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Manganese-Containing Periodic Mesoporous Organosilica with Ionic-Liquid Framework (Mn@PMO-IL): A Powerful, Durable, and Reusable Nanocatalyst for the Biginelli Reaction

Dawood Elhamifar* and Ahmad Shábani[a]

Abstract: The catalytic application of a novel manganese-containing periodic mesoporous organosilica with ionic-liquid framework (Mn@PMO-IL) in the Biginelli reaction was investigated. First, the Mn@PMO-IL nanocatalyst was prepared and characterized by TEM, SEM, X-ray photoelectron spectroscopy, and nitrogen-sorption analysis. The catalyst was then used in the one-pot Biginelli condensation of various aldehydes with urea and alkyl acetoacetates under solvent-free conditions. The corresponding dihydropyrimidone products were obtained in high to excellent yields and selectivities at short reaction times. Moreover, the catalyst was recovered and successfully reused many times with no notable decrease in activity and selectivity.

Introduction

The Biginelli reaction involves one-pot condensation of aldehydes with β-dicarbonyl compounds and urea to synthesize dihydropyrimidones,[1–3] which are very attractive and significant compounds in organic chemistry due to their pharmacological and therapeutic properties such as antibacterial, antitumor, antihypertensive, anti-inflammatory, analgesic, anticancer, antiviral, and anti-HIV activity, as well as efficacy as calcium channel modulators.[2–5] The Biginelli reaction has been traditionally performed under homogeneous conditions with both Brønsted[3,6] and Lewis[3,7,8] acidic catalysts such as HCl, AcOH, trifluoroacetic acid, trifluoromethanesulfonic acid, *para*-toluenesulfonic acid, $TiCl_3$, $BF_3{\cdot}OEt_2$, $ZrCl_4$, $InBr_3$, $InCl_3$, $FeCl_3{\cdot}6\,H_2O$, $NiCl_2{\cdot}6\,H_2O$, $BiCl_3$, Me_3SiCl, $LiClO_4$, LiBr, $Mn(OAc)_3{\cdot}2\,H_2O$, $Cu(OTf)_2$, $CuCl_2{\cdot}2\,H_2O$, $La(OTf)_3$, $Yb(OTf)_3$, $LaCl_3$, and $Sc(OTf)_3$.[3,6–9] However, many of these homogeneous systems are expensive, harmful, and difficult to handle as well as having problems of catalyst recovery and product separation and purification. To overcome these limitations, several strategies using recoverable heterogeneous solid acid catalysts have recently been explored.[10] The reported heterogeneous catalysts have advantages of easy separation and recovery in comparison to their homogeneous counterparts. However, in most cases the activity and efficiency of the catalysts were low, and this necessitates the design and synthesis of highly effective recoverable catalysts for this important three-component reaction.

On the other hand, the fabrication of ordered mesoporous organosilicas (OMOs) in recent decades has been an important achievement in the fields of chemistry and materials science due to the widespread applications of these materials in catalysis, chromatography, gas storage, solid-phase extraction, and so forth.[11] Among the different kinds of OMOs, periodic mesoporous organosilicas (PMOs) have attracted more attention because of their high surface area, high thermal and mechanical stability, and uniform distribution of organic functional groups in their frameworks.[12–14] To date many PMO materials have been prepared by using different functionalized organic precursors and successfully applied as supports for the immobilization and stabilization of organic and inorganic catalysts in chemical processes.[12–16] For example, we recently developed an ionic-liquid-based PMO (PMO-IL) material and investigated its performance in the immobilization and stabilization of palladium and ruthenium catalysts in a number of organic reactions.[16] Our studies showed that the PMO-IL is a powerful and recoverable support for metal catalysts and could be recovered and reused several times with no decrease in activity and efficiency.[16] Considering the aforementioned advantages of PMO-IL nanomaterials and the importance of Biginelli products in drug synthesis, we have now developed a strategy for the preparation of a novel manganese-containing PMO-IL (Mn@PMO-IL) and studied its application in the Biginelli condensation of several aldehydes with urea and alkyl acetoacetates (Scheme 1). The recoverability, reusability, and stability of the catalyst were also studied.

