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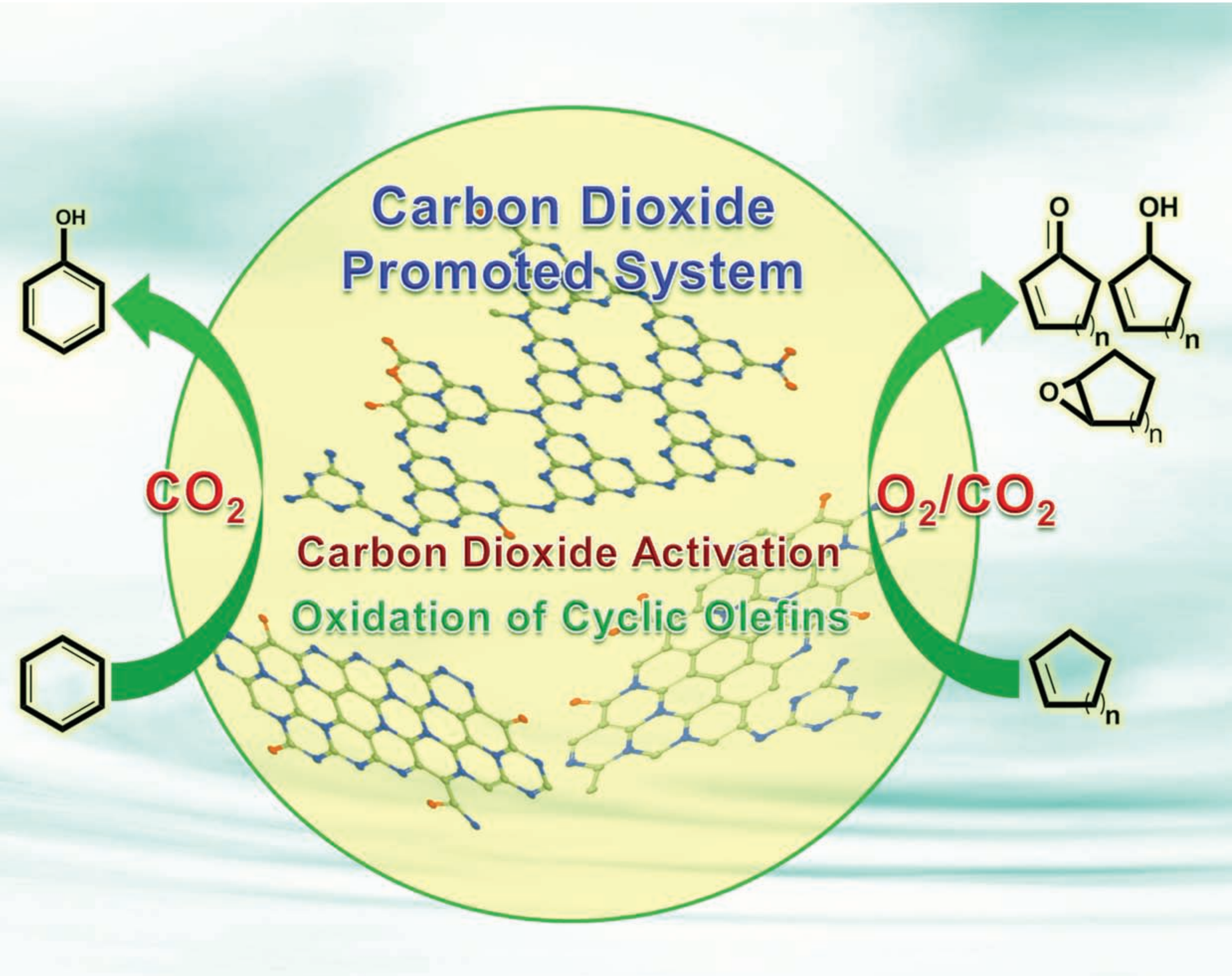

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PAPER

CO_2 activation and promotional effect in the oxidation of cyclic olefins over mesoporous carbon nitrides[†][‡]

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Mesoporous carbon nitrides (MCN) were prepared by a nano-casting method using mesoporous silica as a template with different carbon and nitrogen sources like melamine only (MS-MCN), urea-formaldehyde (UF-MCN) and melamine-glyoxal (MG-MCN). These mesoporous carbon nitride materials possess nitrogen moieties which behave like a CO_2-philic surface facilitating oxidation of cyclic olefins by molecular oxygen in the co-presence of CO_2 below supercritical conditions. The co-presence of CO_2 augmented the conversions of cyclic olefins at low pressures of CO_2, depicting a promotional effect. Approaches towards quantification of promotional effects and insights into the promotional aspects have been studied.

