimal conditions, all the MMT-[TM] + Et₃N catalyst systems produced C₁₀ furoin in high yields (\geq 94%, entries 14-18, Table 4), except for MMT-[MVTM] (entries 19 and 20, Table 4). In a comparative study, we also used these [TM] ILs without being supported on MMT for the coupling reaction and found that the results were nearly identical to those obtained from the supported MMT-[TM] catalyst systems (entries 21-26, Table 4). Also noteworthy is that [MVTM]⁺, which contains an electron-withdrawing vinyl group at the 5-poisiton of the [TM] ring, consistently gave the lowest furoin yield in either

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supported (80%) or unsupported (82%) form. Hence, its inferior catalytic performance can be attributed to the electron-withdrawing substitute that renders low nucleophilicity of the corresponding NHC catalyst.

3.3 Catalytic activity of MMT-[TM] for coupling reaction of HMF to C₁₂ furoin

The supported MMT-[TM] catalysts were also examined for their catalytic performances in catalyzing the self-coupling reaction of HMF to DHMF. Owing to the fact that HMF has a CH₂OH group which could retard or deactivate the NHC catalyst, the self-coupling reaction of HMF is much more challenging than the coupling of FF, thus requiring higher catalyst loadings and more harsh reaction conditions.²⁸ As can be seen from Table 5, when 10 mol% of MMT-[BHTM] and 20 % mol of Et₃N were used at 120 °C for 3 h under solvent-free conditions, the yield of DHMF was only 53 % (entry 1, Table 5). Increasing the MMT-[BHTM] and Et₃N loading to 20 mol% and 40 mol%, respectively, enhanced the DHMF yield to 97% (entry 2, Table 5). On the other hand, variations of other reaction conditions such as solvent (entry 3, Table 5), time (entry 4, Table 5), temperature (entry 5, Table 5), and base (entry 6, Table 5) all led to lower yields of DHMF. Finally, under the optimal conditions (20 mol% MMT-[TM], 40 mol% Et₃N, no solvent, 120 °C, 3 h) based on MMT-[BHTM]), other MMT-supported ILs were shown to perform similarly, achieving high DHMF yields of 97-98% (entries 7-10, Table 5). Again, [MVTM]⁺-based catalyst carrying an electron-withdrawing vinyl group was the least effective, producing DHMF in low yields of 30-78%, depending on the loading of the precatalyst and base as well as temperature (entries 11-13, Table 5).

| Entry | Pre-catalyst (mol %) | Base (mol %) | Temperature (°C) | Time (h) | Solvent | Yield (%) ^b |
|-------|----------------------|-----------------------|---------------------|-------------|---------|---------------------------|
| | | | | | | |
| 1 | MMT-[BHTM], 10 | Et ₃ N, 20 | 120 | 3 | - | 53 |
| 2 | MMT-[BHTM], 20 | Et ₃ N, 40 | 120 | 3 | - | 97 |
| 3 | MMT-[BHTM], 20 | Et ₃ N, 40 | 120 | 3 | DMF | 78 |
| 4 | MMT-[BHTM], 20 | Et ₃ N, 40 | 120 | 1 | - | 93 |
| 5 | MMT-[BHTM], 20 | Et ₃ N, 40 | 80 | 3 | - | 92 |
| 6 | MMT-[BHTM], 20 | DBU, 40 | 120 | 3 | - | 68 |
| 7 | MMT-[HHTM], 20 | Et ₃ N, 40 | 120 | 3 | - | 98 |
| 8 | MMT-[AHTM], 20 | Et ₃ N, 40 | 120 | 3 | - | 98 |
| 9 | MMT-[HMTM], 20 | Et ₃ N, 40 | 120 | 3 | - | 98 |
| 10 | MMT-[AMTM], 20 | Et ₃ N, 40 | 120 | 3 | - | 97 |
| 11 | MMT-[MVTM], 10 | Et ₃ N, 20 | 120 | 3 | - | 32 |
| 12 | MMT-[MVTM], 20 | Et ₃ N, 40 | 120 | 3 | - | 78 |
| 13 | MMT-[MVTM], 20 | Et ₃ N, 40 | 80 | 3 | - | 70 |
| | | | | | | |

Table 5. Experimental Results of HMF Coupling Reaction Catalyzed by MMT-[TM] and Base ^a

^aHMF (0.126 g, 1.00 mmol), nitrogen atmosphere. ^bDetermined by ¹H NMR spectra.

