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A new approach to tailoring edge active groups of graphitic carbon nitrides for catalytic conversion of CO₂ into cyclic carbonates was proposed in this work. To improve the catalytic performance, boron-doped melamine-derived graphitic carbon nitrides (MCNB) with numerous exposed edge defects were prepared by using 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF₄) as the soft template and boron source. Different mass ratios of BmimBF₄ to melamine were explored for MCNB preparation, MCNB(x) (x is the mass ratio) with different polymerization degree, pore structures and boron doping contents were obtained, and the relationship between MCNB properties and corresponding catalytic activities was then investigated. With low polymerization degree, abundant meso-macroporous structure and small amounts of boron (<1.59 atm%) doped in the skeleton, MCNB(0.01) exhibited better catalytic performance and could be suitable for various epoxide substrates with the yield of cyclic carbonates up to 89.0% at 130 °C in 6 h. According to the XPS analysis and DFT calculation results, the active centers were confirmed to be the partially-condensed amino groups in edge defects which were enhanced by moderately doping of boron in the skeleton.

Introduction

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CO₂ conversion into high-value products is of great significance in easing energy and environmental concerns. As an efficient and atom-economy way for CO2 transformation, the cycloaddition with epoxides into cyclic carbonates has attracted extensive attention in both academia and industry, of which the products could be widely used in production of electrolytes, glycols, polar aprotic solvents, pharmaceutical ingredients and fine chemicals in biomedical synthesis.^{1, 2} In recent years, the development of the heterogeneous catalysts has attracted great attention in the literature, such as metalbased catalysts,³ modified molecular sieve,⁴⁻⁶ supported ionic liquids,^{7, 8} and poly(ionic liquids),⁹ etc. Though they have contributed more or less to the catalytic performance, some existing disadvantages including metal residue and low thermal stability still perplex the academia and industry. The stability of catalysts, and the mild and environmental-friendly reaction conditions have always drawn great attention of researchers in fields of catalysis and chemical engineering.¹⁰⁻¹²

The metal-free graphitic carbon nitride $(g-C_3N_4)$ materials could effectively make up for the weakness of traditional

adjustable edge active groups in the structure.^{2, 13-15} In the respect of CO₂ conversion, different methods have been explored to enhance the activity of $g-C_3N_4$, including increase of surface area and dispersity,¹⁶⁻¹⁹ exposure of edge defects,^{17,} ^{20, 21} immobilization of functional groups,²² and doping of other atoms.^{23, 24} According to these reports, the partially-condensed amino groups in edge defects of g-C₃N₄ could function directly or indirectly for the improvement in catalytic activity. Therefore, the key point in developing efficient $g-C_3N_4$ catalysts is digging more edge defects, keeping integrality of active sites, and enhancing the active groups. To create more edge defects and keep their integrality, non-template way has been reported for urea-derived carbon nitrides adjustion by changing polymerization temperatures.^{18, 22} To enhance edge active groups, the introduction of new active components and doping of other atoms were respectively investigated.²²⁻²⁴ Up to date, there is few approach to achieving the above three purposes simultaneously for CO₂ activation.

catalysts due to the combination of thermal stability and

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In recent years, ionic liquids have been used as soft templates in material preparation owning to the unique properties of low melting points, negligible vapor pressures and high decomposition temperatures (some excess 400 °C).²⁵⁻²⁷ In carbon nitride synthesis, ionic liquids not only show great

advantages as soft templates for the precursors with high polymerization temperatures, but also could be used as dopants for doping other atoms. Zhang et al. found that the electronic structures of carbon nitrides as well as their surface properties could be modified by doping phosphorus with 1butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆) as phosphorus source.²⁸ Wang et al. successfully synthesized

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melamine without (left) and with ionic liquids (right).

boron- and fluorine-containing mesoporous carbon nitride polymers for cyclohexane oxidation by using 1-butyl-3methylimidazolium tetrafluoroborate (BmimBF₄) as the soft template.27

Considering the two functions of ionic liquids in modifying materials, they would be promising in tailoring carbon nitrides for CO₂ conversion both as the soft template and heteroatom source. From previous research, boron could enter the C-N condensation scheme replacing carbon as strong Lewis acid sites,²⁹ which might affect the charge distribution and bond length of adjacent groups. BF_4^- was thought to be a good dopant for carbon nitride modification but fluorine was inevitably mixed in when using dicyandiamide as the precursor, which was thought to be unfriendly to environment. To obtain boron-doping and fluorine-free carbon nitrides in this work, melamine with the structure close to carbon nitride unit was adopted as the precursor, and BmimBF₄ was used as the soft template and boron source. Compared with more dense structure in non-template polymerization process of melamine, which goes more directly to melem with less porosity and edge defects (left in Scheme 1),³⁰ that structures with ionic liquids as the soft template could be adjusted for more porosity and edge defects (right in Scheme 1). By changing mass ratios of BmimBF₄ to melamine (B/M), a series of boron-doped melamine-derived carbon nitrides, abbreviated as MCNB(x) (x is the mass ratio), were obtained. First of all, the effect of B/M ratios on the polymerization degrees, pore structures, and

edge active groups of different MCNB materials were studied. Then, the influence of these properties 038/67 catalytic performance for CO₂ conversion into cyclic carbonates was also investigated. Finally, the active centers in edge defects were figured out and the possible reaction mechanism in presence of MCNB catalysts was preliminarily proposed.

