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Manuscript title:

Preparation of mesoporous carbon nitride materials using urea and formaldehyde as precursors and catalytic application as solid bases

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Graphical abstract

Highlights

- Mesoporous carbon nitride prepared using eco-friendly urea and formaldehyde as precursors
- Molar ratio of carbon to nitrogen in mesoporous CN samples is ca. 3.4
- Good activity in various Knoevenagel condensation and transesterification reactions

Abstract:

A series of mesoporous carbon nitride materials have been fabricated using inexpensive and eco-friendly urea and formaldehyde as precursors and mesocellular silica foam (MCF) as a template through a nanocasting approach. Several techniques, including XRD, TEM, elemental analysis, FT-IR, XPS, and CO$_2$-TPD have been applied to characterize the physicochemical properties of the mesoCN materials, and the results show that the materials possess high surface areas (331–355 m$^2$ g$^{-1}$), relatively concentrated pore size of ca. 6 nm, and abundant and multiple nitrogen-containing species. As heterogeneous base catalysts, mesoCN materials demonstrate high catalytic activity and selectivity in both Knoevenagel condensation and transesterification reactions.

Keywords: Carbon nitride; Solid base; Knoevenagel condensation; Transesterification
1. Introduction

Chemical transformation promoted by base catalysis holds an important position in the organic and synthetic chemistry [1]. In particular, C–C bond formation reactions, represented by Knoevenagel condensation, and transesterification, are extensively applied in the production of numerous chemicals including drugs, fragrances, and chemical intermediates [2]. The conventional base catalysts are mainly organic nitrogen-containing compounds (including pyridine, piperidine, etc) [2, 3] and alkali metal hydroxides (e.g. KOH and NaOH) [4, 5]. However, the major disadvantage lies in the difficulty in catalyst/product separation as well as catalyst recycling due to their homogeneous nature. On the other hand, although heterogeneous metal oxides (such as Mg-Al-O and MgO) exhibit outstanding catalyst recyclability, there is still potential metal contamination in reaction system [3, 6].

To circumvent the issue, a series of homogeneous organic bases have been recently immobilized on mesoporous silicas [7-9] and graphene [10]. Owing to their high surface areas along with tunable pore sizes, such heterogeneous materials show excellent catalytic activity in a variety of organic reactions, and thus have been regarded as promising solid base catalysts. Unfortunately, the immobilization demands high-cost silicane coupling agent and the procedure is relatively complicated [11]. In this context, in viewpoints of both fundamental research and industrial application, it is of very interest to develop a new and efficient solid base catalyst.

The past decade has witnessed the robust development of graphitic carbon nitride (g-CN) in multiple research fields. Up to now, g-CN and its based materials demonstrate promising application in photocatalysis [12-14], fuel cells [15, 16], adsorption [17, 18], and heterogeneous catalysis [1, 19-21]. Of particular note is that metal-free g-CN contains abundant and various nitrogen-containing species, which naturally make it to be a typical solid base [3, 22, 23]. More importantly, compared with the bulk g-CN samples prepared by direct pyrolysis, mesoporous g-CN materials possess higher surface areas and much more accessible pores, thus upgrading the catalytic performances of g-CN [24, 25]. Recently, many research groups including ours have successfully prepared several mesoporous g-CN materials using various
precursors [1, 3, 23, 26, 27]. In several base-mediated reactions, it is unambiguous reported that such g-CN materials exhibit good catalytic activity and recycling ability. Despite this success, it should be pointed out that the raw materials adopted for the synthesis of g-CN materials, even reported in other application, are mainly cyanamide, and carbon tetrachloride and ethylenediamine [28, 29]. These compounds are either expensive or highly toxic.

In this work, urea and formaldehyde have been used as cheap and widely available precursors to synthesize mesoporous g-CN (mesoCN) through a hard-templating method. In Knoevenagel condensation reaction between benzaldehyde/acetone and malononitrile, and transesterification reactions of β-keto esters, the mesoCN samples reveal good catalytic activity and selectivity. Finally, the catalytic performance and catalyst preparation of mesoCN have been compared with other reported mesoporous CN based materials.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of MCF material

Mesocellular silica foam (MCF) was prepared using tetraethyl orthosilicate (TEOS) as a precursor and triblock copolymer P123 (EO20PO70EO20) as a soft template [30]. Briefly, 4 g of P123 was completely dissolved into 150 mL of HCl solution (1.6 mol L⁻¹), followed by addition of 4.0 g of 1,3,5-trimethylbenzene and 46 mg of NH₄F. The mixture was vigorously stirred for 1 h at 40 °C. Subsequently, 8.8 g of TEOS was added, and the mixture was further stirred for another 20 h at 40 °C. The obtained suspension was transferred into an autoclave lined by Teflon, and statically heated at 130 °C for 24 h. Afterwards, the precipitate was filtered off, dried overnight, and finally calcined at 550 °C for 5 h.

