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Short communication

Rapid synthesis of cyclic carbonates from CO_2 and epoxides under microwave irradiation with controlled temperature and pressure

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Abstract

The solvent-free synthesis of cyclic carbonates from CO_2 and epoxides were carried out under microwave irradiation with controlled temperature and pressure. In comparison with classical heating of oil bath, microwave was demonstrated to be a more effective energy source, which could offer the highest TOF numbers reported up to now for CO_2 coupling reaction with epoxides in the presence of a novel catalyst consisted of zinc phenosulfonate octahydrate and Bu_4NBr. Pseudo-first order kinetic treatment revealed that the observed reaction acceleration under microwave irradiation mainly derived from the non-thermal effects of microwave that lead to an obvious decrease in activation energy.

Keywords: Ionic liquid; Microwave; Cyclic carbonate

1. Introduction

The development of effective process for chemical fixation of CO_2 has been drawing a huge of attention not only due to the fact that CO_2 is one of the greenhouse gas, but also from an increasing interest to treat CO_2 as an abundant and non-toxic building block for organic reaction. It is no doubt that the direct fixation of CO_2 by coupling reaction with epoxide to cyclic carbonate is one of the most promising routes. Therefore, in spite of the fact that cyclic carbonates, particularly ethylene carbonate and propylene carbonate, are manufactured as scheme 1 in an industrial scale, new findings are still increasing [1a,b]. One of the current developments in this reaction is involved the utilization of ionic liquid as reaction medium or catalyst. CO_2 coupling reaction with a variety of epoxides are reported to be carried out in the presence of pure ionic liquid or ionic liquid-based homogeneous catalyst via chemical or electrochemical processes [2a,f].

Microwave irradiation is now widely accepted as effective and non-conventional energy source for performing chemical reactions [3]. Advantages that derived from the utilization of microwave irradiation as heating source, in comparison with that of classical heating, could include spectacular accelerations, higher yields and higher purity under relative mild reaction conditions. Microwave assisted chemical reaction in the presence of ionic liquids have also been reported [4]. Though recently Nuchter et al. reported the microwave assisted reactions of CO_2 with oxiranes using 1,3-dialkylimidazolium bromide-based ionic liquids as reaction medium [5], attention focused on chemical fixation CO_2 to cyclic carbonate under microwave is still little, and a detail understandings of how this reaction is affected by reaction parameters such as pressure and temperature under microwave irradiation are also unfortunately unavailable.

In this paper, we report the solvent-free coupling reaction of CO_2 with epoxides to produce cyclic carbonate under microwave irradiation with controlled temperature and pressure as well as a kinetic analysis from the perspective of employing different heating source.

2. Experimental

2.1. Apparatus

The apparatus involved in this research was shown in Fig. 1. Reactions concerning microwave were carried out with a custom built IMCR-25003 microwave reactor from IDX Corp. [6], which allows us to set reaction time and temperature, as well as to adjust and maintain CO_2 pressure by using a plunger pump.

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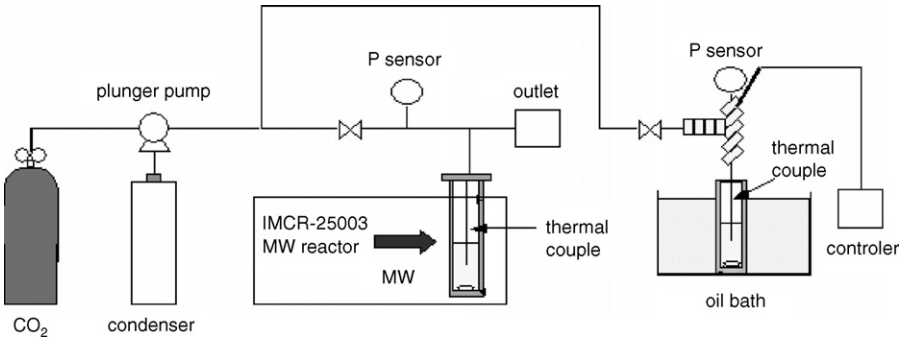


Fig. 1. Schematic representation of the reactor system containing a MW reactor and a conventional oil bath one.