Introduction

Carbon dioxide chemistry has become a more attractive area of research not only because of environmental concerns but also due to its potential utilization as an alternative and economical feedstock.[1–4] The utilization of CO_2 as a chemical feedstock is limited and requires large amounts of energy and/or hydrogen for the abstraction of oxygen. Recently, CO_2 was utilized as a dense phase under so-called supercritical conditions as an activity enhancer, a green alternative for organic solvents [5–11] and as a miscibility enhancer with gaseous reactants like oxygen[12] and H_2.[13] Dense phase CO_2 systems have drawbacks of low reaction rates, high operating pressures and inadequate solubilities.[14] However, Jessop *et al.* have resolved the solubility problem through a switchable system based on 1,8-diazabicyclo-[5.4.0]-undec-7-ene which facilitated organic synthesis and eliminate separation steps by tuning polarities in the presence of carbon dioxide.[15] Another system which elminates the solublity problem is based on a carbon dioxide expanded liquid (CXL) which utilizes partial replacement of dense phase CO_2 with organic solvents.[16] This system mainly focus on behavioral aspects of the expansion of solvents with CO_2. Leitner *et al.*[17] and Beckmann *et al.*[18] have designed certain CO_2-phillic polymers which readily dissolve in carbon dioxide and are considered as new green supports for catalytic systems operating in dense phase CO_2 for oxidation reactions[12] and hydrogenation[19] reactions in homogeneous media.[20]

The alternative way for utilization of carbon dioxide currently evokes great interest as an oxygen source. In our earlier studies we have reported the soft oxidant behavior of CO_2 in the oxidative dehydrogenation of ethylbenzene, toluene and xylene in both gaseous and liquid-phase, respectively.[21–22] The role of CO_2 in these reactions provides several merits such as abstraction of hydrogen from alkanes, alkenes, alcohols and alkyl aromatics through catalytic activation of carbon dioxide to form CO and an oxygen species, acceleration of reaction rate, enhancement of product selectivity, alleviation of chemical equilibrium and suppression of total oxidation.[21] We also reported the promotional effect of CO_2 in oxidation of alkyl aromatics with O_2 as oxidant using a homogeneous Co/Mn/Ni, Br catalyst.[23] The co-presence of CO_2 with O_2 contributed to enhance the reaction rates, higher conversion and selectivities as well. This new system operates under the subcritical pressures of CO_2 and is coined as a carbon dioxide promoted systems (CPS) instead of CO_2 expanded system (CXL) which can be easily discerned by the low pressure *modus operandi* and catalytic CO_2 activation. This inspired us to develop a heterogenous catalytic system which would be able to activate carbon dioxide especially in an oxidation reaction.

As a strategy carbon nitrides were chosen to play a role like a CO_2-phillic surface[24] and as an organocatalyst[25–26] because of high nitrogen contents similar to CO_2-activating organic molecules such as amines, N-heterocyclics, DBU, guanidine, melamine and poryphyrins which were mainly used in carbon dioxide activation for the preparation of cyclic carbonates.[24,27–29] We were intrigued by the report of Antonietti *et al.* on carbon nitride mediated CO_2 activation, in which CO_2 serve as an oxygen source for oxidation of benzene to phenol. In order to judge the

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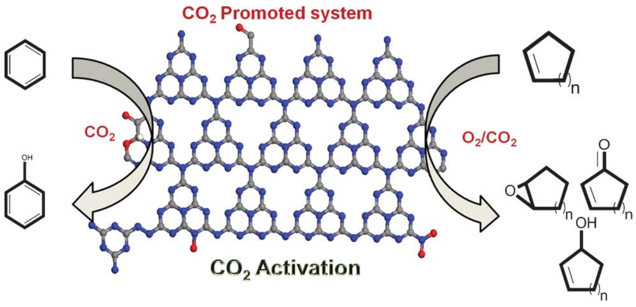
ability of our materials towards CO_2 activation, we have tested the insertion of carbon dioxide into propylene oxide and also the oxidation of benzene to phenol whereby CO_2 served as an oxygen source.

