

Pore Size Architecture of Hexagonal Mesoporous Carbon Nitride (HMCN) for Metal-Free Synthesis of *p*-Hydroxycinnamic Acid

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Abstract

The nanochannels of hexagonal mesoporous carbon nitride (HMCN) base catalytic materials were architected with diameter of 4.7, 5.9, and 7.1 nm using SBA-15 hard templates and these catalysts were represented as HMCN (4.7), HMCN (5.9), and HMCN (7.1), respectively. These materials were characterized by XRD, N_2 sorption, FESEM, EDAX, HRTEM, FTIR and DR UV–Vis spectroscopy. The influence of HMCN catalysts with different pore sizes on *p*-hydroxycinnamic acid synthesis was investigated in metal/pyridine-free reaction conditions. The catalytic experimental results of HMCN (5.9) catalyst with optimum pore diameter of 5.9 nm showed an excellent catalytic performance of 94.5% *p*-hydroxybenzaldehyde conversion with 100% *p*-hydroxycinnamic acid selectivity within 60 min in comparison with other two catalysts, namely HMCN (4.7) and HMCN (7.1).

Graphical Abstract



Keywords HMCN · Pore size · Knoevenagel-Doebner condensation · Heterogeneous catalysis · Metal-free base catalyst

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1 Introduction

p-Hydroxycinnamic acid (*p*-coumaric acid) is a very important ingredient for the synthesis of several drugs and pharmaceuticals as they find their direct applications in antituberculosis, anti-inflammatory, anti-cancer, anti-oxidant, anti-microbial, hepatoprotective, CNS depressant, antibacterial, anti-fungal, anti-malarial, and UV rays absorbent

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[1–5]. Traditionally the *p*-hydroxycinnamic acid is synthesised by Knoevenagel-Doebner reactions using homogeneous base catalysts like aniline, pyridine, hexamethylenetetramine, tri-ethylamine, ammonia and piperidine [6-8], etc. But these catalysts have their own disadvantages of hazardousness, carcinogenic, and unrecoverable from the reaction mixture, because of homogeneous nature. Solid heterogeneous base catalysts such as metal oxides, metal-organic frameworks (MOF), magnetic supports, silica, and polymers have been employed in Knoevenagel-Doebner reaction [9–12] to solve the catalyst recovery issues. Nevertheless these solid catalysts possess drawbacks like low stability (MOF), lack of structural variability (magnetic nanoparticles) or restrictions to reuse (polymers). Hence there is a huge demand in the catalyst preparation to design an environment friendly, efficient, and economical way for p-hydroxycinnamic acid synthesis.

Hexagonal mesoporous carbon nitride (HMCN) opened a new avenue in the field of catalysis and material science owing to its significant properties such as large specific surface area, uniform pore size distribution, high specific pore volume, hydrophobic nature, and high chemical and mechanical stability [13–16]. Very recently HMCN materials are used in base catalytic organic transformations with promising results [17–19]. The great problem in the porous material catalysis is that a catalytic material with similar pore size might not be applicable for different reactants with different molecular sizes. Hence, the architecture on the pore size of HMCN will facilitates the reactants with different molecular sizes to access the basic sites inside the pores of HMCN catalysts.

So herein we report for the first time an efficient environment friendly HMCN catalytic system by architecting the pores with different pore sizes of 4.7, 5.9, and 7.1 nm (Scheme 1) for the synthesis of *p*-hydroxycinnamic acid from *p*-hydroxybenzaldehyde and malonic acid in pyridinefree, metal-free, and environmental friendly conditions. The influence of pore sizes in the HMCN base catalysts was investigated in the *p*-hydroxycinnamic acid synthesis and the experimental results reveal that HMCN (5.9) showed a better catalytic performance with high product isolated yield of 91%, 100% selectivity and maximum *p*-hydroxybenzaldehyde conversion of 94.5% at 60 min compare to other two catalysts, namely HMCN (4.7) and HMCN (7.1). These findings provide insight into the design and development of HMCN catalytic materials with suitable pore size for a wide range of product for the selective catalytic organic transformations.