Results and Discussion

Characterization of MCNB materials

With BmimBF₄ as the soft template and boron source, a series of MCNB materials with different B/M mass ratios (x=0.1, 0.05, 0.03, 0.01) and melamine-derived carbon nitride without addtion of BmimBF₄ (MCN) were prepared. The polymerization degrees, pore structures and edge active groups of all the asprepared MCNB materials were analyzed and detected with different characterization methods.

First of all, TGA curves of all MCNB materials were obtained. From the curves shown in Fig. 1, all MCNB materials had high thermal stability above 500 °C and they all owned one weight loss peak which indicated that all the materials might be pure phase without other unstable impurities. FT-IR spectra and XRD patterns for all the MCNB samples were shown in Fig. 2 and Fig. 3, respectively. All the characteristic peaks of g-C₃N₄ phases were detected in FT-IR spectra. The adsorption bands at 810 cm⁻¹ and 1200–1650 cm⁻¹ could be attributed to the breathing mode of triazine and the stretching mode of C-N heterocycles, respectively.³¹ The broad band at 3000–3700 cm⁻¹ belongs to N–H vibration due to partial condensation and the adsorbed water molecules.^{32, 33} The typical vibration of B-N at 1370 cm⁻¹ is presumably overlapped by that of the C–N stretch.²⁹ With the increase of B/M mass ratios, both of the peaks at 810 cm⁻¹ and in the region of 1240–1650 cm⁻¹ became weaker, illustrating the decrease in polymerization degree of triazine repeating units.³⁴ Compared with MCN, the peaks around 3000–3700 cm^{-1} got more distinct for MCNB(0.01) to MCNB(0.05), meaning more edge -NH groups were exposed



Fig. 1 TGA curves of different MCNB materials prepared with different B/M ratios

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Fig. 2 FT-IR spectra of different MCNB materials prepared with different B/M ratios.



Fig. 3 XRD patterns of different MCNB materials prepared with different $\ensuremath{\mathsf{B/M}}$ ratios.

after BmimBF₄ addition.

In addition, XRD patterns of all the as-prepared MCNB materials were recorded in Fig. 3. All materials owned two typical diffraction peaks at around 27.5° and 13.1°, demonstrating the formation of g-C₃N₄ phases. The peak at around 27.5° could be indexed to the (002) crystal plane of g- C_3N_4 due to the interlayer stacking of melon networks of g- $C_3 N_4, ^{35,\ 36}$ while a minor peak at around $13.1\,^\circ$ could be attributed to the (100) crystal plane of g-C₃N₄ due to the repetitive in-plane tri-s-triazine units.³⁷ Compared with MCN, there was a slight broadening trend for all the characteristic peaks and a slight shift to lower angle for (002) peak after BmimBF₄ addition, indicating the decreased polymerization degree and the expanded interlayer space after boron doping.²⁷ Among MCNB samples, the shift for (002) peak of MCNB(0.01) was more obvious than others, meaning the larger space distance between layers. The lower polymerization degree and larger space distance indicated that more edge defects were easier to reach.³⁸ Whereas, when the B/M mass ratio was raised to 0.10, the (002) peak intensity at 27.5° got a sudden increase, indicating the inter-layer crystalline structure of g-C₃N₄ was less damaged by excessive BmimBF₄ addition though the $(100)^{D}$ beak 106 / Antrahaver crystalline structure was barely distinguished. The less effect on MCNB crystallinity with excess BmimBF₄ addition might be ascribed to self-aggregation of ionic liquids in melamine solution during pre-treatment which caused more ionic liquids condensing alone rather than acting as template during calcination.³⁹⁻⁴¹ Thus, small amounts of BmimBF₄ addition were more suitable to adjust the crystallinity for exposure and access of edge groups, but too much (B/M ratio above 0.1) might have little effect.