Results and Discussion

The PMO-IL was first prepared according to our previously reported procedure[16d] and then treated with a substoichiometric amount of $Mn(OAc)_3{\cdot}2\,H_2O$ in dimethyl sulfoxide to produce the Mn@PMO-IL nanocatalyst (Scheme 1). The Mn@PMO-IL

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[a] *Dr. D. Elhamifar, A. Shábani*
Department of Chemistry, Yasouj University
Yasouj 75918-74831 (Iran)
Fax: (+98) 741-2227574
E-mail: d.elhamifar@yu.ac.ir

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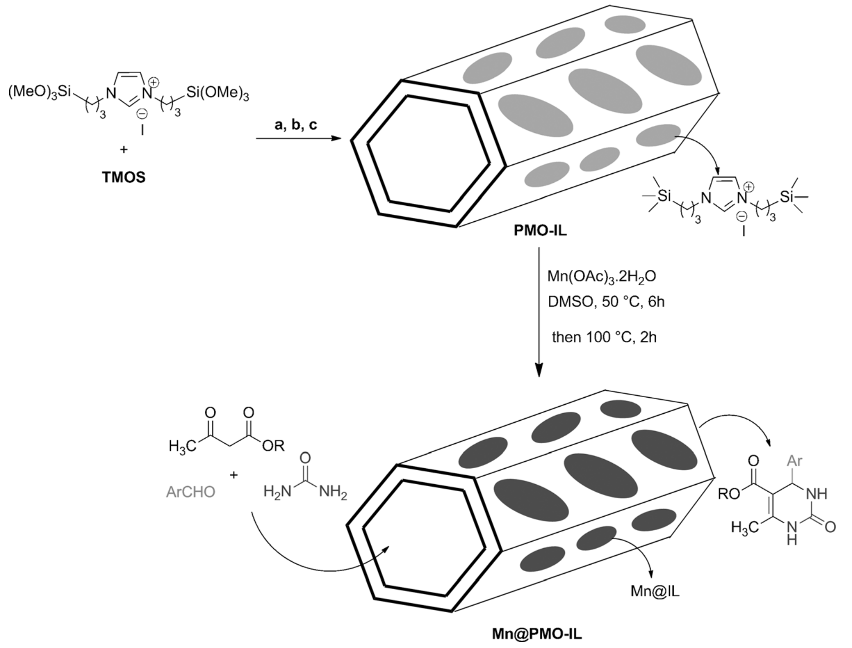


Scheme 1. Preparation of Mn@PMO-IL and its application in the Biginelli reaction. a) H_2O, HCl (2 M), P123, 40 °C, 24 h. b) Static conditions, 100 °C, 72 h. c) Soxhlet extraction of surfactant.

nanocatalyst was characterized to confirm the successful immobilization of manganese acetate in its framework.

Nitrogen adsorption/desorption experiments were performed on the PMO-IL and Mn@PMO-IL materials to compare their surface areas and pore size distributions (Figure 1, Table 1). This revealed a type IV isotherm with H1-type hysteresis loop for both samples, typical of periodic mesoporous materials with high regularity. The BET surface area and pore volume of the Mn@PMO-IL nanocatalyst were both lower than those of its PMO-IL parent (Table 1), confirming successful immobilization of manganese acetate in the material framework. BJH measurements showed a sharp peak and a pore diameter of 10.4 nm for these solid nanostructures, which indicate uniform pore size distributions of the materials (Figure 1 b, Table 1). The excellent regularity of the mesochannels after loading with manganese acetate is proof of the high stability of the PMO-IL nanostructure during the reaction.

Table 1. Structural parameters of PMO-IL and Mn@PMO-IL materials determined from nitrogen-sorption experiments.

