Periodic mesoporous organosilica (PMO-ICS): a highly efficient nanocatalyst for the one-pot multicomponent reactions

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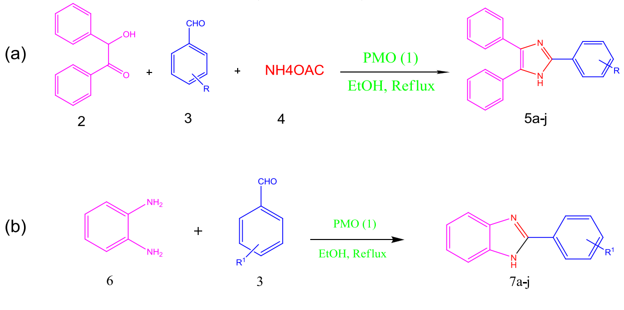
Abstract: Isocyanurate bridging periodic mesoporous organosilica (PMO-ICS) was shown to be a highly active and efficient recyclable catalyst for three-component synthesis of imidazole derivatives from benzoin, different aldehydes and ammonium acetate under mild reaction conditions in short reaction times and good to excellent yields in EtOH. Also, benzimidazole derivatives were efficiently prepared from *o*-phenylenediamine and different aldehydes in the presence of PMO-ICS. Moreover, the catalyst was also recovered and reused at least four times without significant decrease in its reactivity. The PMO-ICS catalyst was characterizred by Fourier transformer infrared (FTIR) spectroscopy, thermogravimetry analysis (TGA), powder X-ray diffraction (XRD) and nitrogen adsorption–desorption isotherms (NADI) techniques as well as scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Keywords: Green chemistry, Heterogeneous catalyst, Periodic mesoporous organosilica (PMO), Multicomponent reactions, Imidazoles.

Introduction

The use of heterogeneous catalysts has become highly desirable in recent years, because they incorporate many green chemistry principles.[1] in 1999, mesoporous organosilica hybrids were prepared from bridged organosilane precursors ((ŔO)$_3$Si–R–Si(OŔ)$_3$; R: organic bridging group, Ŕ: methyl or ethyl). Such mesoporous hybrids prepared from bridged organosilane precursors have been classified as periodic mesoporous organosilica (PMO).[2] PMOs are very attractive as support for heterogeneous solid catalysts in fine chemicals synthesis among others. In addition, other unique properties of PMOs such as high loading of uniform distribution of organic functional groups in their framework, superior thermal stability, non-toxicity, biodegradability, reusability, and stability against air and moisture make them attractive candidate for the widespread applications in catalysis, chromatography, solid-phase extraction, electronic, sensor technology, gas storage, and so forth.[3-7]

In the past years, a few methods have described in the one-pot multicomponent synthesis of 2,4,5-trisubstituted imidazoles and benzoimidazoles based on catalysts such as acetic acid, KH_2PO_4,[8] dodecylbenzenesulfonic acid (p-DBSA),[9] L-proline,[10] $InCl_3\cdot 3H_2O$,[11] $NiCl_2.6H_2O/Al_2O_3$,[12] $KAl(SO_4)_2$,[13] $ZnCl_2$,[14] molecular iodine,[15] Wells-Dawson heteropolyacid supported on silica (WD/SiO_2),[16] However, many of these approaches have limitations in terms of the use of excess amounts of expensive catalysts, product diversity and longer reaction times, unsatisfactory yields, difficult work-up, unavoidable metal pollution, significant amounts of waste materials, and low selectivity. In this work, we wish to report the catalytic application of an isocyanurate-based periodic mesoporous organosilica (PMO-ICS) material as an efficient and green nanocatalyst for the synthesis of 2,4,5-trisubstituted imidazoles and benzoimidazoles under reflux conditions (Scheme 1).



Scheme 1 **(a)** One-pot three-componet reaction of benzoin **2** and different aldehydes **3** with NH_4OAc **4** **(b)** Condensation of different aldehydes **3** with 1,2-phenylenediamine **6.**

Results and discussion

Synthesis of trisubstituted imidazoles catalyzed by Periodic mesoporous organosilica (PMO-ICS)

The synthesis of PMO-ICS has been achieved using known procedure described by Jaroniec and his co-workers. This catalyst was then characterized with some techniques such as infrared (IR) spectroscopy, thermal gravimetric analysis (TGA), powder X-ray diffraction (PXRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM).
BET analysis of PMO-ICS showed specific surface area close to 570 m^2/g, pore size≈ 4.1 and volume pore≈ 5.