Thereafter, the morphology and pore structures were respectively characterized by SEM and TEM. The obtained MCN and MCNB images were respectively shown in Fig. 4 and Fig. 5. All the materials exhibited porous platelet-like structure, consistent with previous reports about g-C₃N₄.⁴² Different from dense layer structure of MCN in Fig. 4, MCNB materials were more bouffant with expanded space between layers (Fig. 4), which agreed well with XRD analysis. The space expansion might result from boron doping in g-C₃N₄ skeletons. Apart from that, all the MCNB samples presented mesomacroporous structures, which could be further verified through N₂ adsorption-and-desorption analysis. Both the isotherms and pore size distribution curves of all MCNB samples were displayed in Fig. S1. The isotherms were type IV with H3 hysteresis loops, indicating the presence of mesopores (mesopores have widths between 2 and 50 nm).⁴³ Besides, the pore-size distribution curves (inset in Fig. S1) of all samples were very wide around pore diameters of 50 nm, indicating the co-existence of meso- and macropores.⁴³ With B/M ratios between 0.01 and 0.05, the proportion of meso-/macropores (pore diameter around 50 nm) in MCNB was higher than that with B/M ratio of 0.1, suggesting that bigger pores tended to occur with less BmimBF₄ addition. This trend could further be proved in Table 1 that both the BET surface area and BJH Desorption average pore diameters decreased with more BmimBF₄ addition and MCNB(0.01) owned the highest BET surface area and average pore diameter. Otherwise, with B/M mass ratio in excess of 0.1, a sudden increase in BET surface area was observed, which might be attributed to extra selfcondensed products out of g-C₃N₄ pore structures from ionic liquids aggregates pre-formed in melamine solution. 40, 44-47



Fig. 4 TEM (a) and SEM (b) images of melamine-derived carbon nitride (MCN) without BmimBF_4 addition.

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Fig. 5 SEM and TEM images of MCNB materials prepared with different B/M mass ratios.

 Table 1 BET surface area, BJH Desorption average pore diameters and C/H mol ratios of MCNB materials

Materials	BET surface area (m²/g) ^a	Average pore diameter (nm) ^b	C/H mol ratio ^c
MCN	10.5	17.8	1.398
MCNB(0.01)	11.1	28.3	1.193
MCNB(0.03)	9.9	23.4	1.173
MCNB(0.05)	7.8	21.6	1.164
MCNB(0.1)	10.3	17.4	1.116
<i>a</i> b c c			(057)

^a BET surface area was obtained from Brunauer–Emmett–Teller (BET) method; ^b Average pore diameters were obtained from Barrett–Joyner– Halenda (BJH) approach; ^C C/H mole ratios were obtained from elemental analysis.

These self-condensed structures of MCNB(0.1) might account for the higher BET surface area than others. That also explained the XRD results that the crystallinity of MCNB was less affected at B/M ratio of 0.1 compared with others.

Furthermore, the C/H mole ratios were also obtained by elemental analysis (Table 1). With addition of BmimBF₄, the C/H mole ratio was reduced from 1.398 to 1.116, indicating that more hydrogen retained because of the lower polymerization degree than MCN. Among MCNB samples, the declining trend of C/H mole ratio while raising B/M ratios might result from the decreased carbon amounts in $g-C_3N_4$ skeleton because of the boron replacement.²⁹ To further explore the active groups in MCNB structure. XPS analysis of both MCN and MCNB materials were conducted for comparison. First of all, no peak was detected from F1s spectrum in Fig. S2, indicating that fluorine atom was scarcely doped in MCNB structure in this work. Hence, the following discussion is mainly about N- and B-containing groups. Three representative carbon nitrides, MCN, MCNB(0.01) and MCNB(0.05), were chosen for comparison. The XPS spectra of N1s and B1s were presented in Fig. 6. As seen from Fig. 6. there existed three kinds of nitrogen components in MCNB structures, including the uncondensed primary nitrogen groups N-H₂ (400.8-401.1 eV), condensed bridge groups C-N(-C)-C or partially-condensed C-N(-H)-C (399.1-399.5 eV) and trazine skeleton nitrogen C = N-C (398.3–398.6 eV), which was consistent with previous reports about g-C₃N₄ edge groups.⁴⁸ Beyond that, B1s spectra confirmed that boron was doped with the binding energy (BE) peak at 191.5 eV, which was reported to be $HN = B(-N)_2$ structure resulting from boron replacement for the original carbon dot.²⁹ Further evidence of the boron doping came from the ¹¹B solid-state MAS NMR measurements. As ¹¹B solid-state MAS NMR displayed in Fig. S3, one sharp peak at -11.69 ppm was observed in MCNB(0.01) and MCNB(0.05), which was more likely corresponded to the bay boron position in the framework structure.²⁹ In addition, the relative percentages of nitrogen components in different MCNB networks were calculated from corresponding XPS spectra. Both of the percentages of amino groups and boron contents were listed in Table 2. Table 2 showed that the sum of uncondensed N-H₂ and partially-condensed C-N(-H)-C (or C−N(−C)−C) percentages increased after BmimBF₄ addition, further confirming the decreased polymerization degree. With B/M ratios raised from 0.01 to 0.05, boron content got higher, while the percentage of uncondensed nitrogen groups became



Fig. 6 XPS spectra of different MCNB materials prepared with different B/M ratios.

	Rela	B content (atm%) ^b			
Samples N–H ₂ C–N(–C)-		C–N(–C)–C or C–N(–H)–C	C=N-C	HN=B(-N) ₂	
MCN	12.7	35.6	51.7	0.32	
MCNB(0.01)	13.1	62.9	24.0	1.06	
MCNB(0.05)	7.2	50.0	42.8	1.59	
^{<i>a</i>} The percentage was calculated according to the relative magnitude of peak					

area in N1s spectra from Fig. 6. ^b B content was determined by XPS analysis.

