Tetrahedron Letters 55 (2014) 3239-3243

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Nano-sized polydopamine-based biomimetic catalyst for the efficient synthesis of cyclic carbonates



Tetrahedro

Zifeng Yang^{a,b}, Jian Sun^a, Xiaomin Liu^a, Qian Su^a, Ying Liu^a, Qian Li^{b,*}, Suojiang Zhang^{a,*}

^a Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China ^b School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, PR China

ARTICLE INFO

Article history: Received 17 January 2014 Revised 26 March 2014 Accepted 10 April 2014 Available online 20 April 2014

Keywords: Polydopamine Carbon dioxide Cyclic carbonates Synergistic catalysis Alkali metal halide

ABSTRACT

Polydopamine (PDA) is a biocompatible and biomimetic material. Herein, nano-sized PDA sphere was prepared and the combination of alkali metal halide and PDA was investigated as a catalyst for the synthesis of cyclic carbonates from epoxide and carbon dioxide. It was found that the activity of PDA could be obviously enhanced in the presence of alkali metal salts. After reaction, the catalyst and the products could be separated easily, and the catalyst was reusable. The origin of the high catalytic efficiency and the reaction mechanism were also discussed.

© 2014 Published by Elsevier Ltd.

Recently, the increasing pressure of CO₂ released by human being promotes a high requirement of C1 conversion. As one of the most important branches of C1 chemistry, the synthesis of cyclic carbonates via the reaction between CO₂ and epoxides (Scheme 1) was investigated intensively,¹ and thus various catalysts have been developed so far including alkali metal halides based binary catalysts,^{2–7} and biomass supported catalysts.⁸ It is worth mentioning that the combinations of low cost, stable, and nucleophilic alkali metal halides with promoters such as β -CD,² cellulose,³ formic acid,⁴ lignin,⁵ amino acids,⁶ and H₂O⁷ provide a good chance in developing cheap and environmentally benign catalysts. It is believed that continuous efforts on the development of new promoters would achieve further enhancement in efficiency under moderate conditions.

Inspired by mussels marine animals which can be glued on the rocks by their mussel adhesive proteins, most recently, Lee et al. introduced a distinctive approach to surface modification in which self-polymerization of dopamine (Fig. 1c) produced an adherent polydopamine (PDA) coating on a wide variety of materials by a simple dip-coating with dopamine solution.⁹ The formed surface modification method has been explored for many applications, including improving the hemocompatibility of biomaterials and tuning the cell behaviors on their surfaces,^{10,11} Li-ion batteries,¹²

enzyme immobilization,¹³ controlled drug release, and water treatment.^{14,15} Thus, it becomes a popular method to confer multi-functionality to solid–liquid interfaces through the formed biocompatible PDA thin films.⁹ Moreover, PDA could be considered as a good promoter for the synthesis of cyclic carbonates because of abundant hydroxyl groups and active N (–NH, –N=) in the structure (Fig. 1b).^{4,7}

Development of cheap, efficient, and environmentally benign catalysts for the synthesis of cyclic carbonates under solvent-free conditions is still an attractive topic. Encouraged by the advantageous properties of PDA, herein, we conducted the reactions in the presence of potassium halide and PDA under solvent-free conditions for the first time, and found that the catalyst showed excellent synergetic effect on the reactions, by which high yields could be obtained for mono- and di-substituted epoxides. We believe that this efficient, stable, and ecologically safe route to synthesize cyclic carbonates has great potential in industrial application.



Scheme 1. Cyclic carbonates synthesis.



^{*} Corresponding authors. Tel.: +86 378 3881589 (Q.L.); tel./fax: +86 10 82627080 (S.Z.).

E-mail addresses: liq@henu.edu.cn (Q. Li), sjzhang@home.ipe.ac.cn (S. Zhang).

The PDA was synthesized according to the method described in Figure 1a.¹⁶ The corresponding results were list as follows. From Figure 2, it can be seen that the size of nano-PDA could be varied from 180 to 630 nm by controlling the dropping rate of ammonia to dopamine. The Fourier transform infrared (FTIR) spectrum of PDA in Figure 3a showed the characteristic spectral peaks of several functional groups, such as N–H, –OH, C–O, C=N, and C–N. XPS results in Figure 3b–d showed that groups such as C–N, C=N, C–O, and N–H could be found in the structure of the corresponding PDA nano-particles. The above results confirmed the structure of synthesized PDA material.