Comparative experiments were also performed using conventional oil bath as heating source.

2.2. Reaction and analysis

In a typical experiment, epoxide substrate and catalyst were charged successively into a self-made autoclave reactor equipped with magnetic stirrer, which was then anchored in the microwave reactor with a tube connected with the plunger pump. CO_2 is introduced through the plunger pump at desired pressure. Then the reaction is allowed to proceed at 70–140 °C for 15–60 min. After the reaction, the reactor was cooled to room temperature and was washed with ethanol for two times. The ethanol phase was combined and analyzed by a gas chromatography equipped with a FID detector using toluene as internal standard (Shimadzu DC-2014, ULBON HR-52 capillary column 25 m × 0.32 mm).

3. Results and discussion

3.1. CO_2 coupling reaction with PO in the presence of various catalysts

Previous studies have revealed that the incorporation of zinc salt with ionic liquids could produce one of the most active catalysts systems for CO_2 coupling reaction with epoxides [2]. Therefore, following this point, four different zinc salts, i.e. $ZnBr_2$ ZnI_2, $Zn(OTf)_2$ and zinc phenosulfonate octahydrate (ZnPO), and five kinds of ionic liquids, i.e. [Emim]Br, [Bmim]Br, [Hmim]Br, Bu_4NBr and Bu_4NI, were involved in our experiments, and their activities for CO_2 coupling reaction under microwave irradiation were investigated using propylene epoxide (PO) as the starting material. Some of the representative results were summarized in Table 1, together with the comparative results obtained using oil bath as heat source. As can be seen, microwave irradiation as heating energy was of higher efficient over oil bath for CO_2 coupling reaction with PO. Depending on the different combination of zinc salt and ionic liquid, microwave irradiation could provide a 11.2–278% increment in term of TOF than that of oil bath (Runs 1–8).

Our results also suggested that ionic liquid have played an important role in CO_2 coupling reaction with PO under microwave irradiation, and an activity order of ionic liquid as Bu_4NI < [Emim]Br ∼ [Bmim]Br ∼ [Hmim]Br < Bu_4NBr was observed (Runs 4–8). Interestingly, it was found that ZnPO, a zinc salt that neglected by most of the previous researches, had the highest activity among the four zinc salts under both microwave and oil bath conditions, which, with the combination with Bu_4NBr, could afford a TOF as 6989 h^{-1} at the yield of 75.9% within 15 min.

3.2. Pressure dependence of CO_2 coupling reaction with PO

As ZnPO/Bu_4NBr had high activity for CO_2 coupling reaction with PO, then it was employed as catalyst to investigate the

Table 1
CO_2 coupling reaction with propylene oxide under microwave irradiation

Run	Zinc salt	IL	Microwave		Oil bath	
			Yield	TOF (h^{-1})	Yield	TOF (h^{-1})
1	$ZnBr_2$	Bu_4NBr	72.2	6732	51.8	4806
2	$Zn(OTf)_2$	Bu_4NBr	70.6	6377	52.7	4767
3	ZnI_2	Bu_4NBr	73.3	6654	62.5	5681
4	ZnPO	Bu_4NBr	75.9	6989	68.3	6383
5	ZnPO	Bu4NI	32.3	2972	22.5	2108
6	ZnPO	[Emim]Br	47.8	4460	12.6	1182
7	ZnPO	[Bmim]Br	49.1	4576	35.8	3309
8	ZnPO	[Hmim]Br	51.3	4733	28.3	2610

Temperature: 100 °C, CO_2 pressure: 3 MPa, time: 15 min, MW: 300 W, PO: 29.9 mmol, zinc salt: 0.013 mmol, IL: 0.65 mmol.

