FULL PAPER



Surfactant-directed one-pot preparation of novel Ti-containing mesomaterial with improved catalytic activity and reusability

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Dawood Elhamifar, Department of Chemistry, Yasouj University, Yasouj, 75918-74831, Iran. Email: d.elhamifar@yu.ac.ir Titanium was incorporated in ionic liquid based periodic mesoporous organosilica to prepare a nanostructured catalyst (Ti@PMO-IL) with high activity. Procedure for the synthesis of Ti@PMO-IL was followed according the simultaneous hydrolysis and condensation of alkylimidazolium ionic liquid, tetramethoxysilane (TMOS) and tetrabutylorthotitanate (TBOT) where a surfactant template was used together with a simple acid-based catalytic aproach. N₂ adsorption isotherm of the Ti@PMO-IL was studied to measure its mean pore volume, pore size distribution and specific surface area. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was applied to identify the chemical bonds present in Ti@PMO-IL. The morphology of this nanomaterial was investigated by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) image was used to study mesoporosity and structure order of the catalyst. The catalytic activity of Ti@PMO-IL was then studied and found to be efficient and reusable to catalyze Hantzsch reaction.

KEYWORDS

Hantzsch reaction, mesoporous organosilica-titania, recoverable catalyst, supported ionic liquid, Ti-based nanocatalyst

1 | INTRODUCTION

Recently, periodic mesoporous organosilicas (PMOs) with organic fragments embedded in the silica walls have become of high interest because of their well-defined ordered mesoporous structure as well as high loading and uniform distribution of organic groups in their pore walls.^[1-4] Especially, metal-loaded PMOs (M@PMOs) are of more interest between chemists due to the advantages of both ordered mesomaterials and supported metal catalysts and thereby their high efficiency in catalytic processes. The M@PMOs nanomaterials are prepared by the treatment of metallic complexes with suitable ligand-containing PMOs or by the co-condensation and hydrolysis of PMO precursors with metal–ligand complex in the presence of structure directing agents.^[5-10] The

M@PMOs prepared through co-condensation method are more stable due to the catalytic metal centers are incorporated in the material network. However, the M@PMOs prepared *via* the first approach are more active in catalytic processes owing to better accessibility of metallic center. More recently, several M@PMOs (M = Mn, Pd, Au, Cu, Rh, Ru, V, *etc*) have been prepared and their catalytic applications have been developed in several organic transformations.^[11] Among these, palladium, gold and manganese based ones are more interested due to their widespread applications in different organic reactions such as reduction, oxidation and coupling processes.

It is worth noting that the ionic liquids (ILs) have unique properties such as excellent thermal and moisture stability, high conductivity, and solvation ability for a

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wide range of organic and inorganic compounds. Therefore, as more recent interesting example, we have prepared a set of ionic liquid-based PMOs-supported metal complexes (M@PMO-IL) followed by the study on their catalytic applications in a number of organic transformations,^[12–14] showing high efficiency, durability, stability and reusability under the reaction conditions applied. Some advantages of PMO-IL nanomaterials in comparison with other PMOs are their high thermal stability, excellent catalytic efficiency and especially their ionic liquid nature making them appealing materials for a wide range of chemical processes. However, the main disadvantage of the most aforementioned M@PMO catalytic systems is the non-chemical immobilization of metallic sources which may cause leaching problems in some cases. Therefore, the preparation of metallic catalysts covalently supported by the ordered mesoporous materials is of significant attention. Interestingly, titanium as a very attractive and important metal has been chemically well incorporated in the body of different nanomaterials. The titanium-containing materials have been extensively used as catalyst for a wide variety of reactions due to their unique physico-chemical properties such as high thermal and mechanical stability as well as excellent catalytic and photocatalytic activities.^[15-21] This noble metal has also been well immobilized in the body of ordered mesoporous materials and successfully applied in a number of chemical processes.^[22-26] Especially, in the oxidation processes such as oxidation of alcohols and epoxidation of alkenes, the Ti-loaded materials play key role. However, to the best of our knowledge, rare reports have been presented on the periodic mesoporous organo-metal-silica, in which both titanium and organic fragments have been incorporated into silica framework.^[27-29] Hence, the preparation of the Ti@PMOs containing active titanium sites and effective organic functional groups with high stability, efficiency and applicability in the catalytic organic reactions is the subject of research interest.