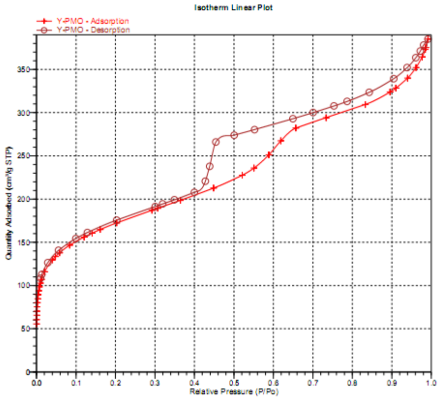


Fig 1 BET analysis of PMO-ICS nanocatalysts

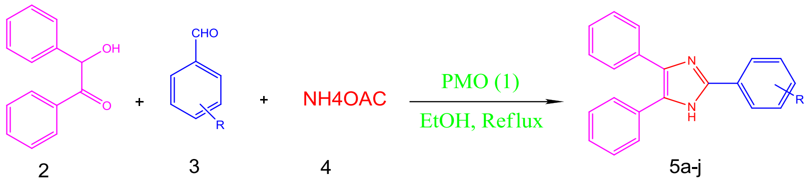
To show the efficiency of Periodic mesoporous organosilica (PMO-ICS) as nanocatalyst, in our preliminary experiments, reaction of 4-chlorobenzaldehyde (1 mmol), benzoin (1 mmol) and ammonium acetate (2.5 mmol) was investigated as model reaction. We investigated the optimal conditions regarding the best amount catalyst, different solvents and temperature for the synthesis of 2,4,5-trisubstituted imidazole derivatives. The results have been summarized in Table 1. It was observed that only 60% of the desired trisubstituted imidazole (**5a)** was formed in the absence of PMO-ICS even under reflux conditions (Table 1, entries 1 and 2). However, the use of PMO-ICS as catalyst, improved the yield of the desired product (**5a**) slightly at room temperature (entry 3). Interestingly, the use of PMO-ICS with 20 mg loading improved yield of the desired product (**5a**) under reflux conditions (entry 4). The study of model reaction in other solvents such as, H_2O and THF using PMO-ICS (1) with 20 mg loading under reflux conditions afforded lower yield of the desired product (**5a**) (entry 5-6). Finally, the effect of catalyst loading on the completion of the reaction was studied (entries 4, 7-8). As it can be seen, 20 mg loading of PMO-ICS as catalyst gave the best results among all. Also it was observed that product (**5a**) was obtained with lower yield and longer reaction time under Solvent-free conditions (entry 9).

Table 1 Optimization of conditions in the reaction of benzoin **2**, 4-chlorobenzaldehyde **3a** and NH_4OAc under different conditions.

Entry	Amount of Catalysts **(1a)**/mg	Solvent	Temp.(°C)	Time (min)	Yeild ^{b} (%)
1	-	EtOH	r.t	240	Trace
2	-	EtOH	reflux	240	60
3	20	EtOH	r.t	180	70
4	20	EtOH	reflux	25	97
5	20	H_2O	reflux	120	45
6	20	THF	reflux	100	80
7	15	EtOH	reflux	90	92
8	25	EtOH	reflux	90	88
9	20	-	100	55	86

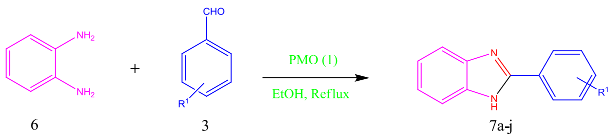
In order to demonstrate the scope of this novel efficient catalyst and protocol, the optimized reaction conditions were developed to other aromatic, heterocyclic or α,β-unsaturated aldehydes (5a-j). The results are listed in Table 2. As it can be seen, quantitative yields were obtained for the desired products (1or 6) under the optimized conditions in short reaction times. Furthermore, after completion of the reaction (monitored by TLC), the catalyst 1 was simply isolated from the reaction mixture by filtration.
At the next stage, 1,2-phenylenediamine was used for more developing of the scope of the invented protocol, through reaction between 1,2-phenylenediamine with various aldehydes. The results are summarized in Table 3. Both aromatic carbocyclic and heterocyclic aldehydes containing electron-withdrawing and electron-donating groups underwent this condensation to furnish trisubstituted imidazoles in high to excellent yields.

Table 2 Isocyanurate bridging periodic mesoporous organosilica (PMO-ICS) catalyzed one-pot three-componet synthesis of imidazoles from benzoin **2**, different aldehydes **3** with NH_4OAc under optimized conditions.



Entry	Aldehyde	Product	Time (min)	Yield (%)
1	4-Chlorobenzaldehyde	**5a**	25	97
2	2-Chlorobenzaldehyde	**5b**	35	81
3	4-Nitrobenzaldehyde	**5c**	35	94
4	Benzaldehyde	**5d**	60	81

Table 3 Condensation of different aldehydes **3** with 1,2-phenylenediamine **6** catalyzed by PMO-ICS under Optimized condition**.**



Entry	R^1 Aldehyde **3**	Product	Time (min)	Yeild^b (%)
1	4-Chlorobenzaldehyde	**7a**	30	93
2	2-Chlorobenzaldehyde	**7b**	30	90
3	4-Nitrobenzaldehyde	**7d**	50	87
4	Benzaldehyde	**7g**	40	92
5	4-Methylbenzaldehyde	**7h**	65	88

Conclusions

We have introduced the catalytic application of a containing isocyanurate-based ordered mesoporous organosilica (PMO-ICS) in the synthesis of benzimidazole and imidazole derivatives. Therefore, the attractive features of this procedure are simple procedure, Low catalyst loading, short reaction times, high yields, elimination of toxic organic solvents, simple workup, reusability and re-activity of the catalyst and simple purification of the products.

Acknowledgment

The authors thank the Research Committee of Iran University of Science and Technology, for financial support of this work.

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