After the structure characterization, the activity of different PDA based catalysts was tested using the reaction of propylene oxide (PO) and CO_2 , and the results are summarized in Table 1. PDA alone showed a little activity for this reaction, and almost no product was detected (entry 1). When using KI alone, the activity is still low (entry 2). It is surprising that the presence of alkali metal halides could result in an obvious increase in the activity of PDA (entries 3–5), and a highest PC yield of 72% as well as 99% selectivity could be realized with KI/PDA (entry 5). Further-

more, the effects of halide anion and alkali metal cation on the reaction in the presence of PDA were tested. It was found that the catalytic activity improved with the increase in leaving ability of halide anion and alkali metal cation (entries 3-8). For example, with the leaving ability increasing from Cl⁻, Br⁻ to I⁻, the corresponding activity order of anion is $Cl^- < Br^- < I^-$ (entries 3–8). Also the activity order of cation is $Na^+ < K^+$, which is in accordance with their leaving abilities (entries 3-8) (see SI, Table S1). Therefore, it can be deduced that the leaving ability is dominant for the activity. In addition, the performance of other bases, such as Na_2CO_3 , K_2CO_3 , and K₃PO₄, combined with PDA is provided in Table 1, entries 11-13. The results showed that their activities are unsatisfactory. Thereafter, the influence of the molar ratio of KI to PDA on the yield of PC was also investigated (Table 1, entries 5, 9, 10) with the total catalyst amount kept constant. Maximum result was obtained at the molar ratio of KI to PDA 1:1. Based on the result, KI/PDA (1:1, molar ratio) was selected for further investigation.

Thereafter, the effect of various conditions on the reaction for the synthesis of PC was carried out using KI/PDA as the catalyst. As can be seen in Table 2, the reaction temperature has an obvious



Figure 1. (a) Schematic illustration of the synthesis of PDA. (b) The suggested structure of PDA. (c) The chemical structure of dopamine.



Figure 2. SEM images of PDA with different diameters (from a to d: 630, 450, 320, and 180 nm).



Figure 3. Characterization of PDA, (a) FTIR spectrum, (b) XPS spectrum, (c) C 1s XPS spectrum and (d) N 1s XPS spectrum of PDA.

Table 1Screening of catalysts for the synthesis of propylene carbonate^a

Entry	Catalyst	PO conv. ^b (%)	PC selec. ^b (%)	Yield (%)
1	PDA	Trace	99	Trace
2	KI	5	99	5
3	KC1/PDA	10	99	10
4	KBr/PDA	13	98	13
5	KI/PDA	73	99	72
6	NaCl/PDA	9	99	9
7	NaBr/PDA	10	99	10
8	NaI/PDA	39	98	38
9 ^c	KI/PDA	42	98	41
10 ^d	KI/PDA	53	99	52
11	K ₂ CO ₃ /PDA	4	99	4
12	Na ₂ CO ₃ /PDA	2	99	2
13	K ₃ PO ₄ /PDA	5	97	5

^a Reaction conditions: PO (10 mmol), PDA (10 mg, 0.06 mmol), KI (10 mg, 0.06 mmol), other metal halide (0.06 mmol), 120 °C, 2 MPa, 1 h.

^b Determined by GC.

^c PDA (6.67 mg), KI (13.33 mg).

^d PDA (13.33 mg), KI (6.67 mg).

effect on the reaction. With temperature increasing from 110 to 140 °C, PC yield increased sharply from 30% to 96% (entries 1–4). Also, prolonging reaction time from 0.66 to 2 h could enhance PC yield from 47 to 99% (entries 4–6, 10, 11). Table 2 also illustrates the effect of pressure on this reaction in the range of 1–4 MPa. The results suggested that the optimized reaction pressure was 2 MPa (entries 6–9). The decrease of PC yield in the high pressure of 4 MPa might be because that too high pressure would reduce PO conversion because of lowered PO concentration in the vicinity of the catalyst, a condition which was not favorable to the reaction

Table 2Optimization of reaction conditions^a

Entry	<i>t</i> (h)	<i>T</i> (°C)	P (MPa)	Yield ^b (%)
1	1	110	2	30
2	1	130	2	91
3	1	140	2	96
4	1	120	2	72
5	0.66	120	2	47
6	1.5	120	2	99
7	1.5	120	1	74
8	1.5	120	3	97
9	1.5	120	4	98
10	2	120	1	92
11	0.66	130	2	65

^a Reaction conditions: PO (10 mmol), PDA (10 mg), KI (10 mg).