The catalytic behaviour of carbonaceous materials have been studied towards oxidation and oxidative dehydrogenation reactions and it is presumed that surface oxygen functionalities serve as active sites for oxidation.[25,30–31] Recently Kakimoto *et al.* have reported a carbon based metal-free catalytic system for oxidation of alcohols using molecular oxygen.[31] In here we are reporting the role of 'N' containing carbonaceous materials especially carbon nitrides for carbon dioxide activation and also towards oxidation of cyclic olefins by molecular oxygen in synergism with CO_2 (Scheme 1). The promotional effect of the co-presence of CO_2 with molecular oxygen has been studied and an insight towards the promotional aspects has been presented.



Scheme 1 Carbon dioxide activation and oxidation of cyclic olefins.

Experimental

Materials and methods

Glyoxal, urea, formaldehyde, propylene oxide, benzene, dimethylacetylene-1,2-dicarboxylate, tetramethyl thiourea, palladium chloride and all the cyclic olefins were purchased from Aldrich and used without further purification; melamine was purchased from TCI. All the solvents used were of analytical grade and used without further purification. Mesoporous carbon nitride (MCN) materials were synthesized *via* a hard templating route by using disk-shaped 2D hexagonal mesoporous silica. The template mesoporous silica, was synthesize by our earlier reported procedure.[32] Three kinds of mesoporous carbon nitrides were prepared by varying the carbon and nitrogen sources and named accordingly; melamine (MS-MCN), urea-formaldehyde (UF-MCN) and melamine-glyoxal (MG-MCN). The appropriate amount of nitrogen and carbon precursor was added to the template in order to polymerize over it to form a porous nanocomposite. The porous nanocomposites obtained were dried and then carbonized at 550° in a nitrogen flow followed by treatment with 3% HF solution in order to remove the silica.

Characterization

Nitrogen adsorption and desorption measurements including surface areas and pore volumes were measured at liquid nitrogen temperature using a Micromeritics porosimeter (model ASAP-2020). Prior to the measurement, the samples were degassed at 160 °C for 5 h. The pore size distribution (PSD) was calculated using the Barrett–Joyner–Halenda (BJH) approach. The specific surface areas were calculated using Brunauer–Emmett–Teller (BET) method and the pore parameters were determined from desorption branches by BJH methods. Raman spectra was recorded on HR 800, Horiba/Jobin-Yvon were employed to analyze the chemical structure of the catalyst. Electron spectroscopy for chemical analysis (ESCA) was recorded on a Sigma Probe ThermoVG, U. K. monochromatic Al–Kα 12 kV, 100 W, 400 micrometre, for a wide scan with pass energy of 50 eV and a step size of 1.0 eV, whereas for a narrow scan with pass energy of 20 eV and a step size of 0.1 eV a Avantage ThermoVG was used. Elemental analysis was carried out on an Elemental analyzer (EA1112, Thermo). Electron energy loss spectroscopy (EELS) was measured by a TEM instrument (JEM 2100F, JEOL). Product analysis was done by gas chromatography (Agilent 6890 N, HP-5 capillary column, FID detector) and further confirmed by GC-MS (Agilent Technologies, GC6890N, MS5975).

Catalytic reaction

Carbon dioxide activation. The reaction between propylene oxide and carbon dioxide was carried out in DMF. In a typical reaction procedure a 100 ml steel autoclave was charged with 5 ml of DMF, 20 mg of catalyst and 1.5 ml of propylene oxide at 80 psi of carbon dioxide. The reaction mixture was heated to 373 K with constant stirring at 300 rpm for a period of 10 h. The aliquots were subjected to GC and GC-MS analysis.

The reaction of benzene to phenol conversion was carried out in a 100 ml stainless steel autoclave fitted with a teflon mantel, 10 ml benzene, 200 mg triethylamine as co-reactant and 100 mg catalyst was placed in the autoclave. The autoclave was then flushed three times with CO_2, pressurized with CO_2 (80 psi), and then heated to 423 K with constant stirring at 300 rpm. The reaction mixture was neutralized with 1 ml HCl and injected directly into the GC–MS (Agilent Technologies, GC6890N, and MS5975).