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lower and MCNB(0.01) owned the largest percentage. Therefore, only a small amount of boron content (boron<1.59 atm%) could be efficient for acquiring more partially-condensed amino groups in edge defects. Too much boron species doped in the g- C_3N_4 skeleton might cause unwanted negative effect to active groups.

Catalytic evaluation of MCNB materials

All the MCNB materials prepared under different B/M ratios were tested for comparison in catalytic activity for CO₂ conversion into cyclic carbonates. With propylene oxide (PO) as model reactant, the cycloaddition reactions were conducted under identical conditions for screening out the best MCNB catalyst. In addition, the suitability of the best catalyst for other epoxides' conversion was also investigated. All yields and selectivities were determined by GC using biphenyl as an internal standard. Yields were given based on epoxides.

First, all the MCNB catalysts were screened by using the model reaction of CO₂ cycloaddition with propylene oxide (PO) into propylene carbonate (PC) under identical reaction conditions. The results were listed in Table 3. Without catalyst participation, PO was hardly converted. With MCN as catalyst, higher catalytic activity was obtained than melamine precursor. After BmimBF₄ addition, the catalytic activity could be improved further, but with the increase of B/M mass ratios from 0.01 to 0.1, the catalytic activity of MCNB exhibited a decreasing trend. Among all the MCNB catalysts, MCNB(0.01) was the best one with PC yield up to 46.9% at 130 °C for 6 h, and MCNB(0.1) was the worst. To further investigate the suitability of MCNB(0.01) as catalyt for other substrates, the cycloaddition of CO₂ with different epoxides, ethylene oxide, epichlorohydrin and isobutylene oxide, were tested successively under given conditions. As the catalytic evaluation results in Table 4 displayed, all the tested substrates exhibited good product yields with MCNB(0.01) as catalyst, especially for epichlorohydrin whose product yield was up to 89.0% at 130 °C for 6 h. Considering the high catalytic activity and suitability for various epoxides, MCNB(0.01) was taken as a promising catalyst for the synthesis of cyclic carbonates in future industry.

The catalytic evaluation results showed the same trend with the above analyzed properties. As a result, $BmimBF_4$ addition enhanced the catalytic activity of melamine-derived carbon nitrides from two aspects. On one hand, the polymerization degree and crystallinity of MCNB were adjusted with $BmimBF_4$ as the role of soft template, which created more exposed edge defects in carbon nitride structure and the partially-condensed groups therein, such as primary amine (NH₂) groups and secondary amino (C–NH–C) groups. These partially-condensed



Scheme 2 The reaction of CO_2 cycloaddition with epoxides into cyclic carbonates.

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Table 3 Catalysts screening for CO ₂ cycloaddition	n with	РО	into∖RG	w Artic	le O	nline	
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Entry	Catalysts	PC yield [%]	PC selectivity [%]	TOF ^f [h ⁻¹]
1	Blank	0.6	98.9	-
2	Melamine ^a	0.4	7.9	0.02
3	MCN ^a	4.8	42.1	0.24
4	MCNB(0.01) ^a	31.0	99.9	1.51
5	MCNB(0.03) ^a	28.4	98.6	1.38
6	MCNB(0.05) ^a	13.0	65.2	0.63
7	MCNB(0.1) ^a	4.9	99.9	0.24
8	MCNB(0.01) ^b	46.9	99.9	1.14
9	MCNB(0.03) ^b	39.8	92.5	0.97
10	MCNB(0.05) ^b	22.1	93.2	0.54
11	MCNB(0.1) ^b	3.1	48.8	0.07
12	MCNB(0.01) ^c	94.2	99.2	0.38
13	MCNB(0.01) ^d	95.7	99.9	1.16

Reaction Condition: PO: 14.3 mmol, temperature: 130 °C, CO₂ pressure: 2.8 MPa; ^{*a*} catalyst (50 mg), 6 h; ^{*b*} catalyst (100 mg), 6 h; ^{*c*} catalyst (100 mg), 36 h; ^{*d*} EO, catalyst (50 mg), 24 h. ^{*f*} TOF: mass of synthesized PC per gram catalyst per hour. All yields and selectivities were determined by GC. Yields were given based on PO reactant.