Sample	BET surface area [$m^2 g^{-1}$]	Pore diameter [nm]	Pore volume [$cm^3 g^{-1}$]
PMO-IL	655	10.4	1.20
Mn@PMO-IL	550	10.4	0.94

Scanning electron microscopy (SEM) images of PMO-IL and Mn@PMO-IL materials were recorded to compare their surface morphologies (Figure 2 a and b). These results showed that PMO-IL has a ropelike structure with high regularity and a diameter of 2–4 μm, while Mn@PMO-IL has a uniform wormlike structure, which indicates that loading with manganese acetate species significantly affects the surface morphology of the mesostructure, although the regularity is maintained. The TEM image of the Mn@PMO-IL material showed a well-ordered rodlike structure of the channels with two-dimensional hexagonal array (Figure 2 c). This observation is in good agreement with the nitrogen sorption experiment and confirms the uniformity and stability of the mesostructure under the applied reaction conditions. In the next study, the Mn@PMO-IL nanomaterial was investigated by X-ray photoelectron spectroscopy (XPS). The XP spectrum showed peaks at binding energies of 103.4 eV (Si 2p), 284.5 eV (C 1s), and 532 eV (O 1s) proving the successful incorporation of the expected elements in the material framework (Figure 3). In addition, Mn $2p_{1/2}$ and Mn $2p_{3/2}$ peaks were observed at 654.2 and 642.6 eV, respectively (Figure 3 a and b), which are reasonably far from those of manganese metal with Mn $2p_{1/2}$ at 649.25 and Mn $2p_{3/2}$ at 638 eV.[17] The Mn $2p_{3/2}$ peak of MnO_2 is observed at 642.2 eV.[17] This means that the manganese in Mn@PMO-ILis strongly bound to electronegative atoms. In other words, the Mn electrons of Mn@PMO-IL sample are more strongly bound than those of MnO_2. Elemental analysis of the Mn@PMO-IL catalyst showed that the manganese loading on the solid surface is 0.3 mmol g^{-1}.

After characterization, the Mn@PMO-IL nanocatalyst was used in the Biginelli condensation of benzaldehyde with urea and ethyl acetoacetate as model reaction (Table 2). This study illustrated that the progress of the reaction is strongly affected by catalyst loading and reaction temperature. The dramatic in-

Table 2. Effect of different parameters on the Biginelli reaction of benzaldehyde with urea and ethyl acetoacetate.[a]

Entry	Catalyst	Catalyst loading	T [°C]	Yield [%][b]
1	Mn@PMO-IL	20 mg (0.6 mol %)	25	<5
2	Mn@PMO-IL	20 mg (0.6 mol %)	45	35
3	Mn@PMO-IL	20 mg (0.6 mol %)	75	97
4	Mn@PMO-IL	15 mg (0.45 mol %)	75	65
5	Mn@PMO-IL	10 mg (0.3 mol %)	75	40
6	PMO-IL	20 mg	75	26
7	SBA-15	20 mg	75	trace
8	Mn@SBA-15	0.6 mol %	75	66
9	Mn@SiO_2	0.6 mol %	75	62

[a] Reaction conditions: benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.5 mmol), 45 min. [b] Yields of isolated products.

