

Periodic mesoporous organosilica: as a novel and efficient nanocatalyst for the one-pot synthesis of 3,3'-arylmethylene-bis-4-hydroxycoumarins in water

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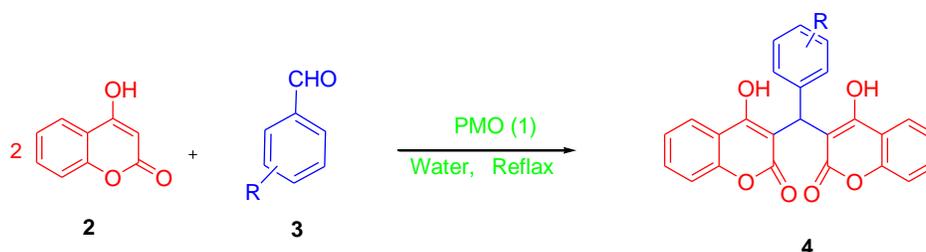
Abstract: Isocyanurate bridging periodic mesoporous organosilica (PMO-ICS) was shown to be a highly active and efficient recyclable catalyst for the synthesis of biscoumarin derivatives from 4-hydroxy coumarin, different aldehydes under mild reaction conditions in short reaction times and good to excellent yields in H₂O. Moreover, the catalyst was also recovered and reused at least four times without significant decrease in its activity. The PMO-ICS catalyst was characterized by Fourier transformer infrared (FTIR) spectroscopy, thermogravimetry analysis (TGA), powder X-ray diffraction (XRD) and nitrogen adsorption-desorption isotherms (NADI) techniques as well as field emission scanning electron microscopy (FESEM). Compared to the classical methodologies, this method illustrated significant advantages including low loading of the catalyst, avoiding the use of toxic transition metals or reactive reagents for modification of the catalytic activity, short reaction times, high to excellent yields, easy separation and purification of the products, and reusability of the catalyst.

Introduction

The use of heterogeneous catalysts has become highly desirable in recent years, because they incorporate many green chemistry principles. In 1999, mesoporous organosilica hybrids were prepared from bridged organosilane precursors ((RO)₃Si-R-Si(OR)₃; R: organic bridging group, R': methyl or ethyl). Such mesoporous hybrids prepared from bridged organosilane precursors have been classified as periodic mesoporous organosilica (PMO). 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 identical 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 extensive applications in catalysis, chromatography, solid-phase extraction, electronic, sensor technology, gas storage, and so forth.¹

In the past years, a few methods have described for the one-pot synthesis of 3,3'-arylmethylene-bis-4-hydroxycoumarins based on catalysts such as molecular iodine,² DBU,³ MnCl₂,⁴ POCl₃ in dry DMF,⁵ Et₂AlCl₃,⁶ SO₃H functionalized ionic liquids,⁷ [bmim][BF₄],⁸ TBAB,⁹ Zn(Proline)₂,¹⁰ SDS,¹¹ refluxing in ethanol or acetic acid,¹² microwave condition,¹³ etc. 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 3,3'-arylmethylene-bis-4-hydroxycoumarins under reflux conditions in H₂O. (Scheme 1)



Scheme 1 One-pot synthesis of 3,3'-arylmethylene-bis-4-hydroxycoumarins from reaction of 4-hydroxycoumarin **2** and different aldehydes **3**.

Results and discussion

The synthesis of PMO-ICS has been achieved using known procedure described by Jaroniec and his co-workers.¹⁴ 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 m²/g, pore size \approx 4.1 nm.