2.1.2. Preparation of mesoCN materials

77 mmol of urea, 77 mmol of formaldehyde (35wt%, a.q.), and 5 mL of deionized water were mixed well. 1.0 g of previously dried MCF powder was added into the solution and stirred for 1 h, and the mixture was then dried at 100 °C for another 9 h in an oil bath. The obtained white composite was calcinated from room temperature to
600 °C with a ramping rate of 2 °C min\(^{-1}\) and hold at the temperature for 3 h under N\(_2\) atmosphere. After the carbonization, the black solid was immersed into 100 mL of NaOH (0.5 mol L\(^{-1}\)) and stirred at 80 °C for 24 h. Afterwards, the dispersion was centrifuged and the black precipitate was rinsed by water (until the pH value of the dispersion reached \(ca.\) 7.0 in order to remove any possible residual NaOH) and ethanol for several times. The obtained material was dried at 60 °C under vacuum for 2 h and the resultant solid was labeled as mesoCN-\(r\), where \(r\) indicated the molar ratio of urea to formaldehyde. The detailed amounts of urea, formaldehyde, and MCF for various mesoCN-\(r\) materials were provided in Table S1.

2.1.3. Preparation of CN/MCF material

116 mmol of urea, 77 mmol of formaldehyde (35wt%, a.q.) solution, and 5 mL of deionized water were mixed well. 1 g of previously dried MCF powder was added into the solution and stirred for 1 h, and the mixture was then dried at 100 °C for another 9 h in an oil bath. The obtained white composite was calcinated from room temperature to 600 °C with a ramping rate of 2 °C min\(^{-1}\) and hold at the temperature for 3 h under N\(_2\) atmosphere. The obtained black sample was labeled as CN/MCF-1.5.

2.2. Sample characterization

X-ray diffraction (XRD) patterns of the mesoCN materials were analyzed by a Rigaku D/max 2500 PC X-ray diffractometer using Ni-filtered Cu-K\(\alpha\) radiation (\(\lambda = 1.5418\) Å). Nitrogen adsorption–desorption isotherms were measured using a Micromeritics ASAP 2020 analyzer. Prior to the analysis, the materials were degassed at 150 °C for 4 h. The specific surface areas were calculated according to the Brunauer–Emmet–Teller (BET) method and the pore size distribution was determined by Barret–Joyner–Halenda (BJH) model. Fourier transform infrared (FT-IR) spectra were recorded by a Bruker Tensor 27 spectrometer. The mass ratio of each sample to KBr was constant at 1:200. X-ray photoelectron spectra (XPS) were analyzed by a Thermo ESCALAB 250XI spectrometer using Mg \(K_\alpha\) radiation as the excitation source. Elementary analysis (EA) was tested by an Elementar Vario EL III analyzer. CO\(_2\) temperature-programmed desorption (CO\(_2\)-TPD) was performed on a Quantachrome ChemBET-3000 analyzer. Prior to analysis, the sample was heated at
300 °C for 1 h under helium gas and then cooled down to the room temperature.

2.3. Catalytic evaluation

Knoevenagel condensation reactions were performed in a two-neck round bottomed flask (25 mL). 5 mmol of benzaldehyde, 5 mmol of malononitrile, 0.4 mL of n-dodecane, and 5 mL of acetonitrile as a solvent were mixed well. 75 mg of catalyst was added into the mixture and the reactions were carried out at 90 °C. After each hour, a small quantity of the reaction mixture was collected, centrifuged and analyzed by GC equipped by a FID detector. Another Knoevenagel condensation reaction was carried out using 10 mmol of acetone and 10 mmol of malononitrile as reactants.

Transesterification reactions of β-keto ester were conducted in a two-neck round bottomed flask. 15 mmol of ethylacetoacetate (EAA), 10 mmol of alcohol, 0.2 mL of n-dodecane, and 3 mL of toluene as a solvent were mixed well. 50 mg of catalyst was added into the mixture and the test was performed at 100 °C. Like Knoevenagel condensation, the catalytic conversions of transesterification were analyzed by GC.

3. Results and discussions

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of various mesoCN materials. Each sample demonstrates a pronounced diffraction peak at ca. 2θ = 25.2 ° with a d-spacing value of 0.353 nm, and a shoulder located at ca. 42 °. The two peaks correspond to the reflection of (002) and (100) planes of disordered graphitic carbon [3, 31], respectively. The assignments of the two diffraction peaks are identical with those reported in mesoporous g-CN prepared using tetrachloride and ethylenediamine as raw materials [11, 24, 32]. From the XRD patterns, it can be found that adjusting the molar ratio of urea to formaldehyde from 0.67 to 1.5, the overall graphitic structure of the materials shows no apparent variation.