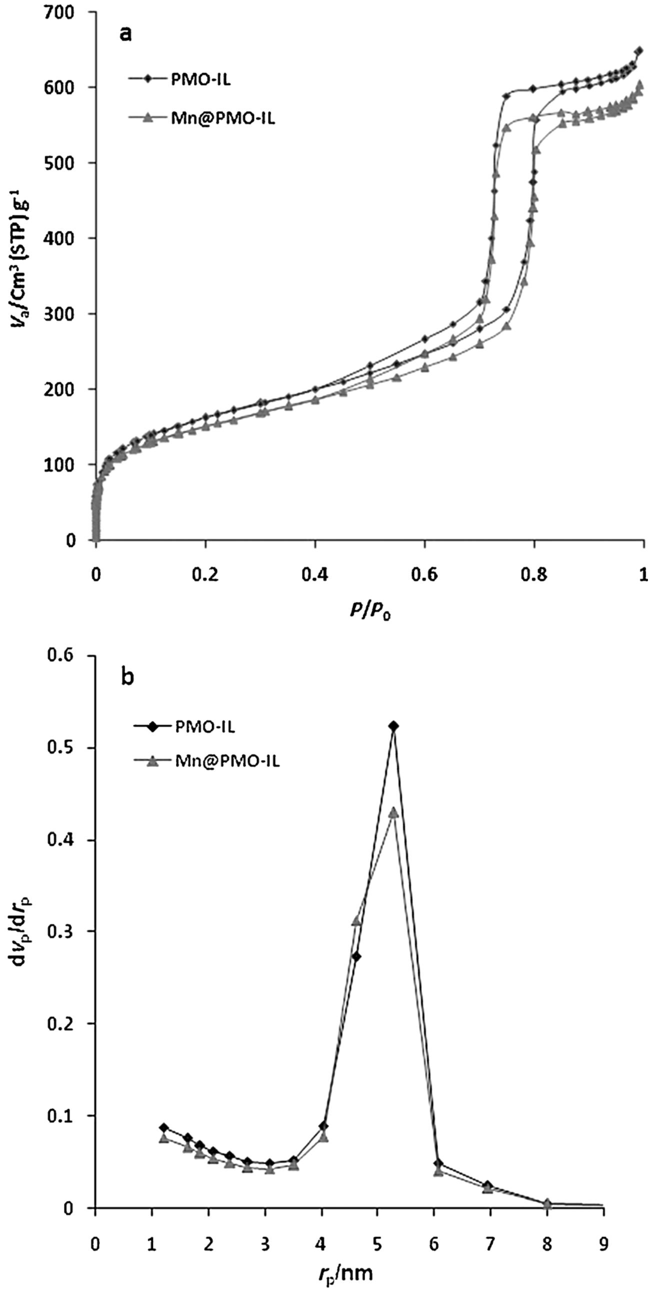


Figure 1. a) Nitrogen adsorption/desorption and b) pore size distribution isotherms of PMO-IL and Mn@PMO-IL.

crease in the rate of substrate conversion on increasing the temperature from 25 to 75 °C confirms that the temperature directly affects the efficiency of the catalyst (Table 2, entries 1–3). On increasing the amount of catalyst from 0.3 to 0.6 mol% a remarkable increase in the yield was observed (Table 2, entries 3–5), which proves that the progress of the reaction is mainly affected by the catalyst loading. To reveal the individual effects of the ionic-liquid groups and manganese sites on the reaction, the efficiency of the Mn@PMO-IL catalyst was compared with those of PMO-IL and an ionic-liquid-free SBA-15 material (Table 2, entry 3 versus entries 6 and 7). In the presence of PMO-IL, 26% of the product was obtained, while SBA-15 gave trace amount of the desired product under the same conditions as the Mn@PMO-IL catalyst. These results clearly showed that the reaction cycle is mainly catalyzed by manganese species immobilized on the PMO-IL nanostructure. Furthermore, the higher activity of PMO-IL in comparison to SBA-15 is attributed to ionic-liquid groups incorporated in the PMO-IL mesochannels, which may catalyze the reaction