2 Experimental

2.1 Synthesis of SBA-15 Templates and HMCN Catalysts

Mesoporous SBA-15 silica template was synthesised by employing optimized procedure with a molar gel composition of TEOS: 0.016 P123: 12.6 HCl: 167 H₂O at different aging temperature of 100, 120, and 150 °C [20]. The solid product obtained from aging process was filtered, washed with deionized water then calcined at 550 °C for 36 h. HMCN catalysts were prepared using SBA-15 templates with different pore diameters. In a typical synthesis, 0.5 g of SBA-15 was added to a mixture of EDA (2.2 g) and CTC (5.4 g) in RB flask. The resultant mixture was refluxed and stirred at 90 °C for 6 h. Then the mixture was dried for 24 h and ground into fine powder. The composite powdered material was pyrolysis at 800 °C in an inert atmosphere for 5 h. HMCN materials were obtained after the removal of silica templates by HF and were labelled as HMCN (x), where x indicates the pore diameter of the materials [21].

2.2 Characterisation

XRD patterns of HMCN samples were recorded on a powder X-ray diffractometer (Rigaku, Smart lab, Japan) using Cu K α (λ = 1.54 Å) radiation. Nitrogen sorption isotherms were measured in Quantachrome (Autosorb 1 sorption analyzer, USA). FESEM images were recorded Hitachi S-4800-TWIN. Transmission electron microscopy was conducted using a FEI-Tecnai G2 20 S-TWIN electron microscope operated at an accelerating voltage of 200 kV. UV–Vis



Scheme 1 Synthesis of *p*-hydroxycinnamic acid using HMCN catalyst

diffused reflectance spectroscopy was performed on a PER-KIN ELMER LAMDA 35, USA, double beam spectrometer in the range of 200-800 nm in ambient conditions. ¹H NMR and ¹³C NMR spectra were recorded on Bruker (AVANCE III, 400 MHz) spectrometer using TMS as an internal standard. LCMS spectrums were recorded using Agilent 1290 series, Mass 6150 quadru pole LCMS.

2.3 Synthesis of p-Hydroxycinnamic Acid

The catalytic performance of HMCN samples was tested on the synthesis of p-hydroxycinnamic acid in Knoevenagel-Doebner reaction under toluene (10 ml) azeotropic reflux condition (105 °C) by taking 1:2 mol ratio of p-hydroxybenzaldehyde (0.0040 mol) and malonic acid (0.0081 mol) with 200 mg of HMCN base catalyst. The catalytic reactions were studied with different reaction conditions such as reaction time, catalyst amount, pore size of the catalyst, and reaction cycle. The reaction mixture were collected, filtered using syringe filter and analysed by gas chromatography (Thermo Scientific TRACE1300, USA) equipped with DB-5 capillary column (30 m \times 0.32 mm \times 1 µm film thickness) and flame ionization detector using nitrogen carrier gas using n-decane as internal standard. The performance of HMCN catalysts is evaluated quantitatively by the conversion of *p*-hydroxybenzaldehyde (conversion %), and the selectivity to p-hydroxycinnamic acid (selectivity %) obtained at the selected conditions. Herein, conversion (%) = ((initial peak area of reactant - final peak areaof reactant)/initial peak area of reactant) $\times 100$; selectivity (%) = (relative peak area of specific product/sum of relative peak area of the all products) $\times 100$. After completion of reaction, the catalyst was recovered by filtration and washed with methanol and hexane. The reaction product *p*-hydroxvcinnamic acid was obtained after the toluene removal by a rotary evaporator and purified by absolute ethanol recrystallization. Product was confirmed by NMR analysis (ESI).

