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# Ionic liquid-based ordered mesoporous organosilica-supported copper as a novel and efficient nanocatalyst for the one-pot synthesis of Biginelli products

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ABSTRACT

The preparation, characterization and catalytic application of a novel copper-loaded ionic liquid-based periodic mesoporous organosilica (Cu@PMO-IL) are described. The mesoporous structure of the Cu@PMO-IL material is characterized by transmission electron microscopy (TEM) and nitrogen adsorption–desorption analysis. The thermal stability of the material is also determined by thermal gravimetric analysis (TGA). The presence of copper species in the material framework is confirmed by X-ray photoelectron spectroscopy (XPS) and elemental analysis (EA). The catalytic application of Cu@PMO-IL nanocatalyst is then investigated in the Biginelli condensation of different aldehydes with urea and alkylacetoacetates under solvent-free conditions and at moderate temperature. Moreover, the stability, reactivity and reusability of the catalyst are improved under applied reaction conditions.



## 1. Introduction

The Biginelli reaction is one of the most important organic processes which is of high interest due to its key role in the production of valuable biologically active compounds such as anti-bacterial, anti-viral, anti-inflammatory, anti-hypertensive, anti-tumor, calcium channel blocker and blood palette aggregation inhibitor drugs [1–4]. Since the discovery of this important reaction by P. Biginelli, numerous successful developments and applications based on this reaction using both Brønsted acid and Lewis acid catalysts under different homogeneous conditions have been reported [1–7]. However, traditional homogeneous systems suffer from problems such as low catalyst recovery, complicated product separation and harsh reaction conditions in most cases. To overcome these drawbacks, several methods have been developed to prepare recoverable heterogeneous catalysts, using various supports, for the Biginelli reaction [8–10]. Among different kinds of supports, silica-based ones are of higher interest due to their availability, high thermal and mechanical stability as well as low cost [9,10]. Especially, ordered mesoporous silica-supported catalysts are of high interest because of their high surface area, superior efficiency, high regularity and selectivity [10]. In general, the most recent approaches have successfully resolved the disadvantages such as low recoverability and reusability of the catalyst. However, in the most cases the low reactivity and high loading of the catalyst as well as the low yield of desired products have been observed. Therefore, the development of new heterogeneous and recoverable acid-based catalytic systems with high reactivity and high efficiency for the Biginelli reaction is necessary.

Periodic mesoporous organosilicas (PMOs) are a new class of functionalized ordered nanoporous materials that are synthesized by the simultaneous hydrolysis and condensation of alkoxysilane precursors bridged to organic groups in the presence of structure directing agents under acidic or basic conditions [11–13]. Recently, these materials have attracted great attention due to their high surface area, tunable pore size and pore volume, excellent lipophilicity and powerful stability [11–13]. To date, many PMOs containing different bridging organic functional groups which vary from aromatics to aliphatics have been prepared and applied as support, catalyst, etc. in several chemical processes [13,14]. In particular, metal-containing PMO materials are very interesting because the metal contents possess unique catalytic activity which can be easily recovered and reused in a typical chemical process [13–16]. Metal-containing PMOs are usually prepared either by the impregnation of metal-complexes onto/into PMO samples containing suitable ligand or by the hydrolysis and co-condensation of a metal-complex-bridged alkoxysilane and tetraalkoxy silane (TEOS

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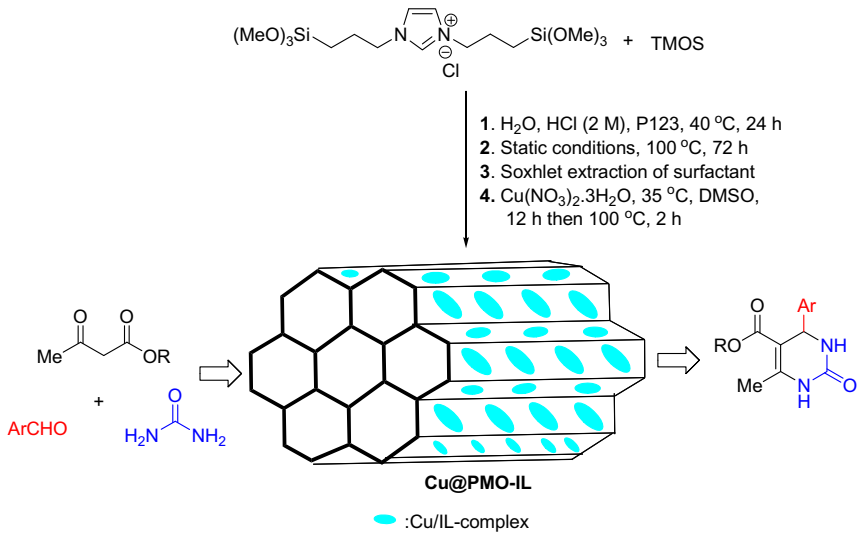


