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### LETTER

Brønsted-Lewis dual acidic ionic liquid immobilized on mesoporous silica materials as an efficient cooperative catalyst for Mannich reaction

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Hong Bo Wang,<sup>‡</sup> Nan Yao,<sup>‡</sup> Long Wang and Yu Lin Hu<sup>\*</sup>

Novel mesoporous silica supported ILs have been prepared and successfully applied as a heterogeneous catalyst in Mannich reactions. The excellent recyclability of the supported catalyst, mild reaction conditions, good to excellent yields, low catalyst loading, and operational simplicity are the important features of this methodology.

Mannich reactions are powerful carbon-carbon bond forming process for the construction of β-aminocarbonyl compounds, which are important intermediates in the production of products.<sup>1,2</sup> pharmaceuticals and natural numerous Traditionally, the common choice in the preparation of these compounds involves the use of protonic acid or lewis acid catalysts, <sup>3</sup> which offer a number of serious disadvantages such as harsh reaction conditions, tedious work-up, corrosive wastes and laborious separation. To overcome this situation, a variety of catalysts have been developed for this reaction, including [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>,<sup>4</sup> HNMPCI/ZnCl<sub>2</sub>/SBA-15,<sup>5</sup> Lipase,<sup>6</sup> (C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>)<sub>2</sub>[BiCl<sub>6</sub>]Cl·H<sub>2</sub>O,<sup>7</sup>TMAC[4]Bu<sup>t</sup>-MNP,<sup>8</sup>ZrOPPAZOSO<sub>3</sub>H,<sup>9</sup>L-FAU zeolite,<sup>10</sup> ZrOCl<sub>2</sub>·8H<sub>2</sub>O,<sup>11</sup> proline and others.12 Unfortunately, most of these methods still suffer from some lacks such as using expensive ligands, toxic reagents, and difficulties recovering and recycling catalysts. Thus, the development of novel catalysts for the Mannich reaction in a highly effective and sustainable manner has attracted much more attention.

lonic liquids (ILs) are a class of green solvents for chemical synthesis and catalysis because of their negligible volatility, potential biological activity, thermal stability, and potential reusability.<sup>13</sup> Some functionalized ILs as catalysts for the three-component Mannich reactions have been reported and

University, Yichang 443002, P. R. China.

E-mail: huyulin1982@163.com.

drawbacks associated with high catalyst loading and catalyst recycling, highly efficient and heterogeneous solid base catalysts are demanded. Very recently, many studies have progressed on preparation and application of supported ionic liquid catalysts via immobilization of ILs on diverse solid supports.<sup>15,16</sup> Properties of these solid IL materials such as high surface area show a remarkable level of catalytic performance. In addition, due to their heterogeneous properties, they have the attractive features of easy separation and recyclability. Mesoporous materials such as MCM-41 possess unique structural features such as their large surface areas, uniform and regular arrangements of pore sizes, and well-defined surface properties. Thus, they are ideal solid supports for immobilization of ILs.<sup>16,17</sup> Based on the above summarizations and inspired by the reports on the acidic nature of mesoporous silica could be improved by the incorporation of some transition metals,<sup>17</sup> catalysts supported on a incorporated mesoporous silica would be conducive to the improvement of Mannich reaction. Herein, we designed and prepared a series of transition metals such as Ti, Sn, and Fe incorporated mesoporous silica MCM-41 supported ionic liquids with different Brønsted and Lewis acid sites. Through investigating the catalytic activities of the supported ILs in the preparation of  $\beta$ -aminocarbonyl compounds, we attempt to explore a novel type of cooperative catalysis system for the direct three-component Mannich reaction (Scheme 1).

presented good catalytic activities.<sup>14</sup> However, because of the

In the preliminary stage of investigation, benzaldehyde, aniline and acetophenone were adopted as the model substrates for investigating the three-component Mannich reaction. The supported ILs developed in our lab were used as the catalysts. Initial screenings were performed in the

College of Materials and Chemical Engineering, Key laboratory of inorganic nonmetallic crystalline and energy conversion materials, China Three Gorges

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<sup>‡</sup> These authors contributed equally to this work

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Scheme 1 Catalytic one-pot three-component Mannich reaction.