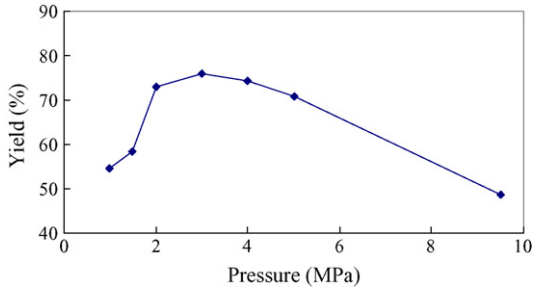


Fig. 2. Pressure dependence of CO_2 coupling reaction with PO.

effects of other reaction parameters on this reaction. To begin with, the influence of CO_2 pressure was examined at 100 °C using 0.013 mmol ZnPO, 0.65 mmol Bu_4NBr and 29.9 mmol PO. The pressure dependence curve was presented in Fig. 2. It was already known that CO_2 pressure was a crucial factor in CO_2 coupling reaction with epoxide when oil bath was used as heating source. Depending on the catalysts involved and the gas–liquid phase behavior of reaction system, optimal yields of cyclic carbonates could be achieved at mild pressure ($ZnBr_2$/[Bmim]Br, 1.5 MPa) [2f], or medium pressure ($ZnBr_2$/*n*-Bu_4NI, 8 MPa) [2e], or supercritical condition ([C_8-mim]Br, 14 MPa) [2c]. As can be seen form Fig. 2, when microwave irradiation was employed as heating source and ZnPO/Bu_4NBr as catalyst, the maximum yield of propylene carbonate at a mild pressure of CO_2 at 3 MPa, similar to that of $ZnBr_2$/[Bmim]Br under oil bath heating.

3.3. Temperature dependence of CO_2 coupling reaction with PO

Then, fixing CO_2 pressure at 3 MPa and using same amounts of ZnPO/Bu_4NBr and PO as mentioned above, effect of temperature was examined and the results were presented in Fig. 3. Within the examined temperature range, yield of propylene carbonate increased with the beginning of 80 °C until achieved the maximum point at 120 °C. However, further temperature increasing to 130 or 140 °C led to a slight decreasing of yield, this indicated maybe some undesired reactions, such as ring opening or polymerization, occurred at high temperature. Therefore, appropriate operational temperature under microwave irradiation could be set below 120 °C for CO_2 coupling reaction with epoxide.

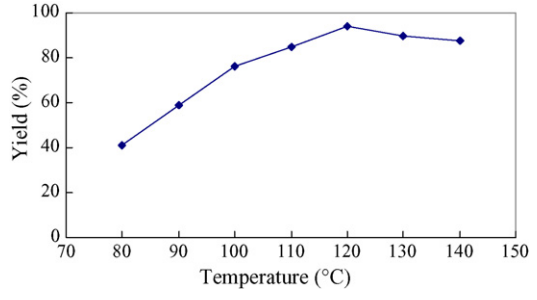


Fig. 3. Temperature dependence of CO_2 coupling reaction with PO.

Table 2
CO_2 coupling reaction with propylene oxide under varied reaction time and PO/Zn ratio

Run	PO/Zn	Time (min)	Yield (%)	TOF (h^{-1})
1	10,000	15	50.7	20,371
2	10,000	30	77.1	15,697
3	10,000	45	88.3	11,825
4	10,000	60	97.0	9,732
5	15,000	60	86.0	12,949
6	20,000	60	70.5	14,548

45 cm^3 reactor was used. Temperature: 120 °C, CO_2 pressure: 3 MPa, MW: 300 W, ZnPO: 0.013 mmol, Bu_4NBr: 0.65 mmol.