On the other hand, the synthesis of the polyhydroquinoline derivatives through Hantzsch reaction has become of significant interest, because such derivatives are known to have biological and different pharmacological activities and used as vital drug in the treatment of angina and hypertension.^[30-32] Traditionally, polyhydroquinolines were synthesized using homogenous acid catalysts in different organic solvents with drawback of being run at high temperature in longtime.^[33] Recently, to overcome such limitations associated with aforementioned systems, many recoverable heterogeneous catalytic systems have been designed and applied for this important transformation. Some of the developed systems include Zn-VCO₃ hydrotalcite, ^[34] poly(4-vinylpyridinium) hydrogen sulfate,^[35] tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$,^[36] clay-supported Ni-nanoparticles,^[37] nano-ZnO,^[38] magnetic Fe₃O₄ nanoparticles,^[39] MgO nanoparticles,^[40] HY zeolite^[41] and Montm-K-10.^[42] The latter catalysts showed several advantages, such as easy recoverability and reusability, good efficiency and high stability under applied conditions, to the traditional ones. However, in some of these systems, hazardous solvents were used and considerable amounts of toxic wastes were delivered, which are their disadvantages. Therefore, it is of high necessary to design and prepare efficient recoverable heterogeneous catalysts for the Hantzsch process working under green-media.

As a part of our efforts, to explore the utility of solidsupported catalysts regarding the importance of the synthesis of heterocyclic compounds in environmental and economic point of view, herein, a novel titanium-containing ionic liquid-based periodic mesoporous organosilica (Ti@PMO-IL) having remarkable properties is prepared and characterized. Moreover, the catalytic application of this noble catalyst is investigated in the synthesis of polyhydroquinolines through Hantzsch reaction (Scheme 1).

2 | RESULTS AND DISCUSSION

The titanium-containing ionic liquid-based PMO (Ti@PMO-IL) was prepared by hydrolysis and co-condensation of 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride. tetramethoxysilane (TMOS) and tetrabutylorthotitanate (TBOT) in the presence of pluronic P123 as structure directing agent under acidic conditions (Scheme 1). The chemical and structural properties of the Ti@PMO-IL material were investigated using several techniques such as TEM, nitrogen adsorption-desorption, DRIFT spectroscopy and SEM.

The TEM analysis of the Ti@PMO-IL was performed to verify its periodicity. As seen in Figure 1, the electrons transmitted along with the hexagonally packed cylindrical mesopores experience lower energy losses compared to those transmitted to their walls. This successfully confirms the ordered mesoporous structure of the Ti@PMO-IL material.

The SEM was used to investigate the surface morphology and particle size of the material. This showed uniform sling-like particles with diameter of about 5 micrometers (Figure 2). These types of mesostructures would be good candidates for the catalysis, chromatography, and microelectronic applications due to their high uniformity and density.

The nitrogen adsorption-desorption analysis of the Ti@PMO-IL nanomaterial illustrated an isotherm of type IV with a hysteresis loop of type H1 indicating a sharp



FIGURE 1 TEM image of the Ti@PMO-IL

capillary condensation step at approximate relative pressure of 0.6, and a very sharp capillary evaporation step centered around 0.4 (Figure 3). Furthermore, it is observed that the adsorption and desorption branches are not exactly parallel, which indicates the 'ink-bottle-like' shape of the pores existing in Ti@PMO-IL nanomaterial. It is important to note that similar adsorption-desorption pattern has been reported for the ordered silicas/organosilicas with large cage-like mesopores.^[43-45] The Brunauer-

FIGURE 2 SEM image of the Ti@PMO-IL

Emmett-Teller (BET) surface area and pore volume of the prepared material were obtained to be 584 m²/g and $0.72 \text{ cm}^3/\text{g}$, respectively.