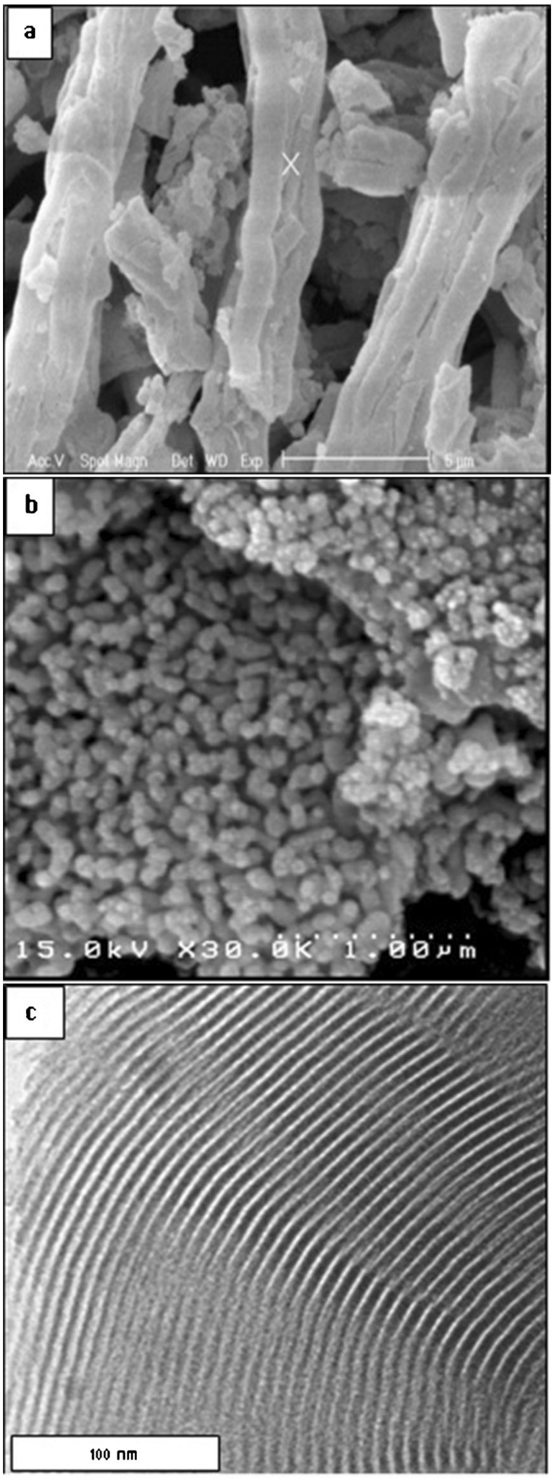


Figure 2. a) SEM image of PMO-IL. b) SEM image of Mn@PMO-IL. c) TEM image of Mn@PMO-IL.

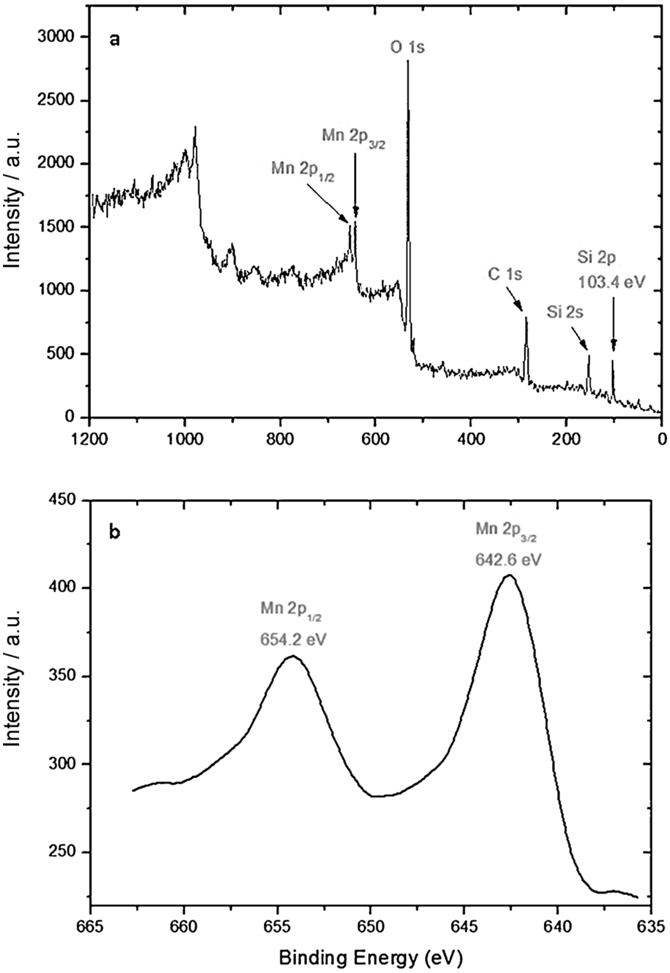
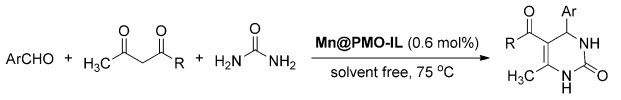


Figure 3. a) XP survey spectrum of Mn@PMO-IL. b) Mn 2p spectrum of Mn@PMO-IL.