3.4. CO_2 coupling reaction with PO under different PO/Zn ratio

PO/Zn ratio and reaction time were another two factors that played important roles in the reaction of CO_2 coupling reaction with PO. Table 2 listed the results of how the yield of product and TOF changed with the varying of PO/Zn ratio and reaction time, with a PO/Zn ratio ranged from 10,000 to 20,000 and reaction time between 15 and 60 min. As can be seen, when the PO/Zn ratio was kept at 10,000, it took just 15 min to reach a yield of 50.7%, and a yield of 97.0% with TOF as 9732 h^{-1} could be achieved within 1 h. To the best of our knowledge, it was the highest number for CO_2 coupling reaction with PO reported up to now. As a reference, the previous record was 5410 h^{-1}, obtained in the presence of $ZnBr_2$/[Bmim]Br with a 95% yield at 1.5 MPa CO_2 [2f]. Increasing the PO/Zn ratio to 15,000 and 20,000 could offer the yields of product as 86.0% and 70.5%, respectively, after 1 h reaction, which further indicated that microwave irradiation can act as an effective heating source for CO_2 coupling reaction with epoxide.

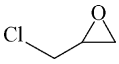
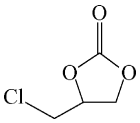
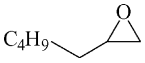
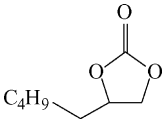
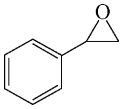
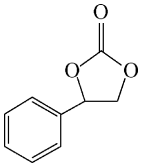
3.5. CO_2 coupling reaction with other epoxides in the presence of ZnPO/Bu_4NBr

Then CO_2 coupling reactions with other epoxides, including chloromethyloxirane, 1,2-epoxyhexane and 1,2-epoxyethylbenzene, were performed under microwave irradiation in the presence of ZnPO/Bu_4NBr and the results were shown in Table 3. As expected, medium to good yields could be achieved within just 15 min with the aid of microwave heating.

3.6. Pseudo-first order kinetic treatment of CO_2 coupling reaction with PO

Microwave effects that resulted from material–wave interactions could be described by thermal effects, which may be easily estimated by temperature measurements, and specific (non-purely thermal) effects. Taking into considerations that our temperature measurements find no any obvious overheating or superheating effects, which were characteristic properties of thermal effects, a perspective from non-thermal effects was then employed to try to explain the observed acceleration of CO_2 coupling reaction with PO under microwave irradiation.

Table 3
CO_2 coupling reaction with other epoxides in the presence of ZnPO/Bu_4NBr

Substrate	Product	Yield (%)	TOF (h^{-1})
		91.5	8451
		70.9	6645
		62.5	5762

Temperature: 120 °C, CO_2 pressure: 3 MPa, ZnPO: 0.013 mmol, Bu_4NBr: 0.65 mmol, substrate: 29.9 mmol.

In general, non-thermal effects can be rationalized by consideration under the Arrhenius law [$k = A\ \exp(-E_a/RT)$] [7,8], where A was pre-exponential factor and E_a was activation energy, and can result from changes in each of the terms in this equation. As the amount of CO_2 was great excessive over PO in our experiment, the concentration of CO_2 can be hypothesized as constant; therefore, the whole system can be treated with pseudo-first order approximation $v = k$ [PO], where v was reaction rate, k was catalytic constant and [PO] was concentration of PO [9].

The results of k for CO_2 coupling reaction with PO obtained, respectively, from microwave and oil bath at temperature ranged from 70 to 100 °C were presented in Table 4. Based on the value of k, first order kinetic plots for microwave and thermal activation was shown in Fig. 4, and the corresponding value of A and E_a were listed in Table 5.

It was clear from Fig. 4 that the above pseudo-first order assumption was very feasible. As can be seen from Table 5, both E_a and A were significantly influenced by microwave irradiation, and decreased remarkably compared with that of oil bath. Since A is representative of the probability of molecular impacts, the decreasing of A meant a negative role of microwave on the reaction rate. Fortunately, this negative effect was simultaneously compensated by the decreasing of activation energy. As a whole, reaction was accelerated under microwave irradiation, especially at low temperature.