The Barrett-Joyner-Halenda (BJH) pore size distribution (Figure 4) showed a sharp peak with mean pore diameter of 3.8 nm indicating the presence of highly uniform mesopores in the material. It is also important to note that a peak with low intensity observed below 2 nm is assigned to micropores. This peak is related to penetration of



FIGURE 3 Nitrogen adsorption-desorption isotherms of the Ti@PMO-IL



FIGURE 4 The BJH pore size distribution of the Ti@PMO-IL

ethylene-oxide side groups of P123 surfactant in the organosilica matrix during material preparation.^[2b] The micropores are located in the wall of mesopores.^[2b] These results are in good agreement with TEM image showing the well-arranged porous structure of Ti@PMO-IL.

The DRIFT spectroscopy of the Ti@PMO-IL was performed to get detailed information about the chemical functional moieties of the material (Figure 5). The C-Si stretching vibrations are observed over the range of 700–800 cm⁻¹. The absorption bands appeared in the ranges 670–680 and 940–965 cm⁻¹ can be assigned to Ti-O-Ti and Si-O-Ti vibrations, respectively.^[46,47] The symmetric and asymmetric stretching vibrations of Si-O-



FIGURE 5 DRIFT spectrum of ordered mesoporous Ti@PMO-IL

Si bonds are observed at 1090 and 925 cm⁻¹. The absorption signals of C=C and C=N bonds of imidazolium ring are observed at 1566 cm⁻¹ and 1634 cm⁻¹, respectively. The absorption peaks in the range of 2900–3050 cm⁻¹ are assigned to the C-H stretching vibrations of aliphatic groups. The band observed around 3100 cm⁻¹ is attributed to unsaturated C-H stretching vibrations. Moreover, the broad peak appeared around 3300 cm⁻¹ is assigned to O-H functional groups. These data strongly confirm the successful incorporation and immobilization of ionic liquid moieties in the material framework.

After the successful characterization of the Ti@PMO-IL, it was employed as a heterogeneous nanocatalyst the one-pot multi-component synthesis for of polyhydroquinoline derivatives under solvent-free conditions, using substituted aldehydes, 5,5-dimethyl-1,3cyclohexanedione (dimedone), alkylacetoacetates and ammonium acetate substrates. The reaction of benzaldehyde with ethyl-acetoacetate, dimedone and ammonium acetate was selected as a model to investigate the effects of different parameters on the reaction progress. The best result was obtained by carrying out the reaction with one molar of aldehyde, ethyl-acetoacetate, dimedone and two molars of ammonium acetate. The reaction did not give the desired product in the absence of catalyst even after 6 hr (Table 1, entry 1), while in the presence of 0.1 mol% of Ti@PMO-IL, 28% yield was obtained at room temperature after 4 h (Table 1, entry 2). The temperature was increased to 45 and 60°C, which resulted in 62 and 80% yields, respectively, using 0.1 mol% of Ti@PMO-IL nanocatalyst (Table 1, entries 3, 4) indicating the beneficial effect of temperature in the reaction progress. It was also found that the catalyst loading plays important role in the conversion rate, the optimal value of which was obtained in the presence of 0.2 mol% of Ti@PMO-IL (Table 1, entries 4-6). Next, the efficiency of the Ti@PMO-IL was compared to ionic liquid-free Ti-SBA-

TABLE 1 Optimization of the reaction conditions^a

Entry	Catalyst (mol %)	Temperature	Time (min)	Yield (%)
1	No catalyst	r.t.	360	Trace
2	Ti@PMO-IL (0.1)	r.t.	240	28
3	Ti@PMO-IL (0.1)	45	60	62
4	Ti@PMO-IL (0.1)	60	60	80
5	Ti@PMO-IL (0.15)	60	40	92
6	Ti@PMO-IL (0.2)	60	20	96
7	Ti@SBA-15 ^b (0.2)	60	20	48
8	TiO ₂ (0.2)	60	20	40

^aConditions: Benzaldehyde (1 mmol), dimedone (1 mmol), ethylacetoacetate (1 mmol) and ammonium acetate (2 mmol).