Table 3. Preparation of dihydropyrimidone derivatives in the presence of Mn@PMO-IL.[a]

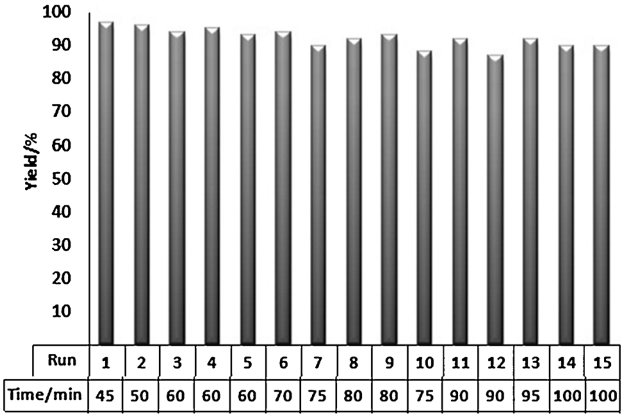


Entry	Ar	R	*t* [min]	Yield [%][b]	M.p.
1	Ph	OEt	45	97	203–205
2	Ph	OMe	45	95	211–213
3	4-Cl-C_6H_4	OEt	50	96	212–214
4	2-Cl-C_6H_4	OEt	65	90	217–220
5	2-Cl-C_6H_4	OMe	65	88	252–254
6	3-Br-C_6H_4	OEt	55	96	193–195
7	3-Br-C_6H_4	OMe	55	97	215–218
8	4-CN-C_6H_4	OEt	60	95	204–206
9	2-NO_2-C_6H_4	OEt	65	87	220–221
10	4-Me-C_6H_4	OEt	45	95	216
11	4-Me-C_6H_4	OMe	45	96	202–204
12	4-MeO-C_6H_4	OEt	45	97	204–206
13	4-MeO-C_6H_4	OMe	45	97	193–195
14	2-MeO-C_6H_4	OEt	55	87	257–259
15	2-MeO-C_6H_4	OMe	55	88	282–284
16	4-OH-C_6H_4	OEt	60	84	228
17	pyrene-1-carbaldehyde	OMe	120	trace	–

[a] Reaction conditions: aldehyde (1 mmol), ethyl/methyl acetoacetate (1 mmol), urea (1.5 mmol). [b] Yields of isolated products.