Table 4 Suitability of MCNB(0.01) for catalytic conversion of other epoxides

Entry	Epoxide	Product	Yield [%]	Selectivity [%]	TOF ^c [h⁻¹]
1 ^{<i>a</i>})))	0	31.0	99.9	1.51
2 ^{<i>a</i>}	$\overset{\circ}{\bigtriangleup}$		59.7	99.2	2.50
3 ^{<i>a</i>}	CI	CIO	89.0	98.0	5.79
4 ^{<i>b</i>}	°∽		34.5	82.9	0.48

Reaction Condition: catalyst (50 mg), epoxides (14.3 mmol), temperature: 130 °C, CO_2 pressure: 2.8 MPa. Reaction time: ^{*a*} 6 h; ^{*b*} 24 h. ^{*c*} TOF: mass of synthesized PC per gram catalyst per hour. All yields and selectivities were determined by GC. Yields were given based on epoxides.

amino groups were active centers for CO_2 cycloaddition with epoxides. Furthermore, with increase of B/M ratios, the proportion of meso-/macropores around 50 nm in MCNB structure declined and MCNB(0.01) owned the largest proportion of meso-/macropores (see Fig. S1). The larger proportion of meso-/macropores is another factor for enhancement of catalytic activity because molecule transportation between different amino groups could be easily done with less diffusion resistance therein. On the other hand, the active centers were also influenced by doped boron atoms with BmimBF₄ as a role of boron source. Both the XPS analysis and catalytic testing results showed that only a small amount of boron doped content (B<1.59 atm%) could be efficient for

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Fig. 7 PC yield and selectivity after each cycle run under reation condition: PO (14.3 mmol), MCNB(0.01) (100 mg), CO_2 pressure (2.8 MPa), temperature (130 °C), time (24 h).



Fig. 8 FT-IR spectra of MCNB(0.01) catalyst before use (fresh) and after use for five runs (used).



Fig. 9 TGA curves of MCNB(0.01) catalyst before use (fresh) and after use for five runs (used).

improving the catalytic activity. Too much addition might be detrimental for the catalytic performance, similar to previous research.²⁹

Recyclability studies of MCNB catalyst

To examine the recyclability of MCNB catalyst, recycling experiments were conducted by using PO cycloaddition with CO_2 as the model reaction with MCNB(0.01) as catalyst at 130 °C, 2.8 MPa for 24 h. After each cycle experiment, the catalyst was easily recovered by simple filtration, and then used for the next cycle. As displayed in Fig. 7, almost no decrease was detected in PC yield (about 72%) and selectivity (over 99%) after five recycle times. indicating that MCNB(0.01) maintained its catalytic activity after use.

In addition, the chemical structure and thermal stability of the catalyst after recycling experiments were also studied. FT-IR spectra and TGA curves of MCNB(0.01) before and after use for five runs were respectively shown in Fig. 8 and Fig. 9. By comparison in FT-IR spectra, all the characteristic peaks of MCNB(0.01) structure remained and there was no obvious change between fresh and used catalyst. Furthermore, TGA curves showed that the decomposition temperature of used catalyst stayed high over 500 $^{\circ}$ C, which was consistent with fresh one.

The recyclability of catalytic activity, chemical structure and decomposition temperature demonstrated the high stability of MCNB catalyst, which was beneficial for the industrial application.

DFT calculation for edge active groups of MCNB materials

According to the previous report, two kinds of boron sites (corner and bay boron) might exist in MCNB structures.²⁹ To figure out the specific function of boron sites in g-C₃N₄ skeleton, DFT calculations were carried out for these two kinds of boron sites of MCNB scheme to compare with that of MCN. The B3LYP/6-311++G(d,p) method has been used for structure optimizations, and subsequent frequency calculations at the same level verify the optimized structures to be ground states without imaginary frequencies (NImag=0). In order to make the calculation more representative, three existing structures of edge groups, with no hydrogen (MCN(C2)), one hydrogen (MCN(CH)), and two hydrogen connected (MCN(H2)), were proposed for comparison. MCNB skeletons with corner and bay boron for different hydrogen-containing structures were respectively marked as MCNB(C2)-I, MCNB(C2)-II, MCNB(CH)-I, MCNB(CH)-II and MCNB(H2)-I, MCNB(H2)-II in Fig. 10. The NPA (natural population analysis) charge distributions by NBO calculations of nitrogen adjacent to boron on the MCNB structures were depicted in Table 5. For the same hydrogencontaining edge groups, the NPA charge values and bond lengths exhibited the same increasing trends from no boron doping to bay boron doping. Obiviously, the charge values changed from -0.450 to -0.710 for MCNB(C2)-II, from -0.575 to -0.848 for MCNB(CH)-II and from -0.744 to -1.032 for MCNB(H2)-II, indicating that electrons are more inclined to transfer from the bay boron site to the nitrogen. According to previous reports,⁴⁹⁻⁵¹ CO₂ could interact with an amine via N-H…O hydrogen bonding or via an interaction between the N lone pair and the C atom of CO₂ and tertiary amines with no hydrogen atom attached to the nitrogen atom have a low reactivity with respect to CO2. Thus, the increased electron