Oxidation of cyclic olefins. All oxidation experiments were performed in a 100 ml autoclave equipped with magnetic stirring and an automatic temperature controller. A typical procedure for the oxidation of cyclic olefins was as follows: cyclic olefin (5 mmol), 10 ml of DMF and 20 mg catalyst was placed in the autoclave fitted with a Teflon mantle. The autoclave was flushed with dioxygen several times followed by adjustment of the pressure ratios 80 psi with appropriate O_2/N_2 or O_2/CO_2 ratios. Under stirring at 300 rpm the autoclave was heated to 373 K and maintained for 10 h. After the reaction, the autoclave was cooled, and the reaction products were analyzed by GC and identified by GC-MS

Recyclability. The catalyst was filtered after the reaction and washed several times with water to remove the DMF followed by 2–3 times washing with ethanol. The catalyst was dried overnight in a vacuum oven at 150 °C and reused for the subsequent cycle in the oxidation of cyclohexene.

Analysis of gaseous mixture after reaction

IR spectra of gases. The gaseous mixture after the oxidation reaction was analyzed by a specially designed setup as shown in Figure S1 (Supplementary Information‡). Initially the IR cell is evacuated followed by connecting with an autoclave equipped with an intermediate valve for controlling the pressure and a moisture trap. The gas is slowly released into the IR cell and analyzed by infrared spectroscopy.

Pauson–Khand. Pauson–Khand reaction was conducted with a small modification of the procedure reported by Chen *et al.*[33] for confirmation of CO formation. The remaining gaseous mixture after oxidation was transferred to another autoclave which was charged with 0.5 mmol of dimethylacetylene-1,2-dicarboxylate, 0.5 mmol *n*-hexene in 10 ml acetonitrile and temperature to 50 °C.

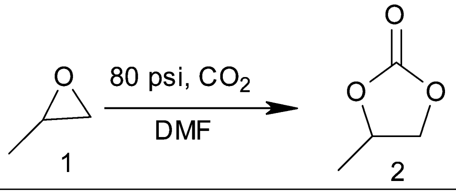
Results and discussion

Spectral and textural properties of MCNs

The elemental analysis of MCN materials MS-MCN, UF-MCN and MG-MCN showed the occurrence of C, H, and N with C : N ratios of 0.6, 2.5, and 5.3, respectively (Table S2‡). In addition, the existence of nitrogen, carbon and oxygen functionalities were also inferred by elemental analysis which were further verified by XPS (X-ray photoelectron spectroscopy) spectra of the MCN materials (Figure S3‡). The O1s binding energy revealed various kinds of oxygen functionalities: C=O at 532.2 eV C–O (533.3 eV), O–H (533.7 eV) and quinine type C=O at 531 eV. The C1s binding energy of MS-MCN shows mainly one carbon species with a binding energy of 288.2 eV, corresponding to a β-C–N=C coordination, whereas the sp^2 C–C was observed at 284 eV, the sp^2 C–N at 285.9 eV, and the sp^2 C=O at 287.4 eV.[34] In the N1s spectrum the main signal shows occurrence of C–N–C groups (398.7 eV) and tertiary nitrogen N–(C)$_3$ groups (400.1 eV). Deconvolution of the N1s XPS signals also reveals a weak additional signal at 402.7 eV, indicative of amino functions carrying hydrogen (C–N–H).[34–35] The EELS spectra (Figure S4‡) of MCNs revealed the presence of ionization edges at *ca.* 284 and 401 eV corresponding to the C–K and N–K shells, respectively. The C and N regions show sharply defined π* and σ* fine structural features, which could be assigned to the sp^2 hybridization (usually observed in "graphitic" structures).[26] The Raman spectra of MCN materials (Figure S5‡) consist of D and G bands in different proportions. The G band lies in the range of 1560–1600 cm^{-1} and indicates E$_2$g in-plane stretching motions of pairs or chains of C-sp^2 bonded atoms. The D band around 1350 cm^{-1}, relates to A$_1$g breathing mode of six fold aromatic rings and only becomes active in the presence of disorder.[36–38] All the characterization results coincide with those reported earlier.[26]

The porous properties of the MCN materials were confirmed by the nitrogen sorption analysis. The N$_2$ sorption shows type IV isotherms with H1-type hysteresis loops (Figure S6‡) which were typical for mesoporous materials having cylindrical type mesostructures.[32] The BET surface areas of materials were around 150–500 cm^3 g^{-1} and pore size distributions were in range of 3–5 nm.

