Bi-functional cationic Zn-porphyrin polymer for efficient synthesis of cyclic carbonates via cooperative activation pathway

Qihua Yang,[a]* **Sanjeevi Jayakumar,**[a] **He Li**[a]
[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Science*
Dalian 116023, China
**Corresponding author: 411-4694447, yangqh@dicp.ac.cn*

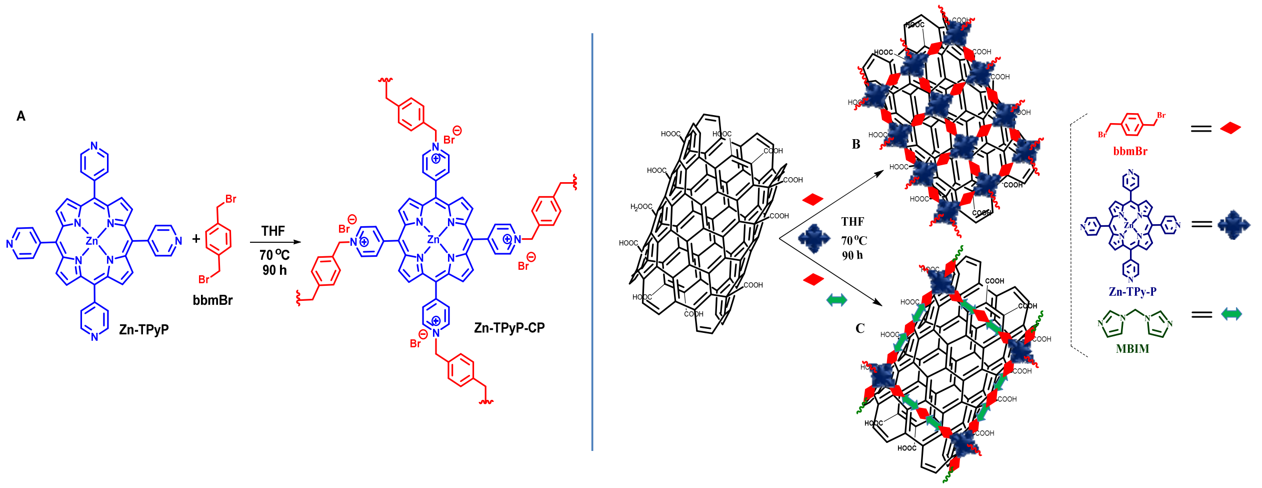
Abstract: Cycloaddition of CO_2 with epoxides to produce a widely applicable biodegradable cyclic carbonate is one of the most interesting processes. Herein, we reported the synthesis of bifunctional cationic porphyrin-based polymers by using a direct reaction of 5,10,15,20-tetrakis(4-pyridyl)porphyrin zinc(II), di(1H-imidazol-1-yl)methane, 1,4-bis(bromomethyl)benzene in the absence or presence of CNTs. The bifunctional catalysts bearing metal Zinc as a Lewis acid and bromine anion as a nucleophilic agent could efficiently catalyze cycloaddition reaction of epoxides and CO_2 under co-catalyst free condition, suggesting the efficient cooperation of zinc and bromine anion during catalytic process. Our studies provide a green rout for the production of cyclic carbonates.

Keywords: Cationic polymer, cycloaddition reaction, CO_2.

1. Introduction

Carbon dioxide is one of the well-known naturally abundant nontoxic, non-flammable, inexpensive and useful renewable C1 resource in organic synthesis.[1] Recently, the conversion of CO_2 waste to valuable chemicals has attracted much research attention. The cycloaddition of CO_2 with epoxides to produce a widely applicable biodegradable cyclic carbonate is one of the most interesting processes. Up to date, different types of solid catalysts for CO_2 cycloaddition reactions have been developed, including immobilized metal complexes/organocatalysts, porous polymers with integrated active sites (ILs or metal complexes etc.) in the network, carbon-based materials and so on[2-4]. Most of solid catalysts still need co-catalysts during the catalytic process for the generation of cooperative activation. The synthesis of solid catalysts possessing cooperative effect remains a difficult task. Herein, we report the synthesis of bi-functional cationic Zn-porphyrin polymer for cycloaddition reaction under co-catalyst free conditions.

2. Experimental



Scheme 1. The general procedure for the synthesis of supported or unsupported cationic polymer.

The synthesis of cationic Zn-porphyrin polymer is outlined in Scheme 1. The usage of CNTs during synthesis process results in the formation of CNTs supported cationic polymer, which may benefit to increase the accessibility of active sites due to nonporous nature of cationic Zn-porphyrin polymer.