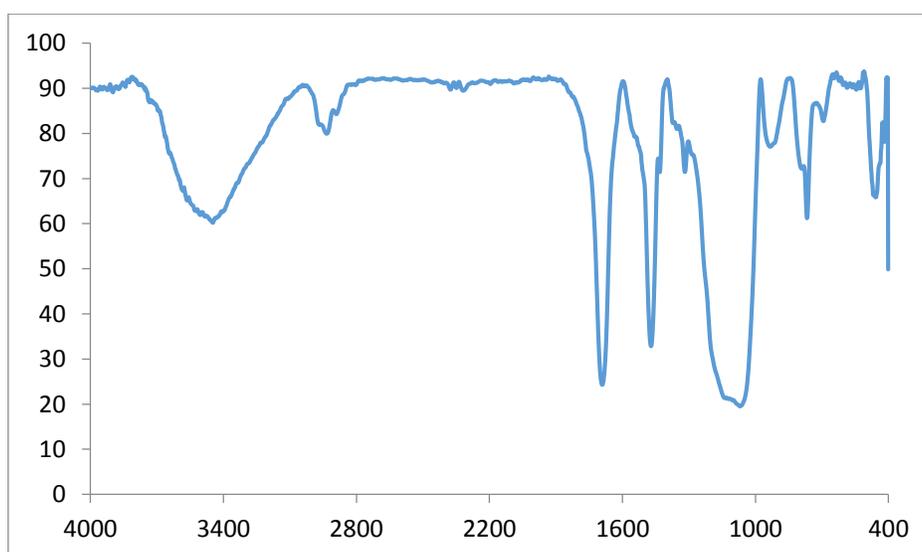


Fig. 1 FT-IR Spectrum of PMO-ICS

To show the efficiency of Periodic mesoporous organosilica (PMO-ICS) as nanocatalyst, in our preliminary experiments, reaction of 4-chlorobenzaldehyde (1 mmol), and 4-hydroxy coumarin (2 mmol) was investigated as model reaction. The reaction conditions were optimized with regard to the best amount catalyst, different solvents and temperature for the synthesis of biscoumarin derivatives. The results have been summarized in Table 1. It was observed that only 20% of the desired product (**4a**) was formed in the absence of PMO-ICS even under reflux conditions after 4h (Table 1, entries 1-2). Interestingly, after addition of 10 mg of the catalyst (**1**) the yield of the desired product **4a** was increased significantly under similar reaction conditions in refluxing H₂O compared to catalyst-free conditions (entry 3). Furthermore, the use of 15 mg of PMO-ICS (**1**) as catalyst loading, improved the yield of the desired product (**4a**) under reflux conditions (entry 4). The study of model reaction in other solvents such as, EtOH and CH₃CN using PMO-ICS (**1**) with 15 mg loading under reflux conditions afforded lower yield of the desired product (**4a**) (entry 6-7). Finally, the effect of catalyst loading on the completion of the reaction was studied (entries 3,4 and 5). As it can be seen, 15 mg loading of PMO-ICS as catalyst gave the best results among all. Also it was observed that product (**4a**) was obtained with lower yield and longer reaction time under solvent-free conditions (entry 8).

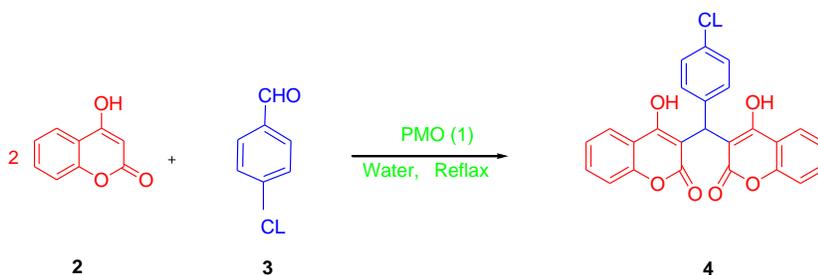


Table 1 Optimization of conditions in the reaction of 4-hydroxy coumarin (**2**) with 4-chlorobenzaldehyde (**3a**) under different conditions^a.

Entry	Catalyst 1 loading (mg)	Solvent	Temp. (°C)	Time (min)	Yield ^b (%)
1	-	H ₂ O	r.t	240	Trace
2	-	H ₂ O	reflux	240	20
3	10	H ₂ O	reflux	20	85
4	15	H ₂ O	reflux	20	94
5	20	H ₂ O	reflux	20	92
6	15	EtOH	reflux	120	41
7	15	CH ₃ CN	reflux	100	35
8	15	-	90	180	45

^aReaction conditions: 4-hydroxy coumarin (**2**, 2 mmol), 4-Chlorobenzaldehyde (**3a**, 1 mmol) in the presence of PMO-ICS (**1**). ^bIsolated Yields.