presence of different anions TsO-, HSO<sub>4</sub>-, CF<sub>3</sub>SO<sub>3</sub>-, TiCl<sub>5</sub>-, CoCl<sub>3</sub>-, SnCl<sub>5</sub>-based MCM-41 supported catalysts (Table 1, entries 1-6). The best results were obtained when the reaction was performed using TiCl5-based MCM-41 supported IL catalyst (Table 1, entry 4). The model reaction was then checked in the presence of other Ti, Sn, or Fe incorporated MCM-41 supported TiCl<sub>5</sub>-based IL catalysts (Table 1, entries 7-9). The investigated catalytic activity studies reveal that the ILSO3H-TiCl<sub>5</sub>@Sn-MCM-41 catalyst shows the best catalytic performance in terms of conversion and yield (Table 1, entry 8). It should be pointed out that in the presence of Ti-MCM-41, Sn-MCM-41 or Fe-MCM-41 supported TiCl<sub>5</sub>-based IL catalysts, the reaction proceeded higher efficiency to give the desired product compared with that of MCM-41 supported IL catalysts. This illustrated that the support plays an important role in the reaction, and these results were consistent with the fact that the acidic nature properties of MCM-41 materials can be improved by incorporating transition metals.<sup>17</sup> The high catalytic efficiency of ILSO<sub>3</sub>H-TiCl<sub>5</sub>@Sn-MCM-41 catalyst may be attributed to superior better dispersion of Lewis and Bronsted sites within Sn-MCM-41 support, suitably superior pore size and pore geometry as described by the N<sub>2</sub> adsorption-desorption isotherms (Fig. S6, ESI<sup>+</sup>). In comparison, a drastic decrease in the catalytic reaction efficiency was observed when common ILs such as ILSO<sub>3</sub>H-TsO, ILSO<sub>3</sub>H-HSO<sub>4</sub>, ILSO<sub>3</sub>H-CF<sub>3</sub>SO<sub>3</sub>, ILSO<sub>3</sub>H-TiCl<sub>5</sub> (Table 1, entries 10-13) or support catalysts such as MCM-41, Ti-MCM-41, Sn-MCM-41, Fe-MCM-41 were used (Table 1, entries 14-17). It is noteworthy that the reaction in MCM-41 catalyst led only very low yield of the product even at prolonged reaction time (Table 1, entry 14), and apparently MCM-41 is not the highly efficient support for the reaction. It was found that the catalytic activities of the supported ILs on the Mannich reaction were dependent on the combined action of incorporated mesoporous silica support and the ionic liquid counter anion. The above results obtained in the reaction may be attributed to the cooperative function of larger surface area, superior pore size, abundant catalytic acid sites after supported on mesoporous silica carrier.<sup>16</sup>

Some reaction parameters including the amount of catalyst and the effect of solvent were studied in detail. Fig. S8 (ESI<sup>+</sup>) shows the effects of the amount of catalyst on the Mannich reaction. Results show that the reaction did not perform without addition of ILSO<sub>3</sub>H-TiCl<sub>5</sub>@Sn-MCM-41. However, a considerable change in the benzaldehyde conversion and product yield were observed when the amount of catalyst was increased to 0.3 g. With further increasing the amount of IL to 0.4 g, the reaction activity was strengthened and a maximum conversion (93%) and yield (92%) were observed. Screening of the reaction conditions revealed that the solvents played an important role on the yield of the desired product (Fig. S9, ESI<sup>+</sup>). Solvents such as CH<sub>3</sub>CN, ethyl acetate, CH<sub>2</sub>Cl<sub>2</sub>, provided slightly lower yields, whereas other solvents such as water and THF produces poor yields. Interestingly, in the absence of solvent, the reaction proceeded smoothly to afford the desired product in good yield of 86%. Further studies established that EtOH was the best choice among the screened solvent systems, with the yield 92% being achieved after 3 h.

To demonstrate the stability and efficiency of ILSO<sub>3</sub>H-TiCl<sub>5</sub>@Sn-MCM-41, recycling experiments for the Mannich reaction were conducted (Fig. S10, ESI<sup>+</sup>). At the end of the reaction, the precipitated catalyst was easily recovered by simple filtration and dried for reusability. The catalytic activity and product yield were well retained in the six consecutive runs, showing the stability and recyclability nature of the catalyst. Scanning electron microscopy (SEM) analysis confirmed that the catalyst displayed obviously unchangeable in the morphology and size before and after reaction (Fig. S4, ESI<sup>+</sup>). Moreover, XRD observation clearly demonstrated the maintained original crystallinity of the catalyst after six runs (Fig. S11, ESI<sup>+</sup>). Particularly, the elemental analysis of the reused catalyst did not show obvious change in the content of the catalyst (Tables S1), which indicated that the catalyst is featured by an outstanding stability in the reaction, and almost no leaching of the catalyst species occurred.

In order to investigate the universality of three-component onepot Mannich reaction catalyzed by ILSO<sub>3</sub>H-TiCl<sub>5</sub>@Sn-MCM-41, different substrates were tested under the optimal conditions (Table S2, ESI<sup>+</sup>). The Mannich reaction of aromatic amines and aldehydes with acetophenone proceeded smoothly to the efficient synthesis of corresponding β-aminocarbonyl compounds at room temperature (Table S2, entries 1-15). Aromatic amines carrying either electron-donating groups (Table S2, entries 2-4) or electronwithdrawing groups (Table S2, entries 5 and 7) were all suitable for this novel heterogeneous catalytic system. However, aromatic amines with electron-donating groups significantly decreased the reaction rate, and longer reaction time was needed to obtain good yields. Interestingly, aromatic aldehydes bearing different substituents, the high performance were obtained with excellent yields (Table S2, entries 5-14). To obtain more insight into the catalytic possibilities of the novel catalytic system, other ketones such as 1-(4-methylphenyl)-ethanone, and cyclohexanone were also studied in the reaction, good yields of the desired products were afforded (Table S2, entries 16 and 17).