3 Results and Discussion

Powder XRD pattern of (a) SBA-15 templates and (b) HMCN materials are shown in Fig. 1. The XRD pattern (a) of SBA-15 templates showed a characteristic peaks due to (100), (110), and (200) reflections due to p6mm symmetry. The XRD pattern (b) of HMCN samples showed a characteristic intense peak at 2Θ value of 0.97 due to (100) reflection and two higher order peaks due to (110) and (200) reflections below 20 value of 2. This clearly indicates the persistence of hexagonal structure having *p6mm* symmetry in the HMCN samples. The XRD peaks of SBA-15 samples shift towards 2O values as the aging temperature increases from 100 to 150 °C. This confirms that as the aging temperature increases the unit cell constant and d-space value increases. The same trend was observed in the HMCN replica materials synthesised from the corresponding SBA-15 templates (Table 1). This result firmly confirms that HMCN samples have an ordered structure and the replication process from SBA-15 template to HMCN is very much successful. The high angle XRD pattern of HMCN (5.9) sample (Fig. 1b, inset) showed a broad peak at 20 value of 24.8 and a weak peak at 44 due to (002) and (100) reflections, respectively. This is similar to the XRD pattern of graphitic CN obtained from turbostratic graphite-like stacking of the conjugated aromatic CN units [20].

Nitrogen adsorption isotherms (a) and pore size distributions (b) of HMCN samples are shown in Fig. 2 and the textural properties are shown in Table 1. Nitrogen adsorption isotherms (a) of HMCN samples exhibit type IV adsorption isotherm with H1 hysteresis loop, which revealed a narrow pore size distribution present in the HMCN materials. The



of a SBA-15 templates and b HMCN catalysts

S. no.	Samples	Catalyst C/N mole ratio in synthetic gel	Catalyst C/N mole ratio in sample by EDAX	$S_{BET} (m^2/g)$	Vp (cm ³ /g)	Dp (nm)	a _o (nm)	d ₁₀₀ (nm)	Total amount of nitrogen (mmol/g) by EDAX
1	SBA-15 (9.0)	_	-	895	1.20	9.0	10.3	8.9	_
2	SBA-15 (10.5)	_	-	653	1.20	10.5	10.9	9.4	_
3	SBA-15 (11.3)	_	-	395	1.10	11.3	11	9.5	_
4	HMCN (4.7)	1.48	2.22	509	0.51	4.7	9.8	8.5	4.92
5	HMCN (5.9)	1.48	2.22	389	0.55	5.9	10.3	8.9	4.90
6	HMCN (7.1)	1.48	2.25	379	0.64	7.1	10.7	9.3	4.78

Table 1 Physicochemical property of different SBA-15 and HMCN samples

The S_{BET} , D_p , and V_p values of SBA-15 are based on the literature (see Ref. [20])

 S_{BET} specific surface area, Vp pore volume, Dp pore diameter, a_o unit cell constant was calculated as, $a_o = 2 \times d_{100}/\sqrt{3}$



pore diameter of HMCN catalysts prepared using SBA-15 templates synthesised at different temperatures increased from 4.7 to 7.1 nm. A shift in the position of capillary condensation step of N2 adsorption isotherms of HMCN samples was observed from low P/P₀ (relative pressure) to high P/P_0 value. This indicates a huge expansion in the pore size of HMCN replica materials as the synthesis temperature of corresponding SBA-15 templates increases. This is in consistent with increase in unit-cell constants and d-space values observed from the XRD patterns of HMCN samples in Fig. 1b [21]. A decrease in specific surface area from 509 to 379 m²/g and increase in specific pore volume from 0.5to 0.64 cm^3/g and pore diameter from 4.7 to 7.1 nm of the HMCN replica materials were observed as increase in the aging temperature of SBA-15 templates used. The change in the pore diameter of the HMCN materials upon increasing the pore diameter of the SBA-15 template is clearly evident from their BJH adsorption pore size distribution (Fig. 2b).