**Scheme 1.** Preparation of the Cu@PMO-IL catalyst and its application in the Biginelli reaction.

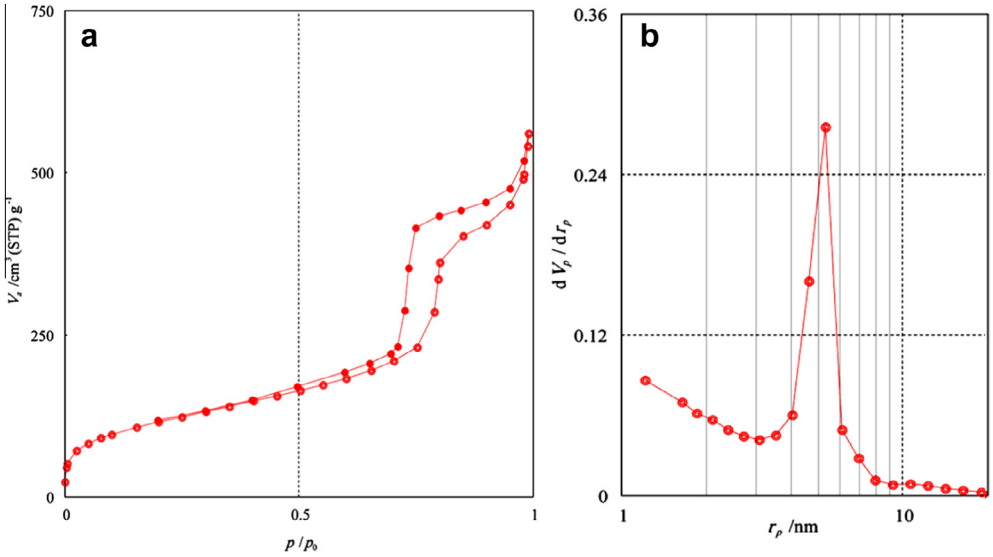


**Fig. 1.** Nitrogen adsorption–desorption isotherm (a) and BJH pore size distribution (b) of the Cu@PMO-IL.

or TMOS) in the presence of surfactant template [13–15]. Along this line, more recently, we have prepared and developed several metal-containing ionic liquid-based periodic mesoporous organosilica materials (M@PMO-IL, M = Pd, Mn, Ru) and studied their catalytic applications in a number of organic processes such as oxidation of alcohols and cross coupling reactions [15,16]. Our study illustrated that, in these transformations, the PMO-IL was a powerful and highly efficient support for the successful immobilization and stabilization of the metal catalysts. The yield and selectivity of the corresponding delivered products were also found to be high to excellent. Moreover, the catalytic systems exhibited high durability and reusability under the applied reaction conditions. In this work, we have developed a protocol for the preparation of a novel copper-containing ionic liquid-based PMO (Cu@PMO-IL) and studied its catalytic efficiency in the one-pot Biginelli reaction of different aldehydes, urea and alkylacetoacetates (Scheme 1). The reactivity, reusability and stability of the catalyst during the reaction process have also been investigated.

## 2. Experimental

### *2.1. Preparation of copper-loaded alkyl imidazolium-based periodic mesoporous organosilica (Cu@PMO-IL) nanocatalyst*

At first the alkyl imidazolium-based periodic mesoporous organosilica (PMO-IL) nanomaterial was prepared by the hydrolysis and co-condensation of tetramethoxysilane (TMOS) and 1,3-bis(trimethoxysilylpropyl) imidazolium chloride in the presence of pluronic P123 surfactant under acidic conditions [15,16]. Typically, pluronic P123 surfactant (2 g) was added to a flask containing deionized water (11.7 g), HCl (2 M, 50 g) and potassium chloride (12.5 g), then the obtained mixture was stirred at 40 °C. After complete dissolution of surfactant, a mixture of tetramethoxysilane (20 mmol) and 1,3-bis(trimethoxysilylpropyl) imidazolium chloride (2.25 mmol) was added to reaction vessel and stirred at the same temperature for 24 h. Then, the obtained mixture was aged for 72 h at 100 °C. After that, the solid material was separated by