The porous properties of the materials were investigated by N2 adsorption–desorption characterization. All the samples present apparent type-IV isothermal curves (Fig. 2A), along with H2 hysteresis loops in the range of p/p0 = 0.6–0.95, indicating that the materials possess typical mesoporous structures.
However, the adsorption curves still rise in the higher relative pressure \((p/p_0 > 0.95)\). This suggests that besides mesopores, there also exist some macroporous structures in the mesoCN materials, which may be attributed to the intraparticle void. The corresponding pore size distribution determined from desorption branches of isotherms shows that the pore size of each sample is relatively narrow, centered at ca. 6 nm. The surface areas and porous parameter are listed in Table 1. The surface area and pore volume of mesoCN-0.67 are 331 m² g⁻¹ and 0.38 cm³ g⁻¹, respectively. It can be found that the surface area and pore volume of mesoCN materials depend on the molar ratio of urea to formaldehyde. That is, as the content of urea is increased, the surface area and pore volume of the final mesoporous materials are improved gradually whereas the pore size shows a monotonous decline from mesoCN-0.67 to mesoCN-1.5.

The reason for this relation between textural parameter and molar ratio of precursors is probably the effect of pore filling in the nanocasting approach. In this work, the precursors used for the fabrication are urea and formaldehyde. When the ratio of urea to formaldehyde (a.q.) is low, the precursor mixture actually contains a lot of water originating from the formaldehyde solution. Although the liquid-phase precursors could completely fill into the mesopores of MCF template, there remain partial solid-phase precursors in the mesopores after drying procedure. This uncompleted filling style, due to the presence of a certain amount of solvent, inevitably brings out potential collapse of carbon-nitride walls during the subsequent etching step [33]. The collapse or shrinkage of walls might damage the partial architecture of mesopores and then result in a decline of surface area or pore volume. However, as the molar ratio of urea to formaldehyde is elevated, the content of original water becomes less, thereby facilitating sufficient filling in the mesopores of MCF, and finally alleviates the decrease of surface area and pore volume. The similar phenomenon, i.e. the impact of ratio of precursors on the textural parameter of negative replica during nanocasting synthetic way, has also been reported by Vinu et al [34]. Wherein, the textual properties including surface areas, and pore volumes of mesoporous carbon nitride materials have a close relation to the molar ratios of
precursors. Consequently, upon adjusting the molar ratio of the precursor, a series of mesoporous materials with tunable textural parameters could be obtained.

The small-angle XRD (SAXRD) patterns of MCF and mesoCN materials are provided in Fig. S1. No apparent diffraction peak has been detected in MCF as MCF itself is foam-like disordered mesoporous silica [35]. The morphology of the materials was observed by TEM. The TEM image of the MCF template (Fig. 3A) reveals a disordered arrangement of polygonal pores (20–30 nm), which is characteristic structure of the MCF material. Also, the pore size detected in the image agrees well with the result of N₂ adsorption–desorption characterization (Table 1 and Fig. S2). In the case of mesoCN, both the images (Fig. 3B) of mesoCN-1.0 and mesoCN-1.5 exhibit irregular foam-like structure. Accordingly, like MCF, the mesoCN-1.5 material also shows no obvious diffraction peak in the SAXRD pattern (Fig. S1). However, at the edges of the samples, there present polygonal-like slices and mesopores between them. Obviously, the mesoCN materials have negatively replicated the original mesostructures of MCF. Meanwhile, the corresponding selected area electron diffraction (SAED) pattern (the inset) shows clear diffraction rings. This confirms that the present mesoCN materials own at least partly graphitic structures, consistent with the above XRD characterization result.

In order to probe their chemical functionality, the mesoporous materials were characterized by FT-IR and the transmittance spectra are depicted in Fig. 4. It is evident that the transmittance for each spectrum is dominated mainly in two regions, i.e. 3500–3200 and 1600–1200 cm⁻¹. The first region is attributed to the stretching vibration of N–H, and O–H bonds of adsorbed water. The other two sharp bands at 1570 and 1295 cm⁻¹ are indexed as N–H deformation modes, and C–N stretching vibration, respectively. In addition, a minor band has also been detected at 2202 cm⁻¹, which is associated with the −N=C=O vibration. In this study, mesoCN materials were prepared using urea and formaldehyde as raw materials. As presumed by Liu et al [31], the two precursors react via a series of self-condensation reactions in the low temperature (~100 °C) and transform into urea-formaldehyde resin. Wherein, the motif unit for the polymer is mainly amide (−CO–NH−) groups. During the
subsequent calcination (~600 °C), the as-synthesized resin undergoes cross-linking stage and final carbonization. Given in this synthetic propose, the above various chemical functionalities, especially C–N groups, can be explained for the mesoCN samples. Despite the resemblance in main bands, the intensity of transmittance (especially the band bands located in 3500–3200 cm⁻¹) seems be related to the molar ratios of the precursors of mesoCN. Naturally, the mesoCN samples prepared by using higher content of urea might possess much more nitrogen-containing species, which are then reflected in the nitrogen-related bands of FT-IR spectra.