through the acidic hydrogen atom on the imidazolium ring (–NCHN–).[9] In another study, the same amount of manganese was immobilized on SBA-15 and amorphous silica materials to afford Mn@SBA-15 and Mn@SiO_2 catalysts. Comparative efficiency tests were then performed on these catalysts in the Biginelli reaction of benzaldehyde with urea and ethyl acetoacetate under the same conditions as before. For the same reaction time as Mn@PMO-IL, Mn@SBA-15 and Mn@SiO_2 gave 66 and 62 % yields of the desired product, respectively (Table 2, entries 8 and 9), which confirms that the efficiency of Mn@PMO-IL is much better than those of Mn@SBA-15 and Mn@SiO_2. These results reveal that PMO-IL is an effective and powerful material for immobilization of the Mn catalyst and indicate the valuable effect of the IL moieties in the catalytic process. These observations may be attributed to the synergistic effect between the PMO-IL and the immobilized manganese catalyst system. On the basis of these studies, 0.6 mol % of Mn@PMO-IL catalyst, 75 °C, and no solvent were chosen as optimum conditions. Under these conditions, the activity of the catalyst was then investigated in the Biginelli reaction of a number of aldehyde substrates with alkyl acetoacetates and urea (Table 3). Benzaldehyde (Table 3, entries 1 and 2) gave excellent yields of the corresponding 1,3-dihydropyrimidinones at short reaction times. The other aromatic compounds bearing electron-withdrawing groups, namely, 4-chlorobenzaldehyde (Table 3, entry 3), 2-chlorobenzaldehyde (Table 3, entries 4 and 5), 3-bromobenzaldehyde (Table 3, entries 6 and 7), 4-cyanobenzaldehyde (Table 3, entry 8), and 2-nitrobenzaldehyde (Table 3, entry 9), also gave excellent yields of Biginelli products. Furthermore, aromatic aldehydes bearing electron-donating groups, such as 4-methylbenzaldehyde (Table 3, entries 10 and 11), 4-methoxybenzaldehyde (Table 3, entries 12 and 13), 2-methoxybenzaldehyde (Table 3, entries 14 and 15), and 4-hydroxybenzaldehyde (Table 3, entry 16), also afforded high yields of the corresponding coupling adducts under the same reaction conditions as above. Significantly, the more sterically demanding *ortho*-substituted compounds, which are usually less reactive substrates in organic transformations, were also smoothly converted to their corresponding products (Table 3, entries 4, 5, 9, 14, and 15). These results illustrate the high performance of the designed catalyst for the preparation of a wide range of Biginelli products bearing different functional groups, which are important in the fields of pharmacology and chemistry. To study the substrate selectivity of the catalyst, the reactivity of a bulky aldehyde, namely, pyrene-1-carbaldehyde, was investigated under the same conditions as the other aldehyde substrates (Table 3, entry 17). After 2 h, only a trace amount of product was observed. This confirms that the reaction mainly occurs inside the pores and proves the high size selectivity of the catalyst, which is due to the location of the reactive catalytic centers inside the mesochannels of PMO-IL.

Since recoverability and reusability of the catalyst are important in both academic and industrial chemistry, the recyclability and reusability of the Mn@PMO-IL catalyst were investigated in the Biginelli reaction of benzaldehyde with urea and ethyl acetoacetate under standard reaction conditions. After the completion of the reaction, 10 mL of hot ethanol was added and the resulting solution was filtered and the residue was washed thoroughly with ethanol. The recovered catalyst (RMn@PMO-IL) was then reused under the same conditions as above for at least 14 reaction cycles and furnished the desired product in high to excellent yield and selectivity (Figure 4), indicating the high stability, durability, and reusability of the catalyst during the reaction process. This can be attributed to the high surface area of the PMO-IL nanomaterial and the ionic-liquid nature of the mesochannels, which effectively immobilize the manganese species and protect them against leaching, agglomeration, and deactivation.[16] Nitrogen adsorption/desorption analysis of the recovered catalyst after five reaction cycles was also performed to verify porosity, stability, and regularity of the mesostructure (Figure S1 of the Supporting Information). The surface area, pore volume, and pore diameter of RMn@PMO-IL were 404 $m^2 g^{-1}$, 0.85 cm^3, and 9.1 nm, respectively (Table S1 of the Supporting Information). Moreover, the BJH isotherm of this material showed a single peak with high intensity, indicating that the regularity of the nanostructure is maintained under the applied reaction conditions. A TEM image of the RMn@PMO-IL nanocatalyst showed a uniform rodlike structure with high regularity, which is in good agreement with the nitrogen-sorption data (Figure 5). These observations strongly confirm high stability of the catalyst during the reaction.



Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Time/min	45	50	60	60	60	70	75	80	80	75	90	90	95	100	100

Figure 4. Reusability of the Mn@PMO-IL catalyst in the Biginelli reaction of benzaldehyde with ethyl acetoacetate and urea.

