Nano-isocyanurate-Periodic mesoporous organosilica (PMO): a heterogeneous catalyst for three-component synthesis of tetrahydrobenzo[*b*]pyrans in water

Mohammad G. Dekamin*, Alireza Rezazadeh-Shendabadi, Abulfazl Seyedsadjadi, Amene Yaghoubi

Department of Chemistry, Iran University of Science and Technology, Pharmaceutical and Biologically-Active Compounds Research Laboratory, Tehran, Iran.

mdekamin@iust.ac.ir

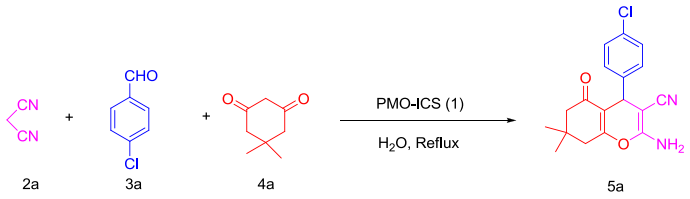
Abstract: Isocyanurate containing periodic mesoporous organosilicas (ICS-PMO) without any post-modification was used as a novel heterogeneous catalyst for synthesis of tetrahydrobenzo[*b*]pyran derivatives via one-pot three-component condensation of aromatic aldehydes with malononitrile (or ethyl cyanoacetate) and dimedone. The catalyst was characterized by FT-IR Spectroscopy, TEM, SEM and BET techniques. Products were obtained in short reaction times with excellent yields in water under reflux conditions. The catalyst could be recycled and reused for several times without noticeably decreasing the catalytic activity.

Keywords: Green chemistry Heterogeneous catalyst; PMO; Tetrahydrobenzo[b]pyran derivatives; Synthesis in water.

Introduction

Green chemistry can be recognized as a pioneering approach, which widely reports intrinsic atom economy, energy savings, waste reduction, easy work-ups, and the avoidance of hazardous chemicals [1]. In this context, the efficiency of heterogeneous catalysis in organic synthesis could be considerably improved by employing nano-sized catalysts due to their extremely small size and large surface to volume ratio [2]. The development of environmentally benign, efficient, and economical methods for the synthesis of biologically interesting compounds remains a significant challenge in synthetic chemistry [3]. Along this line, PMOs have received great attention as heterogeneous catalysts. A PMO is a special type of hybrid organic-inorganic materials, in which organic moieties are integrated into the silica framework. PMOs can be synthesized by using various structure directing agents such as ionic surfactants, oligomeric surfactants, and nonionic block copolymers. Because of uniform distribution of organic bridging groups inside mesopore walls, PMOs become very promising materials for potential applications ranging from highly selective adsorbents and catalysts to sensing devices and hosts for biomolecules.

On the hand, water has been applied in organic reaction as solvent, and it has several advantages such as low cost, safety, non-polluting nature, and operational simplicity [4]. Furthermore, tetrahydrobenzo [*b*] pyran derivatives are an important class of heterocyclic compounds having important pharmaceutical and biological activity. These compounds are used as anticancer, anticoagulant, diuretic, spasmolytic, and, etc [5]. Realizing the importance of 4H-pyran derivatives, several synthetic methods have been reported with the aim of obtaining more biologically potent heterocyclic systems using different catalysts including nano-sized magnesium oxide [6], silica-bonded 1,4-diazabicyclo [2.2.2]octane [7], silica nanoparticles [8], electro generated base, baker's yeast, and amino-functionalized ionic liquid. Other synthetic methods contain of microwaves, ultrasonic radiation, and utilizing additives like hexadecyltrimethylammonium bromide, triethylbenzylammonium chloride, other alkylammonium salts, 4-dodecylbenzenesulfonic acid, and (*S*)- proline. However, limitations of the above methods include poor yields, difficult work-up, and toxic elements. We report herein the synthesis of isocyanurate-PMO (PMO-ICS) as a new catalysis and its application in the synthesis of pyran derivatives (Scheme 1).



Scheme 1 Three-component reaction of malononitrile (2a), 4-chlorobenzaldehyde (3a), and dimedone (4a)

Preparation of isocyanurate-PMO

1 mmol of 1,3,5-tris(2-hydroxy ethyl)isocyanurate and 2 mmol of 4-toluenesulfonyl chloride were poured in a test tube and then dry acetone was added as solvent. This tube was placed in an ultrasonic bath at 60˚C for one hour. In the next stage, MCM-41 (261 mg) was added to test tube and then the reaction mixture was sonicated at 60˚C for 1 hour. The obtained white solid was filtered and dried at 60˚C over night

Preparation of 4H-benzo[b]pyran derivatives

A mixture of aromatic aldehydes (1.0 mmol), malononitrile (1.0 mmol), dimedone (1.0 mmol), and 0.01g isocyanurate containing PMO was stirred under reflux conditions in water. Progress of the reaction was monitored by TLC. After completion of the reaction, mixture was filtered for separation of heterogeneous catalyst.