The chemical composition of mesoCN materials was measured by EA characterization. As listed in Table 1, the calculated chemical formula based on the values of C/N/H element for mesoCN-0.67 is C₃.₆₈NH₂.₀₀. Further comparing the chemical compositions of various mesoCN specimens, it can be seen that the molar ratio of the precursors has significant impact on the content of N element; with the increase of the amount urea fed, the content of N increases progressively. Obviously, the correlation originates from the fact that urea itself serves as the sole N source in the synthesis of mesoCN.

XPS technique was further employed to analyze the surface chemical environment of the materials. For concise, Fig. S3 provides the survey of mesoCN-1.0 and mesoCN-1.5 materials. Each mesoCN sample was constituted by C, N, and O elements. Wherein, the O element is derived from the adsorbed water on the surface of materials, as also detected in the abovementioned FT-IR result. The absence of Si confirms that the original MCF siliceous template has been thoroughly eliminated by NaOH solution. Based on the peak area integrated in Fig. S3, the chemical compositions for mesoCN-1.0 and mesoCN-1.5 materials are C₃.₄₁NOₐ.₂₈ and C₂.₈₅NO₀.₂₂, respectively (note: the hydrogen element cannot be detected by XPS). Apparently, the mesoCN materials own higher concentration of N element on their surface than in the bulk phase (Table 1).

To probe the chemical bonding information, deconvolution of detailed C 1s and N 1s spectra was performed. As depicted in Fig. 5A, the C 1s spectra of mesoCN-1.0 and mesoCN-1.5 can be divided into four independent peaks. The primary peak with
the lowest binding energy at 284.7 eV is assigned to graphitic carbon atoms, i.e. sp2 C–C bond [26]. The peaks located at 286.1 and 287.4 eV are indexed as sp2 C=N and sp3 C–N signals [36], respectively. The last broad peak with the highest binding energy signifies the presence of C–O groups. The multiple carbon bonding states are consonance with the abovementioned FT-IR spectra. In the case N element in mesoCN (Fig. 5B), it can be also divided into four species. The majority is attributed to the N atoms existing in sp3 C–N groups, as reflected by the major peak with a binding energy of 398.2 eV. The second type of N element owns an energy contribution at 400.2 eV, corresponding to sp2 C=N groups [36]. The weak peak at 402.0 eV is associated with the N atoms bonded with O (i.e. N–O), whereas the last peak is assigned with quaternary N species or charging effect of XPS [37]. The above deconvolution results of both C and N 1s spectra agree well with the results reported by Park [36] and Liu [31].

Since all the FT-IR, EA, and XPS characterization results have verified that the present mesoCN materials have abundant and various nitrogen-containing species, it is reasonably deduced that such materials are typical solid bases. Concerning this point, CO2-TPD was applied to study the basicity of the mesoCN materials. As described in Fig. 6, the corresponding CO2-TPD curves of mesoCN materials exhibit broad desorption peaks mainly in the range of 150–400 °C. In order to understand the detailed base distribution of the solid bases, the desorption peaks of CO2-TPD has been deconvoluted. The desorption curve for each material can be separated into three independent peaks. The first peak with the lowest desorption temperature at ca. 125 °C (Peak I) is associated with the physical adsorption, while the peak at ca. 200–250 °C (Peak II) is attributed to weak chemical adsorption that can be assigned to weak basic sites on the surface of the sample. The desorption peak centered at ca. 325 °C (Peak III) is ascribed to relatively strong chemical adsorption associated with the medium-strength basic sites. In the case of CN/MCF-1.5, the predominant desorption of CO2 occurs at the ca. 210 °C. In sharp comparison, the peak position pertaining to the medium-strength base moves towards higher temperatures with respect to mesoCN samples, signifying that mesoCN materials owns superior basic intensity to
the supported CN/MCF-1.5 material. From mesoCN-0.67 to mesoCN-1.5, the Peak II shows no apparent change whereas the intensity of Peak III undergoes substantial improvement. According to the titration experiment of CO₂ and subsequent quantity calculation based on Peak III, the quantity of medium-strength base for mesoCN-1.0, and mesoCN-1.5 is ca. 48, 72, and 115 μmol CO₂ g⁻¹ catal⁻¹, respectively. Therefore, it can be inferred that, the quantity of medium-strength basic sites can be smoothly tuned by adjusting the molar ratio of urea to formaldehyde. More specifically, as the amount of nitrogen-containing urea is increased, the basic quantity of the mesoCN materials is enhanced progressively. Additionally, the variation in basic quantity coincides well with the content of nitrogen element (Table 1) of mesoCN materials.