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density around the nitrogen atom is especially favorable for interaction of primary (NH_2) and secondary (C–NH–C) amino groups with CO_2 .^{49, 52} The interaction between boron and nitrogen will also bring changes in the bond lengths of B-N. The B-N bond length becomes longer than that of MCN(CH) (from 1.350 to 1.411) and MCN(H2) (from 1.348 to 1.411), which causes easier access to CO2. Both the enhancement on electron density and bond length of -N groups after boron replacement was another reason for the increased catalytic activity after BmimBF₄ addition. The reaction mechanism with MCNB as catalysts was proposed in Scheme 3. The boronenhanced nitrogen groups (primary and secondary amino groups) in edge defects of MCNB fragments could activate CO₂ via nucleophilic attack and the primary amino (NH₂) groups might induce C-O bond to easy opening by formation of hydrogen bond. With the contribution of meso-/macropores therein to molecule transportation, the active groups in pore



Fig. 10 Optimized structures by B3LYP/6-311++G(d,p) for Structure A: MCN(C2), MCNB(C2)-I, MCNB(C2)-II; Structure B: MCN(H2), MCNB(H2)-I, MCNB(H2)-II and Structure C: MCN(H2), MCNB(H2)-I, MCNB(H2)-II.

 $\ensuremath{\text{Table 5}}$ NPA charge distributions and the changes of bond length (Å) for different structures

Structure A	MCN(C2)	MCNB(C2)-I	MCNB(C2)-II
NPA Charge	-0.450	-0.470	-0.710
bond length (Å)	1.356	1.360	1.416
Structure B	MCN(CH)	MCNB(CH)-I	MCNB(CH)-II
NPA Charge	-0.575	-0.599	-0.848
bond length (Å)	1.350	1.357	1.411
Structure C	MCN(H2)	MCNB(H2)-I	MCNB(H2)-II
NPA Charge	-0.744	-0.770	-1.032
bond length (Å)	1.348	1.361	1.411



 $\mbox{Scheme 3}$ The possible mechanism for \mbox{CO}_2 conversion into propylene carbonates over MCNB fragments.

edge defects could be easily accessible and this constituted another reason for the effective catalytic performance of MCNB catalysts.

Conclusions

A series of boron-doped melamine-derived carbon nitrides (MCNB) were successfully prepared by adding different amount of BmimBF₄ (B/M mass ratio=0.1, 0.05, 0.03, 0.01) into the preparation process of carbon nitrides. Compared with non-doping melamine-derived carbon nitride (MCN), the addition of BmimBF₄ led to the decrease of polymerization degree with more generated edge defects and more mesomacroporous structures, as well as boron doping in MCNB networks. In addition, MCNB owned better catalytic activity for CO₂ cycloaddition with epoxides than MCN, of which MCNB(0.01) with boron doped content less than 1.59 atm% was the best one and could be suitable for catalytic conversion of various epoxide substrates. The improvement on catalytic activity could be attributed to the increase and enhancement of uncondensed amino groups in edge defects. First, the decreased polymerization degree and the existence of more meso-macroporous structures made more amino groups in edge defects exposed and accessible. Secondly, boron doping enhanced the electron density of hydrogen-containing amino groups which was the active sites for CO₂ and epoxide activation. Thus, it is the combination of edge defects creation and boron doping that contributed to the better catalytic performance. The boron-enhanced amino groups, including primary (-NH₂) and secondary amino groups (C-NH-C) were finally considered to be active centers for activation of epoxides and CO₂ and the boron doping form was confirmed to be $HN = B(-N)_2$ structure with the bay boron sites. This work proposed an effective way to tailor carbon nitride formation for high catalytic activity. Considering the good recyclability in catalytic activity, chemical structure and thermal stability, MCNB is promising to be an efficient heterogeneous catalyst for CO₂ conversion into cyclic carbonates in future industry.

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More relevant exploitation on further improvement of catalytic performance is in progress.

Experimental Section

Preparation of MCNB materials

According to a typical synthetic procedure as described in the literature, $^{\rm 27}$ certain amount (0.1g, 0.05g, 0.03g, 0.01g) of BmimBF₄ and 15 mL deioned water were first added to a 50 mL flask and the mixture was stirred for 10 min. Then 1 g melamine was added in. The final mixture was unsealed and stirred at 80 °C for 5 min. Thereafter, the flask was heated through 90 °C to 100 °C and hold at 100 °C until the water in flask was dried up. The obtained dried white solid was transferred into a crucible and slowly heated over 2 h to a temperature of 360 °C. The material was hold at this temperature for 10 min, heated over 1 h to 500 $^\circ$ C, and tempered at this higher temperature for another 3 h. After cooling in the oven to room temperature, the sample was in sequence washed by diluted hydrogen chloride, deioned water and methanol for the removal of some remaining impurities. Then, the sample was dried in the vacuum oven overnight. Through the above steps, a series of MCNB materials with different B/M mass ratios (x=0.1, 0.05, 0.03, 0.01) and MCN (without addition of BmimBF₄) were successively prepared.