Diffused reflectance UV–Vis spectra (Fig. 3) of HMCN samples exhibited a strong absorbance at *ca*. 330 nm due to $\pi \rightarrow \pi^*$ electronic transition of aromatic 1,3,5-triazine and



Fig. 3 UV-Vis diffused reflectance spectra of HMCN catalysts

 $n \rightarrow \pi^*$ non-bonding electronic transition of nitrogen atoms [22]. FT-IR spectra (Fig. 4) of HMCN samples show three predominant broad bands at *ca*. 1222, 1571 and 3354 cm⁻¹



Fig. 4 FTIR spectra of HMCN catalysts

due to aromatic C–N stretching bands, aromatic ring modes and N–H stretching in the aromatic ring, respectively [20].

The FESEM–EDAX mapping of carbon and nitrogen elemental analysis of HMCN (5.9) sample is shown in Fig. 5. FESEM image (a) of HMCN (5.9) sample showed aggregates of warm like regular rod-shaped particles of *ca*. 2 μ m sizes with co-existence of *ca*. 0.5 μ m particle size. EDAX analysis of HMCN (5.9) sample is provided in Table 1. EDAX results showed that the final product of HMCN catalyst has a higher C/N mole ratio than the actual mole ratio used in the synthesis. This is due to the low thermodynamic stability of nitrogen in the carbon matrix and the nitrogen prefers to stay as nitrogen molecule at high temperature. Elemental mapping analysis (b) and (c) of HMCN (5.9) sample clearly demonstrates that N is homogeneously distributed in the carbon matrix within the HMCN composites.

HRTEM measurement was used to further examine the structural order and morphology of the HMCN materials with different pore diameters and it is shown in Fig. 6. HRTEM images of (a) HMCN (4.7), (b) HMCN (5.9), and (c) HMCN (7.1) samples show a linear array of mesopores arranged in regular tubular channels. The HRTEM analysis



Fig. 5 a FESEM image of HMCN (5.9) and EDAX element mapping of b carbon and c nitrogen



Fig. 6 HRTEM images of HMCN samples a HMCN (4.7), b HMCN (5.9), and c HMCN (7.1)

of HMCN samples prepared from SBA-15 synthesised at 100, 120, and 150 °C showed that the width of mesopore tubular channels are ca. 7.4, 8.3, and 8.9 nm, respectively.

Electronic structure calculations on *p*-hydroxybenzaldehyde and *p*-hydroxycinnamic acid were performed using Gaussian 03W, version 6 with basis set of 6-31++g(d, p)by density functional theory method with B3LYP hybrid functional. The molecular geometry was viewed through Gauss view 3.0. The lowest energy molecular dimension of *p*-hydroxybenzaldehyde and *p*-hydroxycinnamic acid was calculated using three dimensional coordinates and it was found that these molecules exists as planar structure with the dimensions of $0.430 \text{ nm} \times 0.696 \text{ nm}$ and $0.431 \text{ nm} \times 0.976 \text{ nm}$, respectively. It is interesting that the pore sizes of HMCN catalysts synthesised for this study are greater than the molecular dimensions of *p*-hydroxybenzaldehyde and *p*-hydroxycinnamic acid. Hence the catalytic conversion of *p*-hydroxybenzaldehyde to *p*-hydroxycinnamic acid is undoubtedly formed inside the pores of HMCN catalysts rather than on the external surface. The minimum energy conformation of p-hydroxybenzaldehyde and *p*-hydroxycinnamic acid with different pore sizes of HMCN catalysts are depicted in Scheme 2.

The effect of catalysts pore size on the synthesis of *p*-hydroxycinnamic acid was studied at different reaction