Table 1 Cycloaddition of CO$_2$ to propylene oxide over carbon nitride



Entry	Catalyst[a]	Conversion of 1 (%)[b]	Selectivity for 2 (%)[b]
1	MS-MCN	34	90
2	UF-MCN	28	92
3	MG-MCN	25	98

[a] Reaction conditions: 20 mg catalyst, 10 ml DMF, temperature 373 K, 80 psi CO$_2$, 10 h. [b] Estimated by GC.

Carbon dioxide activation over MCNs

Initially catalytic activities of MCNs were tested for CO$_2$ activation in carbonation of propylene oxide to propylene carbonate as a model system. The formation of propylene carbonate in the presence of CO$_2$ inferred the existence of functionality in MCNs for CO$_2$ activation (Table 1).

In order to further confirm the role of MCNs the conversion of benzene to phenol in the presence of CO$_2$ was also investigated. In this reaction carbon dioxide serve as an oxygen source as reported by Antonietti *et al.*[24] All the MCNs showed pretty good activities for the formation of cyclic carbonate and phenol (Table 2). These results are closely related with nitrogen contents of MCNs which serve as Lewis base sites.

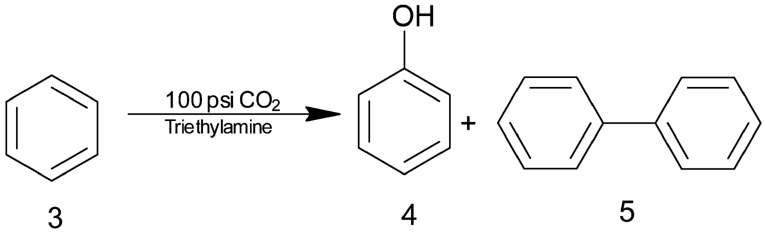
Oxidation of cyclic olefins over MCNs

The catalytic behaviors of MCNs were studied towards oxidation, due to the presence of surface oxygen on the MCNs as observed by elemental analysis, further more spectral analysis by XPS inferred the occurrence of quinone type oxygen which may serve as active sites for oxidation similar to carbonaceous materials.[25,30] However the exact reaction mechanism is uncertain at this stage and further studies are in progress. Oxidation of cyclohexene was carried out with molecular oxygen in the absence and/or presence of CO$_2$ to see the synergetic effect for conversions and selectivities. The investigation on the influence of CO$_2$ in the oxidation of cyclohexene by varying gas ratios in both O$_2$/N$_2$ and O$_2$/CO$_2$ were performed (Table 3).

As shown in (Table 3), at a ratio 0.066 of O$_2$ (entry 1) no conversion of cyclohexene was observed, this might be due to low partial pressure of O$_2$, which was insufficient to achieve the product. A further increase in the O$_2$ ratio increases the product formation (Table 3, entries 2–5). However, gas ratios higher than 0.333 merely increase the conversion of cyclohexene (Table 3, entries 4–5). Hence, the catalytic activity towards other cylic olefins was tested at ratio of 0.333 only.

In all the cases augmented conversions of cyclic olefins were observed in O$_2$/CO$_2$ compared to O$_2$/N$_2$ (Table 3). This promotional effect due to the co-existence of CO$_2$ with oxygen was studied quantitatively and had been calculated as a percentage difference in the conversion of substrate in O$_2$/CO$_2$ and O$_2$/N$_2$; represented as ΔC (%) by following equation (eqn (1)):

Table 2 Catalytic activities of MCNs for phenol production from benzene *via* carbon dioxide activation



Entry	Catalyst[a]	Conversion of 3 (%)[b]	Selectivity of 4 (%)[b]	Selectivity of 5 (%)[b]
1	MS-MCN	30.0	71	29
2	UF-MCN	29.9	89	11
3	MG-MCN	20.7	86	14

[a] Reaction conditions: 200 mg catalyst, 10 ml DMF, temperature 423 K, 80 psi CO_2, 10 h. [b] Estimated by GC.