^b Determined by GC.

because PO was also a reactant. Such an effect of CO₂ pressure on catalytic activity has been observed in other catalytic systems.^{3–6}

With PO as the substrate, experiments were carried out to examine the recyclability of KI/PDA at 120 °C and 2 MPa in 1.5 h. As shown in Figure 4, no decrease in PC yields for six repeated runs indicates the high stability of the catalyst. In addition, the SEM and FT-IR spectrum proved the stability of the catalyst (Figs. 5 and S1).

The above results indicated that KI/PDA was an effective catalyst for the synthesis of PC from PO and CO₂. Next, examinations were carried out in order to screen the applicability of the catalyst to various epoxides, and the results are summarized in Table 3. Among the mono-substituted terminal epoxides (**1a**–**1f**), it was found that with the growth of the substituent chain, the activity order of epoxides is **1a** > **1b** > **1c** > **1d**. On the other hand, **1f** was



Figure 4. Recycling experiment for KI/PDA. Reaction conditions: PO (10 mmol), PDA (10 mg), KI (10 mg), 120 °C, 2 MPa CO_2 , 1 h.

good substrates to give cyclic carbonates in good yield and with excellent selectivity. However, in the case of **1e**, the reaction was carried out with a relatively low yield. To further exemplify the catalytic potential of KI/PDA, disubstituted epoxides were also tested (Table 3, entries 7–9). Disubstituted epoxides such as **1g** showed lower activity than mono-substituted terminal epoxides **1a–1f** (entries 7 vs 1–6), and required a longer time to give **2g**. In particular for **1h**, only 9% cyclic carbonate yield was achieved after 10 h, which is probably due to its higher steric hindrance.¹⁷

As proposed by previous reports, hydroxyl groups in the catalyst play a possible role in accelerating the ring-opening of epoxide by hydrogen bonding.^{4,18} Also it was reported that the signal of the H atom in the hydroxyl group shifts to the downfield in ¹H NMR spectra after hydrogen bonding with epoxide (e.g., PO).¹⁸ In order to make an understanding on the interaction of KI/PDA catalyst and epoxide, NMR detection was carried out using dopamine and PO as model compounds. The ¹H NMR spectra of dopamine determined indicated that PO can form hydrogen bond with the –OH groups of dopamine (see SI, Fig. S2). For further confirmation, the corresponding interactions between dopamine and PO were simulated through the density functional theory (DFT) study (see SI, Scheme S1), which was in accordance with the NMR result.

Based on the discussions above, a possible mechanism for the formation of cyclic carbonates was proposed (Scheme 2). Firstly, the –OH groups of PDA facilitate possibly an electrophilic interaction with the oxygen of the epoxide via hydrogen bonds (a). And the anion of KI gives a nucleophilic interaction to the β -carbon of

Table 3

Cycloaddition of CO₂ to terminal epoxides catalyzed by KI/DPA^a



 $^{\rm a}$ Reaction conditions: epoxide (10 mmol), PDA (10 mg), KI (10 mg) 120 $^{\circ}\text{C},$ CO $_2$ 2 MPa.

^b Determined by GC-MS.

the epoxide (a). The synergistic catalysis roles played by KI and PDA make an easy ring-opening of epoxide. Due to the potential function of PDA on CO_2 activation¹⁹, an alkyl carbonate salt formed (c) in parallel would react with ring-opened intermediate (b) to afford another alkyl carbonate salt (d). Finally, the cyclic carbonate



Figure 5. SEM results for PDA before (a) and after 6th use (b).



Scheme 2. A plausible reaction mechanism for the cycloaddition of CO₂ with epoxide catalyzed by KI and PDA.

is formed by subsequent intermolecular ring-closure and the catalyst is regenerated.

In conclusion, KI/PDA binary catalytic system was used for the synthesis of cyclic carbonates from epoxide and CO₂. The size of PDA could be easily controlled and showed a remarkable effect on the reaction due to the excellent synergetic effect of PDA and KI. Especially, the hydrogen bonding between O atom in PO and hydroxyl groups of PDA can promote the reactions effectively. In addition, the catalyst could also be applicable to other terminal or disubstituted epoxides. The process represents a simple, ecologically safer, and cost-effective route to synthesize cyclic carbonate with high product quality, as well as easy catalyst recycling.

Acknowledgements

The authors are grateful to the support by the National Basic Research Program of China (2009CB219901), and National Science Fund of China (21006117, 21006112 and 21306098).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.04.033.

References and notes

 (a) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T. H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724; (b) Omae, I. *Coord. Chem. Rev.* **2012**, *256*, 1384.

