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Synthesis, characterization, and application of zinc supported on ionic liquid-based periodic mesoporous organosilica (Zn@PMO-IL) in A³-coupling reaction for the synthesis of propargylamines

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Abstract

The present paper shows the preparation of a highly porous periodic mesoporous organosilica (PMO) including the ionic liquid pore walls that supported with zinc ions onto PMO-IL (Zn@PMO-IL). Moreover, the material was characterized using field emission-scanning electron microscopy, transmission electron microscopy, inductively coupled plasma, and N_2 adsorption–desorption. Likewise, the catalytic activity of the Zn@PMO-IL, illustrating a highly efficient nanocatalyst for the synthesis of propargylamines through three-component A^3 -coupling reaction of various aldehydes, amines, and arylacetylene. The results demonstrate an eco-friendly and appealing method with high efficiency and facile work-up procedure. Furthermore, the nanocatalyst can be revived by a simple filtration process and reuse at least five successive runs without considerable reducing in its activity.

Graphic abstract



Keywords Nanocatalysis · Periodic mesoporous organosilica · Ionic liquid · Zinc supported PMO · A^3 -coupling reaction · Propargylamines

Introduction

Development of the environmentally safe, efficient, and economical methods in synthetic chemistry is a vital goal that the scientists are looking for. Amid the appearance of the

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multicomponent coupling reactions especially A^3 -coupling are the promising procedures dealing with the present challenges [1–3]. The A^3 -coupling reaction has exploited as a key factor in the construction of various nitrogen-containing heterocycles, biologically active compounds, and natural products. The propargylamines have been obtained by A^3 -coupling reactions of aldehydes, amines, and alkynes via the formation of C–C bond which is one of the most wellknown coupling reactions [4–12]. Propargylamines are very important intermediates in organic chemistry for the preparation of a various range of nitrogen-containing pharmaceutical active components like as β -lactams, triazolodiazepines,

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pyrrolidines, oxazoles, indolizines, pyrroles, quinolones, and natural products [13–17].

Because of the propargylamines importance, several synthetic methods have been successfully reported for the synthesis of aforementioned compounds under homogeneous conditions. Some of which catalysts consist the salt and complex of the transition metals such as copper [18-20], indium [21], iron [22], zinc [23], nickel [24], iridium [25], silver [26], gold [27], or Cu/Ru^{II} bimetallic systems [23]. Apart from high activity of such homogeneous catalysts in A³-coupling reactions, they have some drawbacks; such as difficulty in recovery the catalyst, use of large amount of catalyst and instability at high temperatures. To overcome the aforementioned inherent limitations, some improvements have been recently applied through combining the advantages of both homogeneous and heterogeneous systems; immobilization or supporting homogeneous catalysts onto the different reusable solid supports such as porous materials [28], polymers [29], zeolites, carbon-based materials [30, 31], MCM-41 [32], montmorillonite [33] and nanoparticles [34].

Among the diversity of the solid supports, the mesoporous hybrids namely periodic mesoporous organosilica (PMO) containing an extraordinary stable ionic liquid (IL) framework, introducing PMO-IL are very attractive support in the fine chemical synthesis [35–37]. Metal-containing PMO hybrid nanomaterials have attracted more attention due to their unique properties including various chemical positions for functionalizing on their backbone, uniform pore sizes, high thermal and mechanical stability, non-toxicity, as well as proper stability in presence of air and moisture. On the other hand, IL contributes dissolving and stabilizing transition-metal catalysts in the coupling reactions as well as exploits in chemoselectivity and diffusability [38, 39]. Therefore, the supported IL considers as a platform for metal immobilization. Immobilization or supporting the transitionmetal catalysts on porous PMO-IL framework can be introduced as a promising research approach in the catalysis area. Hereof, many researches have recently concentrated on the development of eco-friendly and recoverable catalytic systems based on metal-containing PMO-IL for various organic transformations [40-44].

For example, Karimi et al. successfully synthesized gold nanoparticles supported on PMO-IL framework, studying its catalytic activity for one-pot synthesis of propargylamines at 60 °C [45]. In another work, Gholinejad and co-workers reported a copper catalyst supported on PMO-IL framework (Cu@PMO-IL) for the preparation of propargylamines [46]. Although the eye-catching developments have been achieved in this area, it seems that the design of new catalytic systems based on PMO-IL containing a low amount of the used catalyst with mild reaction conditions is still a major challenge for A^3 -coupling reactions.