time viz., 5, 10, 15, 30, 60, 90, 120, 150, and 180 min using 200 mg of HMCN (4.7), HMCN (5.9), and HMCN (7.1) catalysts and they are shown in Fig. 7a-c, respectively. The isolated yield of *p*-hydroxycinnamic acid synthesised using HMCN catalysts was shown in Fig. 8. The three catalysts namely HMCN (4.7), HMCN (5.9), and HMCN (7.1) showed *p*-hydroxybenzaldehyde conversion of 79.8, 94.5, and 91.7%, with selectivity to p-hydroxycinnamic acid of 96.3, 100, and 100%, respectively at 60 min. Since HMCN (4.7) catalyst has smaller pore diameter of 4.7 nm than HMCN (5.9) and HMCN (7.1), it experience a greater diffusion constrain for the reactants to enter into the HMCN (4.7) nanochannels to meet the active sites to get convert into products and the formed product to diffuse out of the channels. This is the reason for the lower conversion (79.8%) and selectivity (96.3%) and isolated yield (55%) for HMCN (4.7) catalyst than HMCN (5.9) and HMCN (7.1). But HMCN (5.9) has the pore size of 5.9 nm with 20.3% greater in pore dimension than HMCN (4.7). The size tuned pores with 5.9 nm, facilitates the faster diffusion of the reactants with less diffusion constrains to adsorb on the active sites to get converted into product and the product formed can easily diffused out. This is the reason for high conversion (94.5%), product selectivity (100%) and isolated yield (91%) within 60 min for HMCN (5.9) compare to HMCN (4.7) and this

Hexagonal Mesoporous Carbon Nitride (HMCN)

Scheme 2 The minimum energy conformation structure of *p*-hydroxybenzaldehyde, *p*-hydroxycinnamic acid and pore size illustrations of HMCN (4.7), HMCN (5.9) and HMCN (7.1) catalysts

Conversion & Selectivity (%)

Fig. 7 Effect of reaction time in the synthesis p-hydroxycinnamic acid on a HMCN (4.7), b HMCN (5.9), and c HMCN (7.1) catalyst





Fig. 8 Effect of pore diameter of different HMCN catalysts on the yield of p-hydroxycinnamic acid

new HMCN (5.9) catalytic reaction system provides much faster reaction rate with high p-hydroxybenzaldehyde conversion with high selectivity to p-hydroxycinnamic acid compare to the earlier reports (Table 2).

The pore diameter of HMCN (7.1) catalyst with 7.1 nm is of 33.8 and 16.9% higher than the pore diameter of HMCN (4.7) and HMCN (5.9), respectively. Hence more number of reactant molecules can enter into the pores without any diffusion constrains. But at the same time, some of the molecules can be diffused out of the HMCN (7.1) nanochannels without adsorption on the active sites, results decrease in p-hydroxybenzaldehyde conversion (91.7%) compare to HMCN (5.9) base catalyst. From this study it is confirmed that the HMCN (5.9) catalyst would be the best choice for high p-hydroxybenzaldehyde conversion with high selectivity to p-hydroxycinnamic acid.

The effect of catalyst amount of HMCN (5.9) on the synthesis of p-hydroxycinnamic acid was studied at 60 min using different catalyst amount viz., 50, 100, 200, 300, and 400 mg and the corresponding product yield was shown in Fig. 9. Initially the yield of *p*-hydroxycinnamic acid is increased gradually from 55 to 91% as increase in the catalyst amount from 50 to 200 mg due to the increase of active basic sites on the catalyst surface in the reaction medium. But there is no increase in the product yield was observed, even after increase in the catalyst amount to 300, 400 mg. Hence from this study, it is observed that 200 mg of HMCN Table 2Comparison of variousbase catalysts used for thesynthesis of p-hydroxycinnamicacid via Knoevenagel–Doebnerreaction

Entry	Catalytic system	Yield (%) ^a	Time (h)	References	
1	Diamino-functionalised MCM-41	85–90	0.25	[23]	
2	Amino-functionalized mesoporous silica	75–85	3	[24]	
3 ^b	Pyridine:piperidine	99	3	[25]	
4 ^c	Pyridine:piperidine	97	0.03	[26]	
5	Pyridine:piperidine	75–85	5	[27]	
6	HMCN (5.9)	91 (100% selectivity)	1	Present work	

Our reaction conditions: *p*-hydroxybenzaldehyde (0.0040 mol), malonic acid (0.0081 mol), HMCN (5.9) (200 mg), toluene (10 ml), reflux temperature

^aIsolated yield

^bUltrasound assisted

^cMicrowave assisted



Fig. 9 Effect of catalyst amount on the synthesis p-hydroxycinnamic acid over HMCN (5.9) catalyst

(5.9) catalyst would be the optimum amount to convert *p*-hydroxybenzaldehyde to *p*-hydroxycinnamic acid. No reaction product was observed in the absence of catalyst under identical conditions. It clearly reveals the importance of the basic active sites of HMCN catalysts in the Knoevenagel type of reactions.

