



## Research Note

# Urea–pyridine bridged periodic mesoporous organosilica: An efficient hydrogen-bond donating heterogeneous organocatalyst for Henry reaction

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## ABSTRACT

Hydrogen-bond donating (HBD) organocatalysts have been employed as an important class of catalysts for the activation of small molecules. However, the use of these catalysts was restricted on account of the self-aggregation of HBD-active species. In this work, a successful approach was developed to construct novel urea–pyridine bridged periodic mesoporous organosilica (PMO) to prevent the unwanted self-recognition and aggregation of urea-based catalytic center by spatial isolation, unleashing its HBD organocatalytic activity along with cooperative effect from the pyridine unit for efficient Henry reaction. The urea–pyridine bridged PMO catalyst presents high structural stability and high catalytic recyclability.

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## 1. Introduction

Electrophile activation by hydrogen-bond donors has emerged as a new catalytic strategy in synthetic organic chemistry including enantioselective catalysis [1–3]. Among various types of organocatalysis, hydrogen-bond donating (HBD) catalysis is a special class of mimetic alternative to Lewis acid activation, which could aid in accelerating nucleophilic attack [4–7]. Urea and thiourea have the potential to be used as double hydrogen-bond donors in organocatalysis. However, the HBD catalytic capability of urea is greatly restricted due to its high propensity to undergo self-dimerization attributed by its oxygen to accept a hydrogen bond in liquid phase homogeneous catalysis [4–8]. This unwanted self-assembly of urea significantly lowers its solubility, resulting in a potential decrease in catalytic reactivity. On the other hand, more soluble thiourea analogue rules out the possibility of self-assembly through strong intermolecular hydrogen-bonding interactions. But, thiourea-based catalysts are often accompanied by poor thermal stability, which limits their applicability in a broad range [8]. In addition, such HBD catalysts are associated with relatively low

turnover efficiency, hindering organocatalytic reactions in large-scale synthesis [9].

The development of new heterogeneous organocatalysts other than metal-based heterogeneous catalysts has attracted a lot of attention owing to their several advantages including the robustness, low toxicity without metal-leaching problem during the reactions, inertness to moisture and oxygen, and simple handling and storage capability in the vicinity of green chemistry [10,11]. Recently, a few successful studies have been reported regarding the incorporation of urea based HBD molecules onto the solid architectures to overcome abovementioned problems. Among these examples, most of the solid HBD catalysts were prepared by the post-modification of the surfaces of various solid supports such as porous organic polymers (POPs) [12], mesoporous silica [13,14], and metal-organic frameworks (MOFs) [15]. However, low stability due to the possibility of structural collapse [16] and the presence of metal ions in the frameworks [17] make MOFs less efficient than other counterparts as the solid supports in heterogeneous HBD catalysis. In addition, the introduction of the urea molecules onto the solid supports by the post-grafting method may still have the possibility of catalytic quenching on account of the dimerization with neighboring urea units on the surface. Furthermore, the post-grafting method often generates unwanted hindrance inside the pore channels of the support materials, making the diffusion of the reaction substrates more difficult [18]. In order to address the problems associated with urea-based organocatalysts,

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we designed a novel periodic mesoporous organosilica (PMO) incorporated with the urea–pyridine group as the organic bridge on the pore walls of mesoporous structure. Through the preparation, we could achieve the hybrid PMO material with high density of organic active groups, while restricting the anchored urea unit from unwanted dimerization in order to unleash its great potential in the HBD catalysis.

## 2. Experimental

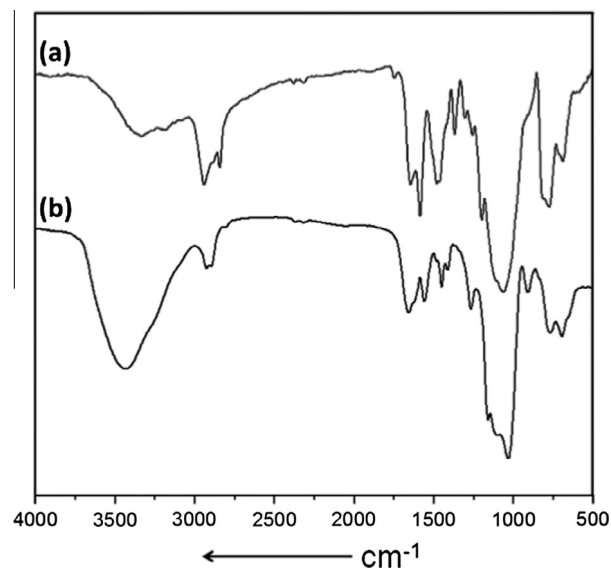
All experimental details are displayed in [Supplementary information \(SI\)](#).

## 3. Results and discussion

In order to prepare a PMO for catalytic applications, it is desirable to have a high degree of functionality within PMO by choosing an organic precursor with at least two terminal alkoxy silanes [19–21]. In the current work, an essential organic precursor (**3**) with two urea linkages was synthesized ([Scheme 1](#)) through the condensation between the amino group of compound **1** and the isocyanato unit of compound **2**. Although the synthesis of this molecule has already been reported [22], it has not been utilized for the preparation of PMO. By using **3** as the organic bridge, a novel PMO was synthesized through the co-condensation [23,24] with tetraethyl orthosilicate (TEOS) using cetyltrimethylammonium bromide (CTAB) as structure-directing agent under basic conditions (see [SI](#) for synthetic details). The obtained **3**-incorporated PMO was denoted as Urea/PMO for further uses.