3.2. Catalyst performance

Initially, Knoevenagel condensation between benzaldehyde and malononitrile was selected as a base-mediated reaction to examine the catalytic performance of mesoCN. A blank test without any catalyst was first performed under 90 °C and the result (Table 2) show the catalytic conversion of benzaldehyde was only 4% at 5 h. Applying mesoCN-0.67 as a catalyst instead, the conversion increases up to 32%. Concerning various mesoCN materials, as the molar ratio of urea to formaldehyde increases, the final catalytic activity increases progressively. The highest catalytic conversion is achieved over mesoCN-1.5, affording a yield of 2-benzylidenemalononitrile as much as 78% at 5 h. In this study, we have also prepared MCF-supported CN catalyst (CN/MCF-1.5) using urea and formaldehyde as starting materials, and the corresponding textural information and chemical composition are summarized in Table 1. Fig. S2 indicates that CN/MCF-1.5 has a remarkable adsorption of N₂, together with a large pore size of ca. 20 nm. Also, the main chemical functionality of CN/MCF-1.5 (Fig. S4) is very similar with that of mesoCN-1.5. Although the CN/MCF-1.5 sample has higher surface area and larger pore volume than mesoCN-1.5 (Table 1), under the same reaction conditions, the catalytic conversion of benzaldehyde obtained over CN/MCF-1.5 is 36%, much lower than that of its counterpart. Since Knoevenagel condensation is a base-mediated reaction, a catalyst having more content of nitrogen species especially along with
higher quantity of active basic sites (Fig. 6) could naturally provide superior activity. As illustrated above, from mesoCN-0.67 to mesoCN-1.5, the quantity of base increases monotonously, which agrees well with the variation in catalytic conversion received over various mesoCN materials. As far as the supported CN/MCF-1.5 material, despite its comparable surface area, either the content of nitrogen element or basic intensity is limited. In this sense, it can be speculated that the essential active sites of mesoporous CN materials in Knoevenagel condensation are medium-strength basis sites.

The mesoCN-1.5 sample was chosen as a reference catalyst for further catalytic evaluation. The influence of reaction time and catalyst weight on the catalyst performance has been investigated subsequently (Fig. 7). At the first 1 h, the conversion of benzaldehyde and selectivity to 2-benzylidemalononitrile are 48% and 98%, respectively. Prolonging the reaction, the selectivity presents no clear change, whereas the conversion elevates gradually but levels off after 5 h. Likewise, the catalytic performance is observed to be dependent on the catalyst amount. The selectivity gained without any catalyst is ca. 81%, probably due to the oxidation of benzaldehyde with ambient oxygen. Upon feeding the catalyst, the conversion increases drastically. As the catalyst weight is up to 100 mg, the reaction offers a best yield of 90%. In addition, the reproducibility of mesoCN-1.5 was examined by consecutive catalytic runs. After each run, the catalyst was rinsed by ethanol for at least three times and then dried in a vacuum oven for 2 h. As shown in Table 2, the catalytic conversion acquired on mesoCN-1.5 is ca. 77%, together with the same selectivity (96%), indicating that the mesoCN catalyst could provide stable catalytic activity. Indeed, according to the various characterization results including XRD, N2 adsorption–desorption, FT-IR, EA, and N 1s XPS (Fig. S5), the structure, textural properties, chemical compositions, and nitrogen species states of regenerated sample after five catalytic runs reveal no significant change. Therefore, the stable physicochemical properties of mesoCN materials are responsible for their high tolerance and recyclability in liquid-phase heterogeneously catalytic reaction.

Besides the Knoevenagel condensation reaction between benzaldehyde and
malononitrile, a condensation between acetone and malononitrile has also been carried out using mesoCN-1.5 as a heterogeneous catalyst. Fig. 8 illustrates the resultant catalytic performance as a function of time. The catalyst demonstrates apparent activity even at 50 °C, and the temperature has an apparent positive effect over the activity of mesoCN. Regarding the product selectivity, the target product is isopropylidenemalononitrile whereas the byproduct is solely isobutenyl methyl ketone, which is derived from self-aldol condensation of acetone catalyzed by basic mesoCN material. With the increase of the temperature, the catalytic conversion increases monotonously at the same reaction time. Meanwhile, it can be observed that the selectivity decreases under higher temperatures, evidencing that mesoCN could also promote aldol condensation besides Knoevenagel condensation. Under 90 °C, the catalytic conversion of acetone reaches ca. 80% and the selectivity is 81% at 3 h of reaction time.

Following the Knoevenagel condensation reactions, we have also carried out a series of transesterification reactions between a β-keto ester (EAA) and alcohols. The transesterification reaction of β-keto ester is a practical transformation to synthesize complex β-keto esters starting from simple β-keto esters [38]. The conventional catalysts are mainly homogeneous organic bases. Herein, the mesoCN-1.5 was subjected to transesterification reactions to further testify its basic activity. As displayed in Fig. 9, for a simple n-butanol, the material exhibits a high conversion of 62% under 100 °C at 6 h (The selectivity to the target complex ester is 100%). Moreover, in addition to n-butanol, various alcohols, including aliphatic and aromatic alcohols, can be smoothly converted by the catalyst under the identical conditions.