Table 3 The influence of CO_2 on oxidation of cyclohexene

Entry	Gas ratio (Psi)	Conversion (%) in O_2/CO_2	Conversion (%) in O_2/N_2	ΔC (%)[a]
1	0.066	0	0	0
2	0.142	16	9	28.0
3	0.230	25	18	16.3.
4	0.333	33	24	15.7
5	0.454	34	24	15.7

Reaction conditions: 20 mg MS-MCN, 10 ml DMF, temperature 373 K, pressure 80 psi, time 10 h; Estimated by GC analysis.[a] Conversion (%) of cyclic olefin.

$$\Delta C(\%)=\frac{\left(C_{O_2/CO_2}\right)-\left(C_{O_2/N_2}\right)}{\left(C_{O_2/CO_2}\right)+\left(C_{O_2/N_2}\right)} \qquad (1)$$

where,

$$C_{O_2/CO_2} = \text{Conversion in } O_2/CO_2, \quad C_{O_2/N_2} = \text{Conversion in } O_2/N_2$$

The oxidation reactions of various cyclic olefins such as cyclopentene, cyclohexene, cyclooctene and cyclododecene were also investigated over MCNs to observe the promotional effect of CO_2 (Table 4). All the catalysts showed higher conversion in the co-presence of CO_2 and positive ΔC (%) values were gained for all the substrates, indicating the enhancement of conversions due to the co-presence of CO_2. The selectivities for products 4, 5 and 6 in O_2/CO_2 (Table 4) were different with those observed in O_2/N_2; the epoxide selectivity in O_2/CO_2 is relatively higher in all cases compared with O_2/N_2.

The higher conversions were observed in the 5 and 6 membered ring olefins (Table 4 entries 1–12) compared with the 8 and 12-membered ring olefins (Table 4 entries 13–24). The low conversion in the case of the large membered rings might be due to diffusion limitation or hampering inside the pores of the catalyst reducing the accessibility of active sites.

Recyclability of catalyst

The recyclability of all the catalyst were tested for oxidation of cyclohexene up to three cycles, and no significant changes in the catalytic activity were observed and the conversions remain almost same (Figure 1). There is a marginal decrease in conversion of each cycle, and this may be due to the physical loss while handling.

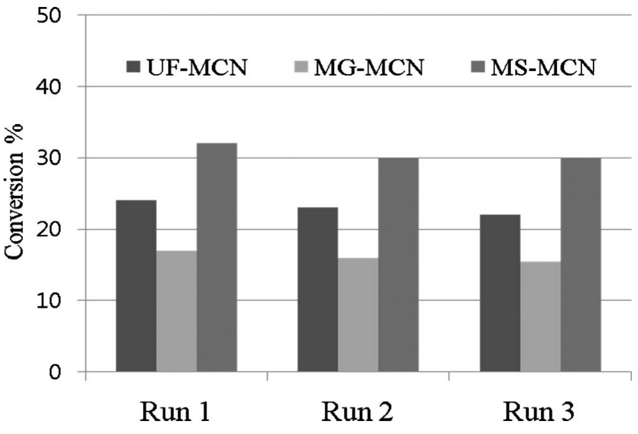
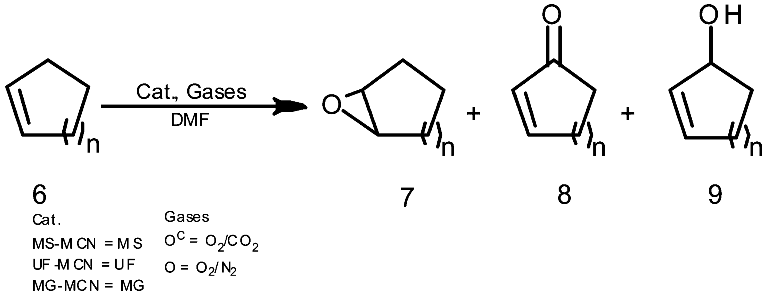


Fig. 1 Recyclability of MCNs in the oxidation of cyclohexene.

Role of CO_2 and promotional aspects

In order to analyze the influence of carbon dioxide in oxidation we carried experiments to analyze the gaseous mixture from the autoclave. The IR spectra of the gaseous mixture after the reaction depicted the existence of additional bands around 2174 cm^{-1} and 2115 cm^{-1} (Figure S7c‡) which may correspond to a gaseous carbon monoxide doublet which is well documented.[39] Whereas no such absorption bands were observed before the reaction (Figure S7a‡). In order to confirm the formation of carbon monoxide from CO_2 during the reaction, IR spectra of