**Table 1** The catalytic three-component Mannich reaction with different catalysts  $^{a}$ 

Entry	Catalyst	Time (h)	Conversion (%) <sup>b</sup>	Yield (%) <sup>c</sup>
1	ILSO <sub>3</sub> H-TsO	6	92	83

	@MCM-41			
2	ILSO <sub>3</sub> H-HSO <sub>4</sub>	6	88	79
	@MCM-41	0	00	75
3	ILSO <sub>3</sub> H-CF <sub>3</sub> SO <sub>3</sub>	6	90	8 1
	@MCM-41	0	50	
4	$ILSO_3H\text{-}TiCl_5$	6	88	8 5
	@MCM-41		00	
5	ILSO <sub>3</sub> H-CoCl <sub>3</sub>	6	64	57
	@MCM-41		04	
6	$ILSO_3H\operatorname{-SnCl}_5$	6	84	81
	@MCM-41		01	
7	$ILSO_3H\text{-}TiCl_5$	4	91	89
	@Ti-MCM-41		51	
8	$ILSO_3H-TiCl_5$	3	93	92
	@Sn-MCM-41			
9	$ILSO_3H-TiCl_5$	4	90	87
	@Fe-MCM-41			
10	ILSO <sub>3</sub> H-TsO	6	86	78
11	ILSO <sub>3</sub> H-HSO <sub>4</sub>	6	87	77
12	ILSO <sub>3</sub> H-CF <sub>3</sub> SO <sub>3</sub>	6	83	72
13	ILSO <sub>3</sub> H-TiCl <sub>5</sub>	6	80	73
14	MCM-41	24	27	21
15	Ti-MCM-41	12	52	49
16	Sn-MCM-41	12	53	51
17	Fe-MCM-41	12	48	44

<sup>*a*</sup> Reaction conditions: benzaldehyde (0.05 mol), aniline (0.05 mol), acetophenone (0.05 mol), catalyst (0.4 g) were stirred in EtOH (10 mL) at room temperature. <sup>*b*</sup> Conversion was determined by LC-MS. <sup>*c*</sup> Isolated yield.

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Based on the above results and the related literatures,<sup>5,7,9,12</sup> a possible mechanism of Mannich reaction is proposed and depicted in Scheme 2. Arylaldehyde is firstly activated by ILSO<sub>3</sub>H-TiCl<sub>5</sub>@Sn-MCM-41 via the coordination of Sn-MCM-41 support with O atom, which can condense with arylamine to give the intermediate imine (III). Meanwhile, the tautomerism of acetophenone and then the coordination with TiCl<sub>5</sub> anion to form the coordinated enolate (I). The imine (III) can be activated by protonation of the SO<sub>3</sub>H, and then reacted with the coordinated enolate (I) undergoes addition to give transition state (IV). Subsequent elimination of the catalyst to afford the desired product. The carbon-carbon bond formation is illustrated in transition state (IV) is considered to be the ratedetermining step. This novel catalyst ILSO3H-TiCl5@Sn-MCM-41 showcases the cooperative catalysis nature. In this case, different substrates can be smoothly converted into the corresponding  $\beta$ aminocarbonyl compounds with low catalyst loading under mild reaction conditions.



Scheme 2 Possible mechanism of Mannich reaction by ILSO $_3$ H-TiCl $_5$ @Sn-MCM-41 cooperative catalysis.

In conclusion, novel multi-functional Ti, Sn, or Fe incorporated MCM-41 supported Brønsted-Lewis acidic ionic liquids were prepared and tested for their catalytic activities in one-pot three-component Mannich reaction. Our studies revealed that Sn incorporated MCM-41 supported dual acidic ionic liquid consisiting SO<sub>3</sub>H cation and TiCl<sub>5</sub> anion displayed excellent catalytic activity in delivering corresponding  $\beta$ -aminocarbonyl compounds in good to excellent yields under mild conditions. Remarkably, the ionic liquids with TiCl<sub>5</sub> Lewis acid anions exhibit better catalytic activities than those of other Brønsted acid or Lewis acid anions, and the novel multi-functional ionic liquid ILSO<sub>3</sub>H-TiCl<sub>5</sub>@Sn-MCM-41 bearing a new cooperative catalysis concept featuring the synergistic effects of the Sn-MCM-41 support, SO<sub>3</sub>H cation and TiCl<sub>5</sub> anion. Moreover, in addition to the tolerance to aromatic amines and aldehydes

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bearing electron-donating or electron-withdrawing groups, the catalyst displayed generality for variability the ketones including acetophenone, 1-(4-methylphenyl)-ethanone, and cyclohexanone. Furthermore, this novel catalytic system can rapidly isolated from the reaction mixture by an external heterogeneous catalysis, and could be successfully recovered by filtration and reused for six runs without significant loss of its catalytic activity. This study provides a new platform based on supported ionic liquids to accomplish the cooperative catalysis comprising the synergistic effects of the supported carriers, cations and anions of ILS.

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### **Graphical Abstract**

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Hong Bo Wang, ‡ Nan Yao, ‡ Long Wang and Yu Lin Hu\*