Results and Discussion

The IR spectrum of isocyanurate-PMO indicates the CH-stretching mode at 2854 and 2926 cm^{-1} and the mode of amidic carbonyl groups related to incorporation of isocyanurate substitution at 1689 cm^{-1} as well comparatively long peak of Si-O-Si bindings at 1078cm^{-1}.

Only a trace amount of the favorable product was obtained under solvent-free conditions even at 100 °C (Table **1** entries1-2). We began to detect the catalytic activity of different amounts of 1, 3, 5- Tris (2-hydroxy ethyl) isocyanurate. An excellent yield was obtained with 8 mol%. The presence of higher amounts of catalyst did not produce higher yields (entries 3-5). Then we investigated the performance of 8 mol% of 1, 3, 5- Tris (2-hydroxy ethyl) isocyanurate to catalyze the reaction in different organic solvents (Table **1** entries 6-11). It is noteworthy to mention that H_2O showed the best result.

Table 1 Optimization of the three-component reaction of dimedone, 4-chlorobenzaldehyde and malononitrile under various conditions [a]**.**

Entry	Amount of Catalyst (mol %)	Solvent	Temp. (°C)	Yield[b] (%)	Time/min
1	_	_	_	Trace	8h
2	_	_	100	Trace	8h
3	8	H_2O	Reflux	92	17
4	3	H_2O	Reflux	80	30
5	12	H_2O	Reflux	92	17
6	8	Aceton	Reflux	50	50
7	8	CCl_4	Reflux	60	40
8	8	DMS	Reflux	50	90
9	8	$CHCl_3$	reflux	50	3h
10	8	_	_	60	30
11	8	H_2O	70	85	40

[a] Reaction conditions: 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), water (3 mL)

[b] Isolated Yield

Both aromatic carbocyclic and heterocyclic aldehydes containing electron-withdrawing and electron-donating groups underwent this condensation to furnish tetrahydrobenzo[*b*]pyrans in high to excellent yields (Table **2)**.

Table 2 Synthesis of derivatives of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-benzo[b]pyran (5) via condensation of dimedone or 1,3-cyclohexanedione, different aldehydes and malononitrile in the presence of PMO-ICS.

Entry	RCHO	product	Time(min)	Yield (%)
1	4-ClC6H4	5a	17	92
2	4-O2NC6H4	5b	12	85
3	C6H6	5c	23	93
4	4-MeC6H4	5d	17	92

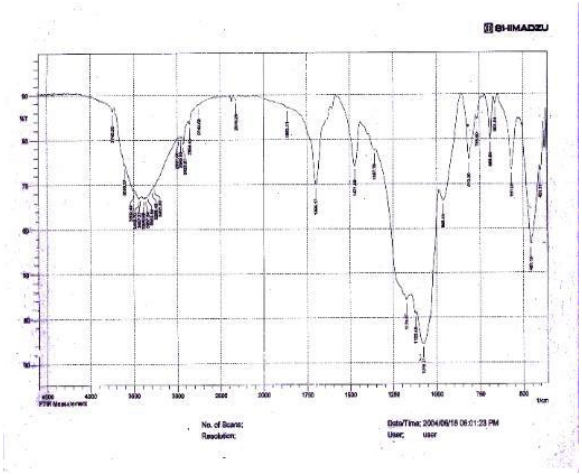


Fig 1 IR spectrum of isocyanurate containing PMO

The surface area and pore diameter obtained 1545.96 and 2.6 nm respectively, using BET analysis was shown in fig **2**.

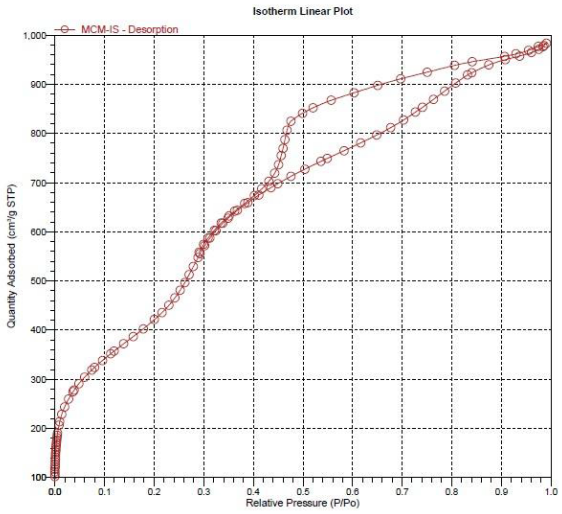


Fig 2 BET analysis of PMO-ICS

Conclusions

In summary, PMO-ICS were prepard by grafting 1, 3, 5-tris (2-hydroxyethyl) isocyanurate into the inner surface of the wall by helping ultrasonic waves. This compound used as heterogeneous catalyst for three-component one-pot synthesis of tetra hydro benzo[b]pyrans in water. The advantages this work short reaction time, excellent yield, recyclability and reusability of catalysis, and the use of water as a green solvent.

Acknowledgment

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

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