Herein, we report the preparation, characterization and application of the zinc immobilized on ionic liquid-based periodic mesoporous organosilica (Zn@PMO-IL) as an efficient nanocatalyst for the one-pot synthesis of propargy-lamines via A³-coupling reaction. To the best of our knowledge, there is no report to date on the use of supported zinc based on PMO-IL for the synthesis of propargylamines.

Results and discussion

Preparation and characterization

The procedure for anchoring the Zn onto PMO-IL (Zn@ PMO-IL) is as follows briefly: first, PMO-IL was prepared by hydrolysis and polymerization of tetramethoxysilane and 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride using Pluronic P123 as a structure-directing agent. Then, Zn metal was immobilized onto the pore walls of PMO-IL through the direct reaction of zinc(II) acetate and imidazolium moieties to prepare the Zn@PMO-IL as nanocatalyst.

After that, the prepared materials were characterized by FE-SEM, TEM, ICP and N_2 adsorption/desorption analyses.

FE-SEM and TEM studies

The surface morphology and structural features of the prepared materials were studied by FE-SEM and TEM analyses. FE-SEM image of Zn@PMO-IL showed it has a rope-like structure with high regularity (Fig. 1) that indicates that the uniformity of the rope-like morphology for PMO-IL is retained.

Furthermore, the TEM image of Zn@PMO-IL exhibited a uniform two-dimensional hexagonal array with a wellordered rod-like structure of the channels (Fig. 2). These results confirmed that immobilizing of metal on PMO-IL



Fig. 1 FE-SEM image of Zn@PMO-IL



Fig. 2 TEM image of Zn@PMO-IL

during the nanocatalyst preparation does not have a notable result on the ordered mesostructures of the PMO-IL scaffold, which is in good agreement with the results obtained by N_2 adsorption–desorption experiment data.

N₂ adsorption-desorption studies

The N₂ adsorption–desorption isotherms and the corresponding pore size distribution curves of PMO-IL and Zn@ PMO-IL at 77 k were evaluated. Their isotherms exhibited a type-IV isotherm pattern with H1 hysteresis loops, which is characteristic of this mesoporous material (Fig. 3). The calculated Brunauer–Emmett–Teller (BET) specific surface areas for PMO-IL and Zn@PMO-IL are 623 and 537 $m^2 g^{-1}$, respectively (Fig. 4). The decrease in surface area of Zn@PMO-IL compared to PMO-IL suggested the successful immobilizing of Zn inside the pores of the PMO-IL. Finally, the Zn content in Zn@PMO-IL was determined to be 0.5 mmol g^{-1} using ICP technique.

Catalytic performance

As mentioned in the previous section, propargylamines are versatile intermediates for the preparation of different nitrogen-containing pharmaceutical active components. Hence, after successful synthesis and characterization of the Zn@PMO-IL as nanocatalyst, we have investigated its catalytic performance as a heterogeneous nanocatalyst for the preparation of propargylamines. To optimize different reaction parameters, the A^3 -coupling of 4-chlorobenzaldehyde (1 mmol), piperidine (1.5 mmol), and phenylacetylene (1.5 mmol) were selected as a model reaction for initial studies (Scheme 1). The summary of optimization studies is presented in Table 1.

At the first stage for optimization, various solvents including toluene, H_2O , $CHCl_3$, and CH_3CN and also solvent-free conditions were tested to identify a suitable solvent that significant yield was observed when $CHCl_3$ was employed.

Subsequently, the effect of reaction temperature on product yield was studied by varying the temperature in $CHCl_3$ and 0.5 mol% of used nanocatalyst. The results showed that the product yield was continually improved with increasing the reaction temperature from 25 °C to reflux temperature of $CHCl_3$. Therefore, the boiling temperature of solvent was chosen as optimal conditions for all further reactions.