Table 4
Catalytic constant k at different temperature

Temperature (K)	$10^4 k$ (s^{-1})	
	MW	Oil bath
343	2.25	1.31
353	4.58	2.40
363	6.54	4.68
373	8.44	7.59

CO_2 pressure: 3 MPa, time: 15 min, PO: 29.9 mmol, ZnPO: 0.013 mmol, Bu_4NBr: 0.65 mmol.

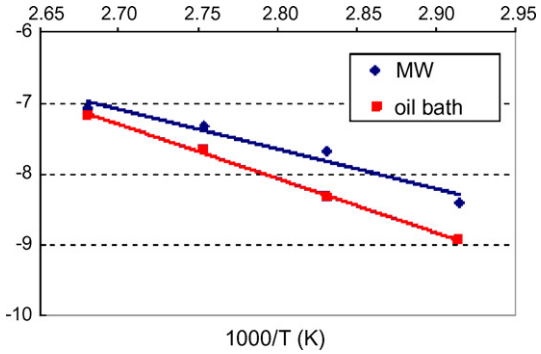


Fig. 4. Pseudo-first order kinetic plots for MW and thermal activation.

Table 5
Results from the Arrhenius plots in Fig. 4

Activation mode	E_a (kJ/mol)	A ($10^3 \times s^{-1}$)
MW	46.2	2.75
Thermal	63.2	5.43

4. Conclusions

In conclusion, we demonstrated herein the rapid and solvent-free synthesis of cyclic carbonates from CO_2 and epoxides under microwave irradiation with controlled temperature and pressure. Our results suggest clearly that microwave irradiation is an effective heating source for CO_2 coupling reaction over oil bath due to its non-thermal effect that affords a marked decreasing of activation energy. Moreover, a novel catalyst consisted of zinc phenosulfonate octahydrate and Bu_4NBr was found which could provide the highest TOFs reported up to now for CO_2 coupling reaction with epoxides under microwave irradiation.

References

[1] (a) M. Ramin, J. Grunwaldt, A. Baiker, J. Catal. 234 (2005) 256;
(b) Y. Du, F. Cai, D. Kong, L. He, Green Chem. 7 (2005) 518.
[2] (a) J. Peng, Y. Deng, New J. Chem. 25 (2001) 639;
(b) H. Yang, Y. Gu, Y. Deng, F. Shi, Chem. Commun. (2002) 274;
(c) H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, Chem. Commun. (2003) 896;
(d) H.S. Kim, J.J. Kim, H. Kim, H.G. Jang, J. Catal. 220 (2003) 44;
(e) J. Sun, S. Fujita, F. Zhao, M. Arai, Appl. Catal. A 287 (2005) 221;
(f) F. Li, L. Xiao, C. Xia, B. Hu, Tetrahedron Lett. 45 (2004) 8307.
[3] A. de la Hoz, A. Diaz-Ortiz, A. Moreno, Chem. Soc. Rev. 34 (2005) 164, and references cited therein.
[4] B.C. Ranu, R. Jana, J. Org. Chem. 70 (2005) 8621, and references cited therein.
[5] M. Nuchter, B. Ondruschka, J. Hoffmann, A. Tied, Stud. Surf. Sci. Catal. 153 (2004) 131.
[6] Details of microwave reactor are available at http://www.idx-net.co.jp/index2.html.
[7] J. Berlan, P. Giboreau, S. Lefeuvre, C. Marchand, Tetrahedron Lett. 32 (1991) 2363.
[8] L. Perreux, A. Loupy, Tetrahedron 57 (2001) 9199.
[9] D.A. Lewis, J.D. Summers, T.C. Ward, J.E. McGrath, J. Polym. Sci. A 30 (1992) 1647.