3.4 Recycling experiments

To examine the recyclability of the current supported MMT-[TM] catalyst system, the better-performing precatalysts MMT-[BHTM], MMT-[HMTM], MMT-[AHTM], MMT-[HHTM] and MMT-[AMTM] were selected to catalyze the FF coupling reaction under the optimal conditions (2 mol% pre-catalyst, 4 mol% Et₃N, 80 °C, 3 h, no solvent) for four consecutive batch runs. At the end of each batch run, an aqueous HCl solution was added to quench the reaction to convert the in situ formed NHC catalyst back to the [TM] precatalyst, in which the [TM]⁺ is re-intercalated back into the interlayers of MMT through cation exchange (Scheme 2). The recycled

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MMT-[TM] was reused to catalyze the FF coupling reaction of the next batch. The results of these recycling experiments were summarized in Table 6, showing that the C_{10} furoin yield was kept nearly constant ranging from 96% to 99% throughout four cycles. Overall, these supported catalysts are both highly effective and readily recyclable.

| Run - | C_{10} furoin yield (%) | | | | | |
|-------|---------------------------|------------|------------|------------|------------|--|
| | MMT-[BHTM] | MMT-[HMTM] | MMT-[AHTM] | MMT-[HHTM] | MMT-[AMTM] | |
| 1 | 99 | 98 | 97 | 98 | 97 | |
| 2 | 97 | 98 | 96 | 98 | 96 | |
| 3 | 98 | 96 | 98 | 96 | 96 | |
| 4 | 98 | 97 | 97 | 97 | 98 | |

Table 6. Recyclability test of MMT-[TM]/Et₃N catalyst system for the FF self-coupling reaction

3.5 The mechanism for the NHC-catalyzed self-coupling reactions of FF and HMF into C_{10} and C_{12} furoins

In the present work, the mechanism of self-coupling reactions of FF and HMF into C_{10} and C_{12} furoins catalyzed by the NHC catalyst was consistent with the reported one.²⁸ As displayed in Scheme 3, thiazolium cation **I**, in combination with a suitable base, to form thiazolin-2-ylidene NHC catalyst **II**. Nucleophilic attack of a FA by **II** generates the carbene-aldehyde zwitterionic adduct **III**, followed by proton transfer, which affords the Breslow intermediate, **IV**. This diamino enol intermediate, functions as an acyl anion equivalent and attacks a second FA molecule, forming zwitterionic adduct **V**. After the proton transfer and the elimination of the furoin product, the NHC catalyst **II** is regenerated.²⁴ Finally, this catalyst was recovered by quenching the reaction with HCl to convert the catalyst back to the precatalyst (as

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Scheme 3. Mechanism of self-coupling reactions of FF and HMF into C_{10} and C_{12} furoins catalyzed by the NHC catalyst.

4. Conclusions

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In summary, through this study we have synthesized and characterized six MMT-[TM] supported precatalysts and employed them, in combination with a suitable base, for the self-coupling reactions of FF and HMF into C_{10} and C_{12} furoins, respectively. Our results showed that such MMT-[TM] catalyst systems, particularly [TM] ILs carrying donating groups on the [TM]⁺, upon activation with Et₃N, exhibit outstanding catalytic performance in both FF and HMF self-coupling reactions. For the FF coupling reaction, optimized conditions (2 mol % pre-catalyst, 4 mol % Et₃N,

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no solvent, 80 °C, 3 h) led to formation of C_{10} furoin in essentially quantitative yield (97-99%). In the case of HMF coupling, use of 20 mol % precatalyst and 40 mol% Et₃N at 120 °C for 3 h also led to near quantitative yield (97-98%) of C_{12} furion. Significantly, this high-yielding, solvent-free coupling catalyst system is also recyclable, thus affording essentially constant high furoin yield of 96% to 99% throughout four catalyst recovery-reuse cycles. Hence, these important features, including the solvent-free process, the quantitative atom-economic and high-yielding coupling reactions, an ease in product isolation and catalyst recovery, and excellent recyclability of the catalyst, highlight the hallmarks of green chemistry possessed by the current supported MMT-[TM] catalyst system.

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