For comparison, the catalytic performances of various mesoporous CN materials for transesterification have been summarized in Table 3. To the best of our knowledge, it covers almost all the previously reported relevant catalyst. It is worth noting that their activity is determined all based on the conversions of alcohols. Under similar reaction conditions (including temperature and catalyst amount), the catalytic activity
received on mesoCN-1.5 is slightly lower than those obtained over other mesoporous materials, although it owns relatively higher nitrogen content to its counterparts. We think that the difference in catalytic activity of CN materials is not merely determined by their nitrogen concentration. For a mesoporous solid base in catalytic application, the contribution of textual properties (including surface area and pore volume) also can substantially improve the final catalytic activity, because a solid base with higher surface area could expose much more accessible active sites in a heterogeneously catalytic reaction. In fact, in the case of textural nature, the surface areas of the present mesoCN samples are ca. 331–355 m² g⁻¹, while the values for other mesoporous carbon nitride materials are almost higher than 500 m² g⁻¹, along with larger pore volume (ca. > 0.65 cm³ g⁻¹). Therein, the higher catalytic conversion obtained over other mesoporous carbon nitride samples should be attributed to their large surface areas and pore volumes than the present mesoCN materials. Notwithstanding, it should be pointed out that, the most advantage of the present mesoCN comparable to other materials lies in its preparation. As mentioned above, the precursors adopted for the mesoporous CN material are generally cyanamide, and CTC and EDA. Although these compounds are classical raw materials, it should be stressed that they are highly toxic, and meanwhile the etching procedure to eliminate silica templates involves hazardous and volatile HF solution. By contrast, the present mesoCN materials are fabricated using inexpensive and relatively safe urea and formaldehyde as precursors. In this viewpoint, the preparation route of mesoCN materials is much more eco-friendly than other reported mesoporous CN samples. Finally, regarding the catalytic versatility in both Knoevenagel condensation and transesterification reaction, it can be assumed that such mesoporous materials could serve as a new solid base for wide base-mediated organic reactions.

4. Conclusion

To conclude, we have prepared a series of mesoCN materials using urea and
formaldehyde as cheap and widely available starting materials via a nanocasting route. The mesoCN materials possess high surface areas and relatively narrow pore size distribution. The average molar ratio of C/N in mesoCN is ca. 3.4, depending on the molar ratio of urea to formaldehyde. In Knoevenagel condensation reactions between benzaldehyde/acetone and malononitrile, such mesoCN samples exhibited good catalytic activities with high selectivities. The catalytic active sites of mesoCN materials are possibly medium-strength basic sites. Furthermore, transesterification reactions between EAA with various alcohols could be smoothly promoted using mesoCN materials, affording a maximum conversion of 68%. It can be anticipated that the metal-free mesoporous g-CN materials could enrich the finding in the heterogeneous base catalysis, and provide a new strategy for the synthesis of mesoporous g-CN catalysts towards wide base-mediated organocatalysis.

Acknowledgments

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References:


Figure Captions

**Fig. 1** Wide-angle XRD patterns of mesoCN-0.67 (a), mesoCN-1.0 (b), mesoCN-1.25 (c), mesoCN-1.5 (d), and recycled mesoCN-1.5 (e) samples.

**Fig. 2** N₂ adsorption–desorption isotherms (A) and pore size distributions (B) of mesoCN materials (up triangle: mesoCN-0.67; circle: mesoCN-1.0; left triangle: mesoCN-1.25; square: mesoCN-1.5; down triangle: recycled mesoCN-1.5 subjected to five catalytic runs).

**Fig. 3** TEM images of MCF (A), mesoCN-1.0 (B), and mesoCN-1.5 (C) materials. The inset is the corresponding SAED pattern of mesoCN-1.5.

**Fig. 4** FT-IR spectra of mesoCN-0.67 (a), mesoCN-1.0 (b), mesoCN-1.25 (c), mesoCN-1.5 (d), and recycled mesoCN-1.5 (e) materials.

**Fig. 5** C 1s (A) and N 1s (B) spectra of mesoCN-1.0 and mesoCN-1.5 materials.

**Fig. 6** CO₂-TPD profiles of CN/MCF-1.5 (a), mesoCN-0.67 (b), mesoCN-1.0 (c), and mesoCN-1.5 (d) materials.

**Fig. 7** Effect of reaction time (A) and weight (B) on the Knoevenagel condensation reaction over mesoCN-1.5. Reaction conditions: 5 mmol of benzaldehyde, 5 mmol of malononitrile, 0.4 mL of n-dodecane, 5 mL of CH₃CN as solvent, and $W_{\text{catal.}} = 75$ mg. The left was collected at 90 °C and the right was tested at 5 h.