In the next step, the influence of the amount of the used nanocatalyst (Zn@PMO-IL) on the reaction was explored and the highest catalytic performance was obtained when 0.5 mol% of Zn@PMO-IL was used in CHCl₃ at reflux



Fig. 3 N₂ adsorption-desorption isotherm for PMO-IL (a) and Zn@PMO-IL (b)



Fig. 4 Pore size distributions for PMO-IL (a) and Zn@PMO-IL (b)



Table 1Screening of differentparameters for the reactionof 4-chlorobenzaldehyde,piperidine, and phenylacetylene

| Entry | Catalyst (amount) | Solvent | Temp./°C | Time /h | Yield/% |
|-------|-----------------------|--------------------|----------|---------|---------|
| 1 | Zn@PMO-IL (0.5 mol%) | Toluene | 60 | 72 | 30 |
| 2 | Zn@PMO-IL (0.5 mol%) | Toluene | Reflux | 36 | 65 |
| 3 | Zn@PMO-IL (0.5 mol%) | H ₂ O | 60 | 36 | 25 |
| 4 | Zn@PMO-IL (0.5 mol%) | H_2O | Reflux | 36 | 40 |
| 5 | Zn@PMO-IL (0.5 mol%) | CHCl ₃ | Reflux | 16 | 95 |
| 6 | Zn@PMO-IL (0.5 mol%) | CH ₃ CN | Reflux | 72 | Trace |
| 7 | Zn@PMO-IL (0.5 mol%) | Solvent-free | 60 | 72 | Trace |
| 8 | Without catalyst | CHCl ₃ | Reflux | 72 | Trace |
| 9 | Zn@PMO-IL (0.75 mol%) | CHCl ₃ | Reflux | 16 | 96 |
| 10 | Zn@PMO-IL (0.5 mol%) | CHCl ₃ | 25 | 72 | 25 |
| 11 | $Zn(Ac)_2$ (1 mmol) | CHCl ₃ | Reflux | 16 | 88 |
| 12 | MgO@PMO-IL (0.5 mol%) | CHCl ₃ | Reflux | 72 | Trace |

conditions. In addition, the model reaction was examined in the absence of Zn@PMO-IL and trace of the desired product was detected (Table 1, entry 8). This observation confirms the vital role of the nanocatalyst for the reaction completion.

Finally, after optimization of different parameters in the A³-coupling reaction, we decide to synthesize propargylamines under obtained optimum conditions with various substrates to find the general applicability of this catalytic system. Results are summarized in Table 2. As can be seen from Table 2, various aldehydes including both electron-withdrawing and -donating groups (such as -NO₂, -Cl, -Br, -OMe, -CN) in reaction with morpholine (or piperidine) and phenylacetylene were converted to the corresponding propargylamines in good to excellent yields.

Table 2 Synthesis of various propargylamines using Zn@PMO-IL



| Entry | R | Х | Product | Time /h | Yield/% ^a |
|-------|-------------------|-----------------|------------|---------|----------------------|
| 1 | Н | CH ₂ | 4 a | 20 | 92 |
| 2 | 4-Cl | CH ₂ | 4 b | 16 | 95 |
| 3 | 4-Br | CH ₂ | 4c | 16 | 90 |
| 4 | 4-NO ₂ | CH_2 | 4d | 24 | 80 |
| 5 | 4-CN | CH ₂ | 4 e | 24 | 85 |
| 6 | 4-OMe | CH ₂ | 4 f | 16 | 95 |
| 7 | 4-Cl | 0 | 4g | 16 | 95 |
| 8 | 4-Br | 0 | 4h | 16 | 92 |
| 9 | 4-OMe | 0 | 4i | 16 | 95 |
| 10 | 4-NO ₂ | 0 | 4j | 24 | 80 |
| 11 | 4-CN | 0 | 4k | 24 | 82 |

Reaction conditions: aldehyde (1 mmol), piperidine or morpholine (1.5 mmol), and phenylacetylene (1.5 mmol) in 5 cm³ of CHCl₃ in the presence of Zn@PMO-IL (0.5 mol%) at reflux condition. ¹H and ¹³C NMR spectra were found in accordance with the ones described in Ref. [45] ^aIsolated yield

Proposed reaction pathway

On the basis of some related literatures [4, 11], a plausible mechanism for A³-coupling reaction in the presense of Zn@PMO-IL was proposed in Scheme 2. According to the suggested mechanism, C–H activation of the alkyne

by the nanocatalyst generates zinc acetylide. It is noteworthy that the metal acetylide formation is a common step in A^3 -coupling reaction. Subsequently, the iminium ion generated from the reaction of aldehyde and amine reacts with zinc acetylide to yield corresponding propargylamine product with the regeneration of the nanocatalyst.