Table 4 Oxidation of cyclic olefins and the promotional effect of CO_2



Entry	n	Cat.	Gases	Conversion of 6 (%)	Selectivity (%)[a] 7	8	9	ΔC (%)
1	1	MS	OC	40	37	24	29	12.6
			O	31	30	22	40	
2	1	UF	OC	35	38	24	38	11.6
			O	28	28	23	42	
3	1	MG	OC	24	40	27	32	11.6
			O	19	32	25	40	
4	2	MS	OC	33	30	21	49	15.5
			O	24	25	16	53	
5	2	UF	OC	24	38	23	39	14.2
			O	18	30	21	44	
6	2	MG	OC	17	40	27	33	17.2
			O	12	31	22	40	
7	4	MS	OC	21	>99	—	—	27.0
			O	12	>99	—	—	
8	4	UF	OC	15	94	—	—	36.0
			O	7	98	—	—	
9	4	MG	OC	12	>99	—	—	26.0
			O	7	>99	—	—	
10	8	MS	OC	17	>99	—	—	30.0
			O	9	>99	—	—	
11	8	UF	OC	13	87	—	—	30.0
			O	7	78	—	—	
12	8	MG	OC	9	>99	—	—	28.5
			O	5	>99	—	—	

Reaction conditions: 20 mg catalyst, 10 ml DMF, temperature 373 K, pressure 80 psi, gas ratio 0.333, time 10 h; Product analyzed by GC and GC-MS.[a] Trace amount of diol was observed.

a synthetic mixture of 5% CO in helium was recorded which revealed similar a absorption pattern, conforming the exsistence of CO (Figure S7b‡) in the gaseous mixture after the reaction. It is presumed that the mode of operation responsible for the promotional effect is due to activation of carbon dioxide by formation of carbamate as reported earlier, the carbon dioxide not only serve as oxygen source but also produce carbon monoxide which is in consonance with an earlier report on carbon nitride systems.[24] The further confirmation of CO formation was also investigated similar to Antonietti *et al.* by the Pauson–Khand reaction. The formation of Pauson–Khand product further confirms the formation of CO (Scheme S8‡).

Conclusions

The mesoporous carbon nitride materials have been successfully synthesized by a hard templating method. The synthesized MCNs show catalytic activity towards activation of carbon dioxide which was evidenced by cycloaddition of CO_2 to propylene oxide and conversion of benzene to phenol. The MCN materials show catalytic activity towards the oxidation of cyclic olefins by molecular oxygen. The presence of carbon dioxide in the oxidation system revealed a promotional effect with higher conversions of cyclic olefins. An approach towards quantitative estimation of the promotional effect has been made to understand the synergistic effect of carbon dioxide in the oxidation system. The insight into promotional aspects revealed that the carbon dioxide is acting as a source of oxygen which is inferred by formation of carbon monoxide and surface carbamate.

Acknowledgements

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References

1 J.-S. Chang, K.-W. Lee and S.-E. Park, ed., *Carbon dioxide utilization for global sustainability*, Elsevier, Netherlands, 2004.
2 M.-J. Choi and D.-H. Cho, *Clean: Soil, Air, Water*, 2008, **36**, 426–432.
3 G. A. Olah, A. Goeppert and G. K. S. Prakash, *J. Org. Chem.*, 2008, **74**, 487–498.
4 C. He, G. Tian, Z. Liu and S. Feng, *Org. Lett.*, 2010, **12**, 649–651.