The FT-IR spectrum ([Fig. 1](#)) of Urea/PMO displays many characteristic peaks for various functionalities such as C=O and C–N stretching from the urea–pyridine unit in the range of 1600–1400  $\text{cm}^{-1}$  and C–H stretching at 2950–2850  $\text{cm}^{-1}$ , providing clear evidence of the successful integration of precursor **3** into the organosilica framework. The spectrum ([Fig. 1b](#)) also shows characteristic peaks of the Si–O stretching at 1084 and 1231  $\text{cm}^{-1}$  and the Si–C stretching at 962  $\text{cm}^{-1}$ , indicating the formation of silica network [25,26]. The predominant band ranging from 1670  $\text{cm}^{-1}$  to 1640  $\text{cm}^{-1}$  was attributed to the bending frequency of surface adsorbed  $\text{H}_2\text{O}$  molecules, which unfortunately masked few other signals from the urea–pyridine unit. Although we pretreated the Urea/PMO at 120 °C under vacuum of  $10^{-6}$  mbar, we were still unable to remove the surface adsorbed water completely. Furthermore, a broad band around 3426  $\text{cm}^{-1}$  was attributed to the O–H stretching vibration of hydrogen-bonded silanols on PMO.

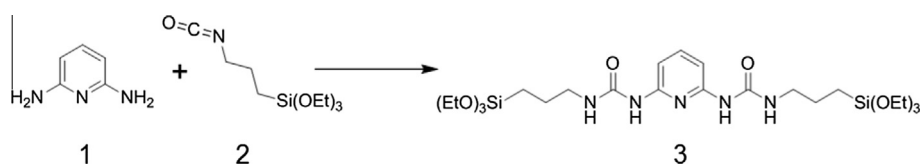
The  $^{13}\text{C}$  cross-polarization magic angle spinning (CP MAS) NMR spectrum of Urea/PMO ([Fig. 2a](#)) exhibits strong signals ranging from 10 to 43 ppm, which could be attributed to different aliphatic primary and secondary carbon atoms from the organic bridging unit (**3**). Strong signals from aromatic carbons on the pyridine ring could be identified at  $\sim 105$  ppm as well as in the range from 140 to 160 ppm. In addition to these signals, one strong signal at  $\sim 152$  ppm was assigned to the carbonyl carbon from the urea linkage. These clear observations further support the successful incorporation of compound **3** into the silica framework. The same



**Fig. 1.** FT-IR spectra of (a) compound **3** and (b) Urea/PMO.

characteristic signals ([Fig. 2a](#)) were also observed from the recovered Urea/PMO\_U catalyst after 6 consecutive cycles of catalysis, reflecting good stability of the organic moiety within the silica framework even after prolonged catalytic usage.  $^{29}\text{Si}$  CP MAS NMR spectrum of Urea/PMO ([Fig. 2b](#)) shows major signals centered at  $-110$  and  $-100$  ppm as well as a small shoulder at  $-90$  ppm, which could be attributed to the silicon species of  $\text{Q}^4$  [ $(\equiv\text{SiO})_4\text{Si}$ ] and  $\text{Q}^3$  [ $(\equiv\text{SiO})_3\text{Si}(\text{OR})$ ] respectively [27,28], where R represents Et or H. In addition to these signals, Urea/PMO also displays one more peak at  $-64$  ppm, corresponding to the  $\text{T}^3$  resonance from silicon species attached to the organic group [ $-\text{CH}_2-\text{Si}(\text{OSi}\equiv)_3$ ]. Apart from  $\text{T}^3$  signal, the spectrum does not display any other signals corresponding to  $\text{T}^0$ ,  $\text{T}^1$  and  $\text{T}^2$  [27,28]. This is solid evidence in support of complete integration of the organic precursor into the silica framework through the hydrolysis of terminal alkoxy silanes. The  $^{29}\text{Si}$  CP MAS NMR spectrum of Urea/PMO\_U ([Fig. 2b](#)) is essentially similar to that of Urea/PMO, revealing the stable urea–pyridine unit in the polysiloxane network.

The isothermal  $\text{N}_2$  adsorption/desorption measurements were carried out for Urea/PMO and the same catalyst (Urea/PMO\_U) after 6 consecutive cycles of catalysis in order to determine their surface areas and pore size distributions ([Table 1](#)). Urea/PMO illustrates a typical type IV isotherm ([Fig. S1 in the SI](#)) under the lowest pressure, which accounts for the presence of mesopores. The Brunauer–Emmett–Teller (BET) surface area of Urea/PMO was measured to be  $951 \text{ m}^2 \text{ g}^{-1}$ . The pore size distribution indicates a narrow distribution of mesopores ([Fig. S1 in the SI](#)) with an average pore diameter of 3.8 nm calculated by employing Barrett–Joyner–Halenda (BJH) model. A slight decrease in the BET surface area ( $892 \text{ m}^2 \text{ g}^{-1}$ ) with no remarkable change in the isotherm pattern was observed for reused Urea/PMO\_U catalyst ([Fig. S1 in the SI](#)), indicating the preservation of the mesopores after the catalysis. The pore diameter was found to be 3.8 nm for reused



**Scheme 1.** Schematic representation of the synthetic route for the preparation of organic silane precursor (**3**).

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