3. Results and discussion

Table 1. Catalytic performance of supported and unsupported cationic polymer in the synthesis of cyclic carbonate with PO and CO_2 under solvent free conditions.[a]

Catal.	**S/C**	**Yield (%)**	**Sel. (%)**	**TOF (h^{-1})**
Zn-TPy + TBAB[b]	1450	54	>99	299
ZnTPy-CP	1450	64	>99	471
ZnTPy/CNTs-50	1450	73	>99	602
ZnTPy/CNTs-30	1450	79	>99	706
ZnTPy/CNTs-15	1450	89	>99	945
ZnTPy/CNTs-5	1450	99	>99	1065
ZnTPy-BIM4/CNTs-5	1450	98	>99	1650
ZnTPy-BIM12/CNTs-5	1450	94	>99	1216
ZnTPy-BIM4/CNTs-5[c]	7100	95	>99	2602

[a] Reaction condition: catalyst (0.069 mol%) , PO (13.27 mmol), S/C = 1450, 120 ºC, 1.5 MPa, 2.5 h. [b] Zn-TPy (6.2 mg, 0.069 mol%), TBAB (11.7 mg, 0.28 mol%), PO (13.27 mmol), 120 ºC, 1.5 MPa, 2.5 h. [c] ZnTPy-BIM4/CNTs-5 (0.014 mol%), PO (13.27 mmol), S/C = 7100, 120 ºC, 1.5 MPa, 6 h.

The cationic polymer, ZnTPy-CP, could catalyze the reaction to afford 64% conversion of PO. Under similar conditions, homogeneous catalyst Zn-TPy gave PO conversion of 54% using TBAB as co-catalyst (the molar ratio of Br to Zn is ca. 4, similar to that of heterogeneous system). The TOF of ZnTPy-CP was over 1.5 fold that of Zn-TPy, indicating that close contact of porphyrin Zn(II) and bromide anion in cationic polymer could enhance the cooperation activation of epoxide and CO_2 during catalytic process. The BET surface area of ZnTPy-CP is only 16 m^2/g, therefore, most of active sites were buried in the matrix of cationic polymer and could not be accessed by reactants. The diffusion barrier of reactants and products was also a big issue for nonporous materials.

For increasing the BET surface area and decreasing diffusion resistance, cationic polymers were supported on CNTs. ZnTPy/CNTs-50 showed higher PC yield (73% versus 64%) and TOF (602 h^{-1} versus 471 h^{-1}) than those of pure cationic polymer. CNTs had no activity in cycloaddition reaction. This indicated that higher activity of supported cationic polymer was mainly attributed to the increment in BET surface area. Because cationic polymer had no porosity, only outer surface of ZnTPy/CNTs-50 contributed to the catalytic activity. Thus decreasing the thickness of polymer layer on CNTs would increase the dispersion degree of active sites. Thus, the loading content of cationic polymer on CNTs was tuned from 50 wt% to 5 wt %. Based on TEM characterizations, the polymer thickness on CNTs decreased with polymer loading decreasing. To our delight, the PC yield increased monotonically from 73% to 99% as polymer loading decreased from 50 wt% to 5 wt%. The similar tendency was also observed for TOF. This was mainly due to high dispersion degree of active sites and fast diffusion rate of reactants and products.

4. Conclusions

In summary, cationic polymer and CNTs supported cationic polymer were facilely prepared by a one-pot reaction approach, in which the relative amount of porphyrin zinc(II) and quaternary ammonium bromide could be facilely adjusted by controlling the monomer ratio in initial synthesis. Under co-catalysts free conditions, these bifunctional catalysts could efficiently catalyse the cycloaddition reaction of CO_2 and epoxides via a cooperative reaction pathway with porphyrin zinc(II) as lewis acid site and bromine anion as a nucleophilic agent. The catalytic activity of cationic polymer was increased greatly by supporting on CNTs, mainly attributed to the increase of BET surface area.

References

1. T. Sakakura, J.-C. Choi, H. Yasuda, Chem. Rev. 107 (2007) 2365.
2. C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adan, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.* 135 **(**2013) 1228.
3. X.L. Meng, Y. Nie, J. Sun, W.-G. Cheng, J.Q. Wang, H.-Y. He, S.J. Zhang, Green Chem. 16 (2014) 2771.
4. S. Zhang, J. Sun, X. Zhang, J. Xin, Q. Miao, J. Wang, Chem. Soc. Rev. 43 (2014) 7838.