On the basis of the structure, physicochemical properties, and catalytic testing results of the HMCN materials, the excellent catalytic performance of HMCN is attributed to the following two factors. On the one hand, the combinations of Brönsted and Lewis active basic centres (Scheme 3) of HMCN catalysts catalyse the Knoevenagel–Doebner type condensation reaction more effectively [20]. On the other hand, the unique surface textural properties of HMCN material play a key role to obtain an excellent catalytic activity with high selectivity to *p*-hydroxycinnamic acid. The uniform pore channel with optimum pore size (5.9 nm) of HMCN material facilitates the easy diffusion of reactants and products elution from the nanochannels, which reduces the internal mass transfer resistance. Hence HMCN catalysts



Scheme 3 Schematic wall structure of HMCN

having suitable pore size makes more opportunity for the reactants to access the active sites of HMCN catalysts.

The formation mechanism of *p*-hydroxycinnamic acid is illustrated in Scheme 4. At first the acidic proton from the active methylene group of malonic acid is abstracted by the Lewis basic sites of carbon nitride. Then the produced compound (I) undergo nucleophilic attack to the carbonyl carbon of compound (II) to form oxyanion (III). The oxyanion abstract H⁺ from the protonated Lewis basic site of HMCN catalyst produces compound (IV) and the catalyst is regenerated. The compound IV leads to the formation of *p*-hydroxycinnamic acid with the elimination of water and CO₂.

The HMCN (5.9) catalyst recycle test was conducted after the separation of catalyst from the reaction mixture by filtration, and washing first with toluene and then with methanol



Scheme 4 The formation mechanism of *p*-hydroxycinnamic acid

and dried at 100 °C. The recovered catalyst was reused for the next reaction run in order to study the catalyst lifetime and stability. It was observed that conversion of *p*-hydroxybenzaldehyde and selectivity to *p*-hydroxycinnamic acid is not much affected even after six cycles as shown in Fig. 10.

4 Conclusions

The size of nanochannels of HMCN catalytic materials were architected with the diameter of 4.7, 5.9, and 7.1 nm using SBA-15 hard templates synthesised at different temperatures. The influence pore diameter of HMCN catalysts on

p-hydroxycinnamic acid synthesis was investigated in a nonconventional metal-free, pyridine-free, eco-friendly reaction conditions. HMCN (4.7), HMCN (5.9), and HMCN (7.1) showed *p*-hydroxybenzaldehyde conversion of 79.8, 94.5, and 91.7%, with selectivity to *p*-hydroxycinnamic acid of 96.3, 100, and 100%, respectively at 60 min. The low catalytic performance of HMCN (4.7) than HMCN (5.9) and HMCN (7.1) catalysts is due to the smaller pore diameter of 4.7 nm, experiences greater diffusion constrain for the reactants to enter into nanochannels. The high catalytic performance of HMCN (5.9) catalyst with 94.5% *p*-hydroxybenzaldehyde conversion and 100% *p*-hydroxycinnamic acid selectivity compare to other catalysts is due to easy diffusion



Fig. 10 Reusability test of HMCN (5.9) catalyst in the synthesis of p-hydroxycinnamic acid

of *p*-hydroxybenzaldehyde into HMCN nanochannels with suitable pore size of 5.9 nm. The low catalytic performance of HMCN (7.1) catalyst compare to HMCN (5.9) is due to the large pore size of 7.1 nm, facilitates reactants to diffuse much faster rate and some of them can easily diffusion out without adsorb on the reactive sites. These findings suggest that the methodology adopted here could also offer many opportunities for the synthesis of organic molecules with different molecular sizes such as paraffins, aromatics, vitamins and amino acids.

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