**Fig. 8** Catalytic performance of mesoCN-1.5 in Knoevenagel condensation reactions between acetone and malononitrile. Reaction conditions: 10 mmol of acetone, 10 mmol of malononitrile, 0.3 mL of n-dodecane, 3 mL of toluene as solvent, and $W_{\text{catal.}} = 50$ mg.

**Fig. 9** Catalytic performances of mesoCN-1.5 in transesterification reactions between EAA with various alcohols. There was no byproduct in each case; namely the selectivity to the target complex β-keto was 100%. Reaction conditions: 15 mmol of EAA, 10 mmol of alcohol, 0.2 mL of n-dodecane, 5 mL of CH₃CN as solvent, $W_{\text{catal.}} = 50$ mg, and $T = 100$ °C.
Fig. 1 Wide-angle XRD patterns of mesoCN-0.67 (a), mesoCN-1.0 (b), mesoCN-1.25 (c), mesoCN-1.5 (d), and recycled mesoCN-1.5 (e) samples.

Fig. 2 N₂ adsorption–desorption isotherms (A) and pore size distributions (B) of mesoCN materials (up triangle: mesoCN-0.67; circle: mesoCN-1.0; left triangle: mesoCN-1.25; square: mesoCN-1.5; down triangle: recycled mesoCN-1.5 subjected to five catalytic runs).
**Fig. 3** TEM images of MCF (A), mesoCN-1.0 (B), and mesoCN-1.5 (C) materials. The inset is the corresponding SAED pattern of mesoCN-1.5.

**Fig. 4** FT-IR spectra of mesoCN-0.67 (a), mesoCN-1.0 (b), mesoCN-1.25 (c), mesoCN-1.5 (d), and recycled mesoCN-1.5 (e) materials.
Fig. 5 C 1s (A) and N 1s (B) spectra of mesoCN-1.0 and mesoCN-1.5 materials.

Fig. 6 CO₂-TPD profiles of CN/MCF-1.5 (a), mesoCN-0.67 (b), mesoCN-1.0 (c), and mesoCN-1.5 (d) materials.
Fig. 7 Effect of reaction time (A) and weight (B) on the Knoevenagel condensation reaction over mesoCN-1.5. Reaction conditions: 5 mmol of benzaldehyde, 5 mmol of malononitrile, 0.4 mL of n-dodecane, 5 mL of CH₃CN as solvent, and W_{catal.} = 75 mg. The left was collected at 90 °C and the right was tested at 5 h.

Fig. 8 Catalytic performance of mesoCN-1.5 in Knoevenagel condensation reactions between acetone and malononitrile. Reaction conditions: 10 mmol of acetone, 10 mmol of malononitrile, 0.3 mL of n-dodecane, 3 mL of toluene as solvent, and W_{catal.} = 50 mg.
Fig. 9 Catalytic performances of mesoCN-1.5 in transesterification reactions between EAA with various alcohols. There was no byproduct in each case; namely the selectivity to the target complex β-keto was 100%. Reaction conditions: 15 mmol of EAA, 10 mmol of alcohol, 0.2 mL of n-dodecane, 5 mL of CH3CN as solvent, \( W_{\text{catal.}} = 50 \) mg, and \( T = 100 \) °C.

Table 1 Texture parameters and chemical composition of mesoCN materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m² g⁻¹)</th>
<th>Pore size (a nm)</th>
<th>( V_{p}^b ) (cm³ g⁻¹)</th>
<th>N [wt%]</th>
<th>C [wt%]</th>
<th>H [wt%]</th>
<th>Chemical formula c</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCF</td>
<td>362</td>
<td>20.1</td>
<td>2.08</td>
<td>0</td>
<td>0</td>
<td>1.61</td>
<td>–</td>
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<tr>
<td>mesoCN-0.67</td>
<td>331</td>
<td>7.0</td>
<td>0.38</td>
<td>19.52</td>
<td>61.62</td>
<td>2.79</td>
<td>C₃.₆₈NH₂.₀₀</td>
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<tr>
<td>mesoCN-1.0</td>
<td>338</td>
<td>6.6</td>
<td>0.40</td>
<td>20.15</td>
<td>61.37</td>
<td>3.34</td>
<td>C₃.₅₅NH₂.₃₂</td>
</tr>
<tr>
<td>mesoCN-1.25</td>
<td>347</td>
<td>6.3</td>
<td>0.42</td>
<td>20.56</td>
<td>59.03</td>
<td>3.35</td>
<td>C₃.₃₅NH₂.₂₈</td>
</tr>
<tr>
<td>mesoCN-1.5</td>
<td>355</td>
<td>6.2</td>
<td>0.55</td>
<td>21.49</td>
<td>55.82</td>
<td>3.01</td>
<td>C₃.₀₃NH₁.₉₆</td>
</tr>
<tr>
<td>mesoCN-1.5 ( d )</td>
<td>367</td>
<td>6.4</td>
<td>0.60</td>
<td>20.57</td>
<td>56.71</td>
<td>4.25</td>
<td>C₃.₂₁NH₂.₈₉</td>
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<tr>
<td>CN/MCF-1.5</td>
<td>410</td>
<td>22.9</td>
<td>0.77</td>
<td>7.84</td>
<td>25.15</td>
<td>1.147</td>
<td>C₃.₇₄NH₂.₀₅</td>
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</table>