Characterization of MCNB materials

The chemical structures of the materials were analyzed by Fourier transform infrared (FT-IR) spectroscopy (Thermo Nicolet 380) with anhydrous KBr as the standard. X-ray diffraction (XRD) were conducted by a SmartLab (9) X-ray diffractometer (Rigaku, Japan) with Cu K α radiation (λ = 0.1541 nm). Thermogravimetric analysis (TGA) were performed on a DTG-60H thermal analyzer (Shimadzu, Japan) at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere using an empty crucible as the reference. Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images were respectively taken by a SEM (JSM6700F, JEOL) and a TEM instrument (JEM2100F, JEOL). Isotherms of N₂ adsorption and BET surface areas were obtained by N₂ physisorption test using a Micromeritics Porosimeter (ASAP-2020 HD88). Elemental analysis (C/H/N) was operated on a Vario EL Cube elemental analyzer. The distribution of surface active groups was achieved through an X-ray photoelectron spectroscope (XPS) (ESCALAB250Xi). ¹¹B solid-state MAS NMR was recorded on a Bruker Avance III HD 500M NMR. All the yields and selectivities were examined via a GC (Agilent 6820) with a TCD detector. The composition of the products was identified by using GC-MS (Agilent 6890/5973B). The density functional theory (DFT) calculations were carried out using the Gaussian 09 program.

General procedure for catalytic conversion of epoxides by MCNB catalysts

First, 14.3 mmol of propylene oxide and certain amount of MCNB were put in a 25 ml stainless steel reactor equipped with an automatic temperature control system at room temperature. Then the reactor was charged with CO_2 to 1.0

MPa pressure before being heated. When the viceactor owas heated to the target temperature, the CO_2 : pressure for a certain time. After the reaction, the reactor was cooled down to room temperature and the excess CO_2 was released slowly. The products were separated from the remaining mixture and analyzed by GC and GC-MS. The cycloaddition of CO_2 with other epoxides, ethylene oxide, epichlorohydrin and isobutylene oxide, were conducted with the same procedure.

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References

- J. Bayardon, J. Holz, B. Schäffner, V. Andrushko, S. Verevkin, A. Preetz and A. Börner, *Angew. Chem. Int. Ed.*, 2007, 46, 5971-5974.
- S. Yin, J. Han, T. Zhou and R. Xu, *Catal. Sci. Technol.*, 2015,
 5048-5061.
- 3 J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, *Green Chem.*, 2015, **17**, 1966-1987.
- 4 B. Mousavi, S. Chaemchuen, B. Moosavi, Z. Luo, N. Gholampour and F. Verpoort, New J. Chem., 2016, 40, 5170-5176.
- 5 S. Verma, R. B. N. Baig, M. N. Nadagouda and R. S. Varma, *Green Chem.*, 2016, **18**, 4855-4858.
- 6 R. R. Kuruppathparambil, R. Babu, H. M. Jeong, G.-Y. Hwang, G. S. Jeong, M.-I. Kim, D.-W. Kim and D.-W. Park, *Green Chem.*, 2016, **18**, 6349-6356.
- Q. He, J. W. O'Brien, K. A. Kitselman, L. E. Tompkins, G. C.
 T. Curtis and F. M. Kerton, *Catal. Sci. Technol.*, 2014, 4, 1513-1528.
- 8 B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang and S.-J. Zhang, *Green Chem.*, 2015, **17**, 108-122.
- 9 X. Wang, Y. Zhou, Z. Guo, G. Chen, J. Li, Y. Shi, Y. Liu and J. Wang, *Chem. Sci.*, 2015, 6, 6916-6924.
- 10 R. Babu, A. C. Kathalikkattil, R. Roshan, J. Tharun, D.-W. Kim and D.-W. Park, *Green Chem.*, 2016, **18**, 232-242.
- 11 R. Ma, L.-N. He and Y.-B. Zhou, *Green Chem.*, 2016, **18**, 226-231.
- 12 N. Pasupulety, K. Gunda, Y. Liu, G. L. Rempel and F. T. Ng, *Appl. Catal. A- Gen.*, 2013, **452**, 189-202.
- 13 Y. Wang, X. Wang and M. Antonietti, Angew. Chem. Int. Ed., 2012, 51, 68-89.
- 14 Y. Gong, M. Li, H. Li and Y. Wang, *Green Chem.*, 2015, **17**, 715-736.