^bSanta Barbara Amorphous (SBA).

15 and TiO_2 heterogeneous catalysts with the same Ti loading and conditions. Interestingly, the latter catalysts delivered low to moderate yields of the desired products under the same conditions and time as Ti@PMO-IL (Table 1, entry 6 *versus* entries 7, 8). These observations successfully confirm the valuable role of ionic liquid moieties in the reaction progress.

After the reaction conditions were optimized, the substrate scope and versatility of the catalyst were examined VILEY Organometallic 5 of 8 Chemistry

using various aldehydes, alkyl-acetoacetates, dimedone, and ammonium acetate. For all reactions, the work-up involved simply quenching with ethanol, then filtration and recrystallization in a suitable solvent. The results are summarized in Table 2. As shown, both electrondonating groups (such as Me and MeO) containing substrates and electron-withdrawing groups (such as Cl and NO₂) bearing aromatic aldehydes were used and delivered the corresponding polyhydroquinolines in high to excellent yields within short reaction times at 60° C. These data confirm the high efficacy of the designed titanium-based nanocatalyst for the preparation of different derivatives of biologically useful polyhydroquinolines.

The recyclability and reusability of the Ti@PMO-IL nanocatalyst were also studied under applied conditions based on the aforementioned test model (Table 3). After each run, hot ethanol was added into reaction vessel and the obtained mixture was filtered followed by washing the catalyst with ethanol. The recovered catalyst was

TABLE 3 Recyclability of the catalyst in the Hantzsch reaction

Run	Time (min)	Yield (%)	Run	Time (min)	Yield (%)
1	20	96	6	30	90
2	20	95	7	33	90
3	24	94	8	33	88
4	28	95	9	35	86
5	28	92	10	35	85

TABLE 2 Ti@PMO-IL-catalyzed four-component Hantzsch reaction for the synthesis of polyhydroquinolines^a

	$ \begin{array}{c} 0\\ R_1 \\ 1\\ R_2 \\ 0\\ 3\end{array} $	$H_{4}OA$	Ac Ti-PMO-IL (0.2 m solvent free, 60 °	$rac{c}{c}$ $rac{c}$ $rac{c}{c}$ $rac{c}{c}$ $rac{c}{c}$ $rac{c}{c}$ $rac{c}{$	R_2	
Entry	R ₁	R ₂	Product	Time (min)	Yield/ % ^b	M. p. [°C]
1	Ph	Et	5a	20	96 ± 0.7	206-208
2	2-Cl-Ph	Et	5b	35	88 ± 0.9	202-206
3	2,4-Cl-Ph	Et	5c	35	87 ± 0.7	242-246
4	Ph	Me	5d	20	95 ± 1	250-253
5	4-MeO-Ph	Me	5e	26	93 ± 0.8	260-263
6	4-Me-Ph	Me	5f	25	93 ± 1	266-271
7	2,4-Cl-Ph	Me	5 g	35	85 ± 0.8	211-213
8	3-OEt,4-OH-Ph	Me	5 h	35	86 ± 0.7	237-239
9	4-NO ₂ -Ph	Me	5i	15	95 ± 0.9	238-240

^aReaction conditions: Aldehyde 1 (1 mmol), alkyl-acetoacetate (1 mmol), dimedone (1 mmol), ammonium acetate (2 mmol). Ti@PMO-IL (0.2 mol %), 60 °C. ^bIsolated yield. applied in the next runs. The results showed that it could be recovered and reused at least for nine times without notable reduction in its performance. A hot filtration test was next performed. For this, after the progress of about 40% of the reaction, hot ethanol was added and the obtained mixture was immediately filtered followed by the removal of solvent and allowing the reaction of residue to be continued at 60°C. After 1 hour, a further conversion of only 5% was observed. The catalyst-free filtrate was also analyzed by atomic absorption and the result showed no existence of titanium species in this solution. These results proved strong durability of the chemically-supported Ti-based catalyst and also confirmed that it operates in a heterogeneous pathway.