Conclusion

A manganese-containing imidazolium-based periodic mesoporous organosilica (Mn@PMO-IL) was prepared and characterized, and its catalytic performance was investigated in the Biginelli reaction. Nitrogen-sorption analysis and TEM images showed high regularity and uniform pore size distribution of the catalyst. The catalyst was effectively applied in the Biginelli reactions of various aldehydes with urea and alkyl acetoacetates, which gave the corresponding products in high to excellent yields and selectivities. Moreover, the catalyst was successfully recovered and reused at least 14 times without notable decrease in activity and selectivity. The nitrogen adsorption/desorption data and TEM image of the recovered nanocatalyst (RMn@PMO-IL) clearly showed high regularity and uniform pore size distribution of the mesochannels. These observations could be attributed to the ionic-liquid nature of the mesostructure, which protects catalytic manganese species against any leaching, destabilization, and deactivation. Other advantages of this catalyst system include high surface area, high conversion rate, solvent-free conditions, easy product separation, and high catalyst durability. Investigations of other applications of this catalyst system are underway.

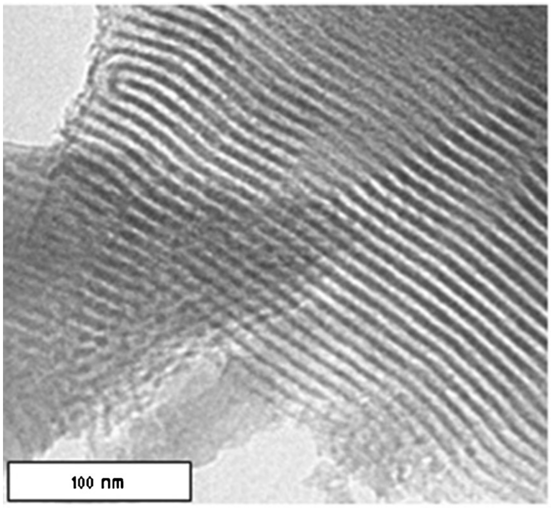


Figure 5. TEM image of RMn@PMO-IL catalyst after the fifth reaction cycle.

Experimental Section

Preparation of Mn@PMO-IL nanocatalyst

Firstly, the PMO-IL nanostructure was prepared according to our previous procedure.[16d] Then 1 g of this material was homogeneously dispersed in DMSO and treated with $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol) at 50 °C for 6 h and then at 100 °C for 2 h. After cooling the reaction solution to room temperature, the product was filtered and washed thoroughly with ethanol to remove unsupported $Mn(OAc)_3{\cdot}2H_2O$. The resulting powder was dried at 60 °C for 12 h under vacuum to give Mn@PMO-IL.

General procedure for the Biginelli reaction with Mn@PMO-IL nanocatalyst

Aldehyde (1 mmol), alkyl acetoacetate (1 mmol), and urea (1.5 mmol) were added to a round-bottomed flask with stirring at 25 °C for 5 min, and then 0.6 mol% of Mn@PMO-IL nanocatalyst was added and the resulting mixture stirred at 75 °C in an oil bath for an appropriate time (see Table 3). After completion of the reaction, 5 mL of hot ethanol was added and the solution was filtered while hot. The filtrate was cooled to precipitate a solid product.

The crude product was then recrystallized from 96% ethanol to give pure crystals in high to excellent yields.

General procedure for the recovery of Mn@PMO-IL nanocatalyst in the Biginelli reaction

Typically, the Biginelli reaction of benzaldehyde (5 mmol), ethyl acetoacetate (5 mmol) and urea (7.5 mmol), was performed in the presence of 0.6 mol% of Mn@PMO-IL nanocatalyst under standard conditions. After the completion of the reaction, 10 mL of hot ethanol was added and the solution was filtered, then the residue was washed thoroughly with ethanol. The obtained material was dried at 80 °C and denoted as recovered catalyst (RMn@PMO-IL). The RMn@PMO-IL was reused under the same conditions as above for at least 14 reactions and gave the desired product in high yield with no decrease in activity and selectivity.

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Keywords: Biginelli reaction · heterogeneous catalysis · ionic liquids · manganese · mesoporous materials

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