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Journal Name

- J. Liu, H. Wang and M. Antonietti, *Chem. Soc. Rev.*, 2016, 45, 2308-2326.
- 16 F. Goettmann, A. Thomas and M. Antonietti, *Angew. Chem. Int. Ed.*, 2007, **46**, 2717-2720.
- 17 M. B. Ansari, B.-H. Min, Y.-H. Mo and S.-E. Park, Green Chem., 2011, 13, 1416-1421.
- 18 M. B. Ansari, H. Jin and S.-E. Park, *Catal. Sci. Technol.*, 2013, **3**, 1261-1266.
- 19 Z. Huang, F. Li, B. Chen, T. Lu, Y. Yuan and G. Yuan, Appl. Catal. B-environ, 2013, 136–137, 269-277.
- 20 J. Mao, T. Peng, X. Zhang, K. Li, L. Ye and L. Zan, *Catal. Sci. Technol.*, 2013, **3**, 1253-1260.
- 21 Q. Su, J. Sun, J. Wang, Z. Yang, W. Cheng and S. Zhang, *Catal. Sci. Technol.*, 2014, 4, 1556-1562.
- J. Xu, F. Wu, Q. Jiang and Y.-X. Li, *Catal. Sci. Technol.*, 2015, 5, 447-454.
- Z. Huang, F. Li, B. Chen and G. Yuan, *Catal. Sci. Technol.*, 2016, 6, 2942-2948.
- 24 D.-H. Lan, H.-T. Wang, L. Chen, C.-T. Au and S.-F. Yin, *Carbon*, 2016, **100**, 81-89.
- 25 J. Wang, J. Luo, S. Feng, H. Li, Y. Wan and X. Zhang, *Green Energ. Environ.*, 2016, **1**, 43-61.
- 26 Y. Wang, X. Wang, M. Antonietti and Y. Zhang, *ChemSusChem*, 2010, **3**, 435-439.
- 27 Y. Wang, J. Zhang, X. Wang, M. Antonietti and H. Li, Angew. Chem. Int. Ed., 2010, 49, 3356-3359.
- 28 Y. Zhang, T. Mori, J. Ye and M. Antonietti, J. Am. Chem. Soc., 2010, 132, 6294-6295.
- 29 Y. Wang, H. Li, J. Yao, X. Wang and M. Antonietti, *Chem. Sci.*, 2011, **2**, 446-450.
- 30 Y. Zheng, J. Liu, J. Liang, M. Jaroniec and S. Z. Qiao, *Energ. Environ. Sci.*, 2012, 5, 6717-6731.
- 31 B. V. Lotsch and W. Schnick, Chem. Mater., 2006, 18, 1891-1900.
- J. Hong, X. Xia, Y. Wang and R. Xu, J. Mater. Chem., 2012, 22, 15006-15012.
- 33 Y. Wang, J. Hong, W. Zhang and R. Xu, *Catal. Sci. Technol.*, 2013, **3**, 1703-1711.
- 34 J. Xu, Y. Li, S. Peng, G. Lu and S. Li, Phys. Chem. Chem. Phys., 2013, 15, 7657-7665.
- C. Fettkenhauer, G. Clavel, K. Kailasam, M. Antonietti and D. Dontsova, *Green Chem.*, 2015, 17, 3350-3361.
- 36 A. Kumar, P. Kumar, C. Joshi, S. Ponnada, A. K. Pathak, A. Ali, B. Sreedhar and S. L. Jain, *Green Chem.*, 2016, 18, 2514-2521.
- B. Lin, G. Yang, B. Yang and Y. Zhao, *Appl. Catal. B-Environ*, 2016, **198**, 276-285.
- 38 X. Song, H. Tao, L. Chen and Y. Sun, *Mater. Lett.*, 2014, 116, 265-267.
- 39 Z. Miskolczy, K. Sebők-Nagy, L. Biczók and S. Göktürk, *Chem. Phys. Lett.*, 2004, **400**, 296-300.
- 40 T. Singh and A. Kumar, J. Phys. Chem. B, 2007, 111, 7843-7851.
- 41 J. Wang, H. Wang, S. Zhang, H. Zhang and Y. Zhao, J. Phys. Chem. B, 2007, **111**, 6181-6188.
- 42 G. Xin and Y. Meng, New J. Chem., 2013, 2013, 1-5.

- 43 Q. Xiang, J. Yu and M. Jaroniec, J. Phys. Chem. Com. 2011, 315 7355-7363. DOI: 10.1039/C7GC00279C
- 44 M. Blesic, M. H. Marques, N. V. Plechkova, K. R. Seddon, L. P. N. Rebelo and A. Lopes, *Green Chem.*, 2007, **9**, 481-490.
- 45 Y. Wang and G. A. Voth, J. Am. Chem. Soc., 2005, **127**, 12192-12193.
- 46 S. Chen, S. Zhang, X. Liu, J. Wang, J. Wang, K. Dong, J. Sun and B. Xu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5893-5906.
- 47 J. Bowers, C. P. Butts, P. J. Martin, M. C. Vergara-Gutierrez and R. K. Heenan, *Langmuir*, 2004, **20**, 2191-2198.
- 48 D. R. Miller, J. Wang and E. G. Gillan, *J. Mater. Chem.*, 2002, **12**, 2463-2469.
- 49 R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650-653.
- 50 P. D. Vaidya and E. Y. Kenig, *Ind. Eng. Chem. Res.*, 2008, **47**, 34-38.
- 51 K. R. Roshan, B. M. Kim, A. C. Kathalikkattil, J. Tharun, Y. S. Won and D. W. Park, *Chem. Comm.*, 2014, **50**, 13664-13667.
- M. D. Soutullo, C. I. Odom, B. F. Wicker, C. N. Henderson,
 A. C. Stenson and J. H. Davis, *Chem. Mater.*, 2007, 19, 3581-3583.

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