3 | EXPERIMENTAL SECTION

3.1 | General procedure for the preparation of the Ti@PMO-IL

The Ti@PMO-IL was prepared by the simultaneous hydrolysis and condensation of 1,3-bis(3-trimethoxysilylpropyl) imidazolium chloride ionic liquid (IL), tetramethoxysilane (TMOS) and tetrabutylorthotitanate (TBOT) in the presence of P123 surfactant under acidic conditions. The procedure of Ti@PMO-IL synthesis is typically follows as: pluronic P123 (1.5 g) and KCl (8 g) were added to a solution containing 9.5 g of distilled water and 41.6 g of HCl (1.4 M) under stirring at 35°C. After a homogeneous solution was prepared, a mixture of 1,3-bis(3-trimethoxysilylpropyl) imidazolium chloride (1.8 mmol) and tetramethoxysilane (14 mmol) was added and stirred for 45 min. Next, 5 mmol of TBOT was added drop-wise and the resulting mixture was stirred for 24 h while keeping the same temperature. The obtained mixture was transferred into a Teflon-lined autoclave and heated at 100°C for 72 hr under static conditions. After cooling the reaction mixture to room temperature, it was filtered and completely washed with ethanol and deionized water. The block co-polymer P123 was extracted by acidic ethanol using Soxhlet apparatus. The obtained powder was dried at 70°C for 12 hr under vacuum and denoted as Ti@PMO-IL. By using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) the loading of Ti was calculated.

3.2 | General procedure for the synthesis of polyhydroquinolines through Hantzsch reaction using Ti@PMO-IL nanocatalyst

The synthesis of polyhydroquinolines was performed assisted by a magnetic stirrer in a round-bottom flask fitted with a condenser and placed in a temperature controlled oil bath. Typically, the flask was charged with aldehyde (1 mmol), dimedone (1 mmol), ammonium acetate (2 mmol) and methyl/ethylacetoacetate (1 mmol) in the presence of 0.2 mol% Ti@PMO-IL nanocatalyst. The mixture was stirred at 60°C and the reaction progress was monitored by TLC. After the reaction was completed, it was stopped followed by the addition of 10 ml of hot EtOH. The obtained mixture was hotly filtered and the catalyst was separated. Then, some ice species were added into filtrate to precipitate or crystallize the desired products. The pure products were obtained after the recrystallization of crude ones in EtOH.

4 | CONCLUSION

In summary, a novel concept for the preparation, characterization and application of Ti-containing ionic liquidbased PMO (Ti@PMO-IL) was developed. The nitrogen adsorption-desorption analysis and transmission electron microscopy showed that the prepared material is mesostructure and highly ordered. In addition, the SEM image illustrated the uniform sling-like particles for the Ti@PMO-IL. The DRIFT spectroscopy confirmed the successful incorporation and/or immobilization of ionic liquid and titanium moieties in this mesostructure. Next, Ti@PMO-IL was successfully applied in the preparation of biologically active polyhydroquinolines through Hantzsch reaction under solvent free conditions, which resulted in the corresponding products with excellent yield and selectivity. The catalyst was recovered several times and reused without significant decrease in efficiency. In fact, this methodology effectively combined the advantages of ionic liquids, ordered mesoporous materials, solvent-free media and chemicallyimmobilized metal catalysts for the easy separation of products and the recycling of catalyst. According to the aforementioned advantages of the present catalyst, some of its applications in other organic processes are underway in our laboratories.

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CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

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