Reusability test

The recoverability and reusability of the catalysts are a very important issue in catalyzed reactions. Therefore, in this part of our study, reusability Zn@PMO-IL as nanocatalyst was studied using the model reaction when the conditions were optimized. Once the reaction was finished (monitored by TLC), the catalyst was separated through a simple filtration process, washed several times with deionized water, and dried under vacuum for next same reaction. The results showed that Zn@PMO-IL is able to reuse at least five cycles without much drop in its catalytic performance (Fig. 5).

Leaching test

Zinc leaching from Zn@PMO-IL as nanocatalyst into reaction solution was checked by ICP analysis to survey the heterogeneity of our catalytic processes. Negligible leaching (less than the detection limit) was detected under the applied reaction conditions. These results truly confirmed the high stability, strong attachment of metal center onto the PMO-IL framework, and also heterogeneous nature of our catalytic system.

Conclusions

In summary, we have prepared a zinc metal supported on periodic mesoporous organosilica with an ionic liquid framework (Zn@PMO-IL) and confirmed it by different techniques such as SEM, TEM, ICP, and N₂ adsorption–desorption analyses. SEM, TEM, and N₂ adsorption–desorption demonstrate that the nanocatalyst has a uniform twodimensional hexagonal pore structure with high regularity. Zn@PMO-IL was then employed as a highly efficient nanocatalyst for one-pot synthesis of propargylamines. The present procedure illustrated the high reactivity for various



Fig. 5 Recyclability test of Zn@PMO-IL during the model reaction

substrates in all reactions in described coupling reaction, which gave the corresponding propargylamines in good to excellent yields. Moreover, reusability studies showed that the nanocatalyst can be recovered from reaction media and successfully reused several consecutive runs without significant loss of its catalytic performance, which confirmed its high efficiency and stability. It is worth noting that the leaching experiment by ICP analysis confirmed the strong attachment of zinc metal to PMO-IL framwork and nanocatalyst works in a heterogeneous pathway.

Experimental

The chemicals were purchased from the commercial sources. Fourier transform infrared spectroscopy (FT-IR) on KBr pellets of the compounds was recorded on a Bruker vector 22 in the range of 400 and 4000 cm⁻¹. ¹H and ¹³C NMR spectra were measured with Bruker DRX-400 Avance instrument (400.13 and 100.61 MHz, respectively), in CDCl₃. Thermogravimetric analysis (TGA) was conducted from room temperature to 800 °C under N₂ atmosphere using BAHR Thermoanalyse (GmbH STA 503). The particle size and morphology of the synthesized materials were examined using transmission electron microscopy (TEM; Zeiss-EM10C-100 kV), field emission scanning electron microscopy (FE-SEM; MIRA3 XMU) and N2 adsorption-desorption analysis (Belsorp, BELMAX, Japan). The metal content in the catalyst was measured by induced coupled plasma (ICP; VARIAN VISTAPRO instrument). The progress of the reactions was monitored by thin-layer chromatography (TLC) using silica gel SIL G/UV 254 plates. Melting points were measured by employing the capillary tube method with an Electrothermal 9100 apparatus. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

Preparation of precursors and catalyst

Imidazolium ionic liquid (IL), PMO, and PMO-IL were prepared based on our previous work [47]. For the synthesis of Zn supported on PMO-IL (Zn@PMO-IL) as catalyst, 0.2 g PMO-IL was dispersed in 1 cm³ DMSO. In the following, Zn(Ac)₂ (0.1 mmol) was added and the mixture was stirred at 50 °C for 6 h, and then at 100 °C for 2 h. Finally, the mixture was cooled to room temperature and washed with EtOH several times and dried under vacuum.

General procedure for A³-coupling reaction

Typically, Zn@PMO-IL as catalyst (0.5 mol%) was added to a mixture of aldehyde (1 mmol), amine (1.5 mmol), and phenylacetylene (1.5 mmol) in 5 cm³ CHCl₃. Then, the mixture

was heated to the reflux temperature of the solvent. The progress of the reaction was monitored using TLC (*n*-hexane/ EtOAc, 3:1 ratio). At the end of the reaction time, the solvent was evaporated under reduced pressure and the product was obtained by plate chromatography to afford propargylamines. The products were characterized using ¹H and ¹³C NMR spectroscopy and the spectra were found in accordance with the ones described in Ref. [45].

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