In order to demonstrate the scope of this novel efficient catalyst and protocol, the optimized reaction conditions were developed to other aromatic and heterocyclic aldehydes. The results are listed in Table 2. As it can be seen, good to excellent yields were obtained for the desired products (**4a-e**) under the optimized conditions in shorter reaction times. Furthermore, after completion of the reaction (monitored by TLC), the catalyst **1** was simply isolated from the reaction mixture by filtration.

Table 2 Isocyanurate bridging periodic mesoporous organosilica (PMO-ICS) catalyzed one-pot synthesis of biscoumarin derivatives.

Entry	Aldehyde 3	Product 5	Time (min)	Yield ^{b,c} (%)
1	4-Chlorobenzaldehyde (3a)	4a	15	96
2	2-Nitrobenzaldehyde (3b)	4b	40	90
3	4-Nitrobenzaldehyde (3c)	4c	15	90
4	4-Pyridine carbaldehyde (3d)	4d	20	88
5	Benzaldehyde (3e)	4e	20	94

Reaction conditions: 4-hydroxy coumarin (**2**, 2 mmol), 4-chlorobenzaldehyde (**3a**, 1 mmol) in the presence of 15 mg PMO-ICS (**1**) and H₂O (1.5 mL).

Experimental

General

All chemicals were purchased from Merck or Aldrich and used as received except for benzaldehyde which a fresh distilled sample was used. Field emission scanning electron microscopy (FESEM) images was obtained using Sigma instrument of Zeiss Company, Germany. The BET specific surface area of the catalyst was obtained using an equipment ASAP 2020TM micromeritics. Thermal gravimetric analysis (TGA) was performed by means of Bahr company STA 504 instrument.

General procedure for the synthesis of PMO-ICS

The synthesis of PMO-ICS (**1**) has been achieved using known procedure described by Jaroniec and his co-workers. In a typical experiment, 2.0 g of Pluronic P123 (Aldrich, average Mw \cong 5800 Dalton) was dissolved in a mixture of 20 mL of deionized water and 60 g of 2 M HCl solution. Then, 0.01 mol (3.08 g) of tris [3-trimethoxysilyl] propyl] isocyanurate (ICS, Aldrich) and 0.01 mol tetraethoxysilane (TEOS, 3.12 g)) was added dropwise into that solution. The obtained mixture was stirred at the constant rate and room temperature for 20 h. The mixture was aged at 100 °C for 48 h without stirring. The solid was filtered off and washed thoroughly with hot EtOH/H₂O (60 mL of EtOH 96% and 2 mL of 12 M HCl) using a soxhlet apparatus for 72 h to remove the surfactant molecules. The obtained white powder was dried in air at 100 °C overnight.

General procedure for the synthesis of biscoumarin derivatives

In a 5 mL round-bottomed flask, 4-hydroxy coumarin (**2**, 2 mmol), 4-chlorobenzaldehyde (**3a**, 1 mmol) and 15 mg PMO-ICS (**1**) were added to H₂O (1.5 mL). The obtained mixture was stirred at reflux conditions for times indicated in Table 2. After completion of the reaction monitored by TLC (eluent: EtOAc: n-hexane), ethylacetate (3 mL) was added and the obtained mixture was heated and filtered off to separate the solid catalyst **1**. Hexane was added dropwise to the filtrate at 50 °C to give pure crystals of the desired products **4a-e** in 88–96% yields based on the starting aldehyde.

Conclusions

We have reported the catalytic application of a containing isocyanurate-based ordered mesoporous organosilica (PMO-ICS) in the synthesis of biscoumarin derivatives. Therefore, the noteworthy features of this method 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.

Acknowledgements

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