- (a) Huang, J. W.; Shi, M. J. Org. Chem. 2003, 68, 6705; (b) Song, J. L.; Zhang, Z. F.; Hu, S. Q.; Jiang, T.; Han, B. X. Green Chem. 2009, 1031, 11; (c) Song, J. L.; Zhang, Z. F.; Han, B. X.; Hu, S. Q.; Li, W. J.; Xie, Y. Green Chem. 2008, 10, 1337.
- Liang, S. G.; Liu, H. Z.; Jiang, T.; Song, J. L.; Yang, G. Y.; Han, B. X. Chem. Commun. 2011, 2131.
- Tharun, J.; Mathai, G.; Kathalikkattil, A. C.; Roshan, R.; Kwak, J. Y.; Park, D. W. Green Chem. 2013, 15, 1673.
- . Wu, Z. L.; Xie, H. B.; Yu, X.; Liu, E. H. ChemCatChem 2013, 5, 1328.
- Yang, Z. F.; Sun, J.; Cheng, W. G.; Wang, J. Q.; Li, Q.; Zhang, S. J. Catal. Commun. 2014, 44, 6.
- 7. Sun, J.; Ren, J. Y.; Zhang, S. J.; Cheng, W. G. Tetrahedron Lett. 2009, 50, 423.
- (a) Zhao, Y. N.; He, L. N.; Wang, J. Q. Chem. Lett. 2008, 19, 286; (b) Sun, J.; Wang, J. Q.; Cheng, W. G.; Zhang, J. X.; Li, X. H.; Zhang, S. J.; She, Y. B. Green Chem. 2012, 14, 654; (c) Tharun, J.; Hwang, Y.; Roshan, R.; Ahn, S.; Kathalikkattil, A. C.; Park, D. W. Catal. Sci. Technol. 2012, 2, 1674; (d) Roshan, K. R.; Mathai, G.; Kim, J.; Tharun, J.; Park, G. A.; Park, D. W. Green Chem. 2012, 14, 2933.
- Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Science 2007, 318, 426.
- (a) Wei, Q.; Li, B.; Yi, N.; Su, B.; Yin, Z.; Zhang, F.; Li, J.; Zhao, C. J. Biomed. Mater. Res. A 2011, 96, 38; (b) Zhu, L. P.; Jiang, J. H.; Zhu, B. K.; Xu, Y. Y. Colloids Surf. B Biointerfaces 2011, 86, 111; (c) Joung, Y. K.; You, S. S.; Park, K. M.; Go, D. H.; Park, K. D. Colloids Surf. B Biointerfaces 2012, 99, 102.
- (a) Ku, S. H.; Lee, J. S.; Park, C. B. Langmuir 2010, 26, 15104; (b) Rim, N. G.; Kim, S. J.; Shin, Y. M.; Jun, I.; Lim, D. W.; Park, J. H.; Shin, H. Colloids Surf. B Biointerfaces 2012, 91, 189; (c) Shin, Y. M.; Lee, Y. B.; Shin, H. Colloids Surf. B Biointerfaces 2011, 87, 79.
- 12. Ryou, H.; Lee, Y. M.; Park, J. K.; Choi, J. W. Adv. Mater. 2011, 23, 3066.
- 13. Sureshkumar, M.; Lee, C. K. Carbohydr. Polym. 2011, 84, 775.
- 14. Yu, B.; Wang, D. A.; Ye, Q.; Zhou, F.; Liu, W. Chem. Commun. 2009, 6789.
- 15. Xi, Z. Y.; Xu, Y.; Zhu, L. P.; Wang, Y.; Zhu, B. K. J. Membr. Sci. 2009, 327, 244.
- 16. Ai, K. L.; Liu, Y. L.; Ruan, C. P.; Lu, L. H.; Lu, G. Q. Adv. Mater. 2013, 25, 998.
- Whiteoak, C. J.; Kielland, N.; Laserna, V.; Escudero-Adan, E. C.; Martin, E.; Kleij, A. W. J. Am. Chem. Soc. 2013, 135, 1228.
- 18. Wang, J. Q.; Sun, J.; Cheng, W. G.; Dong, K.; Zhang, X. P.; Zhang, S. J. Phys. Chem. Chem. Phys. 2012, 14, 11021.
- (a) Yang, Z. Z.; He, L. N.; Gao, J. Energy Environ. Sci. 2012, 5, 6602; (b) Yang, Z. Z.; He, L. N.; Peng, X. Y. Green Chem. 2010, 12, 1850; (c) Yang, Z. Z.; He, L. N.; Zhao, Y. N. Energy Environ. Sci. 2011, 4, 3971.