5 B. Subramaniam, C. J. Lyon and V. Arunajatesan, *Appl. Catal., B*, 2002, **37**, 279–292.

6 W. Leitner, E. Dinjus and F. Gaßner, *J. Organomet. Chem.*, 1994, **475**, 257–266.

7 P. G. Jessop, T. Ikariya and R. Noyori, *Science*, 1995, **269**, 1065–1069.

8 S. Kainz and W. Leitner, *Catal. Lett.*, 1998, **55**, 223–225.

9 A. O. Chapman, G. R. Akien, N. J. Arrowsmith, P. Licence and M. Poliakoff, *Green Chem.*, 2010, **12**, 310–315.

10 B. Subramaniam and M. A. McHugh, *Ind. Eng. Chem. Process Des. Dev.*, 1986, **25**, 1–12.

11 S. P. Nalawade, F. Picchioni and L. P. B. M. Janssen, *Prog. Polym. Sci.*, 2006, **31**, 19–43.

12 T. Seki and A. Baiker, *Chem. Rev.*, 2009, **109**, 2409–2454.

13 E. J. Beckman, *J. Supercrit. Fluids*, 2004, **28**, 121–191.

14 G. Musie, M. Wei, B. Subramaniam and D. H. Busch, *Coord. Chem. Rev.*, 2001, **219–221**, 789–820.

15 P. G. Jessop, D. J. Heldebrant, X. Li, C. A. Eckert and C. L. Liotta, *Nature*, 2005, **436**, 1102–1102.

16 P. G. Jessop and B. Subramaniam, *Chem. Rev.*, 2007, **107**, 2666–2694.

17 W. Leitner, *Nature*, 2000, **405**, 129–130.

18 E. J. Beckman, *Chem. Commun.*, 2004, 1885–1888.

19 Z. K. Lopez-Castillo, R. Flores, I. Kani, J. P. Fackler and A. Akgerman, *Ind. Eng. Chem. Res.*, 2002, **41**, 3075–3080.

20 I. Kani, M. A. Omary, M. A. Rawashdeh-Omary, Z. K. Lopez-Castillo, R. Flores, A. Akgerman and J. P. Fackler, *Tetrahedron*, 2002, **58**, 3923–3928.

21 J.-S. Chang, V. P. Vislovskiy, M.-S. Park, D. Y. Hong, J. S. Yoo and S.-E. Park, *Green Chem.*, 2003, **5**, 587–590.

22 M. S. Park, J.-S. Chang, D. S. Kim and S.-E. Park, *Res. Chem. Intermed.*, 2002, **28**, 461–469.

23 D. Raju Burri, K.-W. Jun, J. S. Yoo, C. W. Lee and S.-E. Park, *Catal. Lett.*, 2002, **81**, 169–173.

24 F. Goettmann, A. Thomas and M. Antonietti, *Angew. Chem., Int. Ed.*, 2007, **46**, 2717–2720.

25 Dang S. Su, J. Zhang, B. Frank, A. Thomas, X. Wang, J. Paraknowitsch and R. Schlögl, *ChemSusChem*, 2010, **3**, 169–180.

26 A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Muller, R. Schlogl and J. M. Carlsson, *J. Mater. Chem.*, 2008, **18**, 4893–4908.

27 N. Eghbali and C.-J. Li, *Green Chem.*, 2007, **9**, 213–215.

28 B. Barkakaty, K. Morino, A. Sudo and T. Endo, *Green Chem.*, 2010, **12**, 42–44.

29 E. A. Prasetyanto, M. B. Ansari, B.-H. Min and S.-E. Park, *Catal. Today*, 2010, **158**, 252–257.

30 M. Ansari, E. Prasetyanto, J. Lee and S.-E. Park, *Res. Chem. Intermed.*, 2010, **36**, 677–684.

31 Y. Kuang, N. M. Islam, Y. Nabae, T. Hayakawa and M.-a. Kakimoto, *Angew Chem. Int. Ed.*, 2010, **49**, 436–440.

32 Sujandi, S.-E. Park, D.-S. Han, S.-C. Han, M.-J. Jin and T. Ohsuna, *Chem. Commun.*, 2006, 4131–4133.

33 Y. Tang, L. Deng, Y. Zhang, G. Dong, J. Chen and Z. Yang, *Org. Lett.*, 2005, **7**, 1657–1659.

34 M. Aono, S. Aizawa, N. Kitazawa and Y. Watanabe, *Thin Solid Films*, 2008, **516**, 648–651.

35 P. Petrov, D. B. Dimitrov, D. Papadimitriou, G. Beshkov, V. Krastev and C. Georgiev, *Appl. Surf. Sci.*, 1999, **151**, 233–238.

36 Y. G. Cao, X. L. Chen, Y. C. Lan, J. Y. Li, Y. P. Xu and T. Xu, *Appl. Phys. A: Mater. Sci. Process.*, 2000, **71**, 465–467.

37 A. C. Ferrari and J. Robertson, *Philos. Trans. R. Soc. London, Ser. A*, 2004, **362**, 2477–2512.

38 X. R. Liu, P. V. Zinin, L. C. Ming, T. Acosta, S. K. Sharma, A. K. Misra and S. M. Hong, *Journal of Physics: Conference Series*, 2010, 215.

39 R. A. Gardner and R. H. Petrucci, *J. Am. Chem. Soc.*, 1960, **82**, 5051–5053.