\( a \) Determined by the desorption branches. \( b \) Total pore volume. \( c \) Measured by EA. \( d \) Recycled catalyst subjected to five catalytic runs.
**Table 2** Catalytic results of Knoevenagel condensation reactions over mesoCN and CN/MCF-1.5 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conv. (%)</th>
<th>Sel. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>4</td>
<td>81</td>
<td>3</td>
</tr>
<tr>
<td>mesoCN-0.67</td>
<td>32</td>
<td>96</td>
<td>31</td>
</tr>
<tr>
<td>mesoCN-1.0</td>
<td>45</td>
<td>97</td>
<td>44</td>
</tr>
<tr>
<td>mesoCN-1.25</td>
<td>62</td>
<td>96</td>
<td>60</td>
</tr>
<tr>
<td>mesoCN-1.5</td>
<td>81</td>
<td>96</td>
<td>78</td>
</tr>
<tr>
<td>CN/MCF-1.5</td>
<td>36</td>
<td>95</td>
<td>34</td>
</tr>
<tr>
<td>mesoCN-1.5 &lt;sup&gt;b&lt;/sup&gt;</td>
<td>77</td>
<td>96</td>
<td>74</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 5 mmol of benzaldehyde, 5 mmol of malononitrile, 0.4 mL of <i>n</i>-dodecane, 5 mL of CH<sub>3</sub>CN as solvent, <i>W</i> <sub>catal</sub> = 75 mg, <i>t</i> = 5 h, and <i>T</i> = 90 °C. <sup>b</sup> Recycled catalyst in the fifth catalytic run.

**Table 3** Comparison of catalytic activity over various mesoporous CN catalysts for transesterification reaction between EAA and <i>n</i>-butanol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursor</th>
<th>&lt;i&gt;T&lt;/i&gt;</th>
<th>&lt;i&gt;S&lt;/i&gt; &lt;sub&gt;BET&lt;/sub&gt;</th>
<th>&lt;i&gt;V&lt;/i&gt; &lt;sub&gt;p&lt;/sub&gt;</th>
<th>&lt;i&gt;t&lt;/i&gt;</th>
<th>Conv. (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN-FDU12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>CTC+EDA</td>
<td>100</td>
<td>702</td>
<td>1.40</td>
<td>7</td>
<td>74</td>
<td>[39]</td>
</tr>
<tr>
<td>CN-H-SBA15&lt;sup&gt;b&lt;/sup&gt;</td>
<td>HMTA&lt;sup&gt;f&lt;/sup&gt;</td>
<td>110</td>
<td>788</td>
<td>0.68</td>
<td>6</td>
<td>70</td>
<td>[40]</td>
</tr>
<tr>
<td>mpg-C&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>cyanamide</td>
<td>110</td>
<td>440</td>
<td>1.20</td>
<td>5</td>
<td>98</td>
<td>[1]</td>
</tr>
<tr>
<td>MCN-1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>CTC+EDA</td>
<td>110</td>
<td>505</td>
<td>0.55</td>
<td>6</td>
<td>69</td>
<td>[41]</td>
</tr>
<tr>
<td>MCN-3&lt;sup&gt;e&lt;/sup&gt;</td>
<td>CTC+EDA</td>
<td>110</td>
<td>645</td>
<td>0.67</td>
<td>2</td>
<td>90</td>
<td>[22]</td>
</tr>
<tr>
<td>mesoCN-1.5</td>
<td>urea + formaldehyde</td>
<td>100</td>
<td>355</td>
<td>0.55</td>
<td>6</td>
<td>60</td>
<td>this work</td>
</tr>
</tbody>
</table>

<sup>a</sup> mesoporous carbon nitride using mesoporous silica FDU-12 as a template. <sup>b</sup> prepared using mesoporous silica SBA-15 as a template. <sup>c</sup> prepared using colloid silica nanoparticles as hard template; the reactant alcohol was benzyl alcohol. <sup>d</sup> prepared using SBA-15 as a template. <sup>e</sup> prepared using mesoporous silica IBN-4 as a template. <sup>f</sup> hexamethylenetetramine.