Molecular Catalysis xxx (xxxx) xxx-xxx



Contents lists available at ScienceDirect

Molecular Catalysis



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

Solventless synthesis of cyclic carbonates by direct utilization of CO_2 using nanocrystalline lithium promoted magnesia

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ARTICLE INFO

Keywords: Carbon dioxide Lithium promoted magnesia Cyclic carbonate 4-(Chloromethyl)-1,3-dioxolan-2-one Epichlorohydrin

ABSTRACT

Cyclic carbonates are industrially important chemicals. In this work, an efficient synthesis of cyclic carbonate was achieved by cyclization of epoxide with CO_2 using nanocrystalline lithium promoted magnesia (Li-MgO), without using any co-catalyst or solvent. A series of Li-MgO were prepared by gel combustion method and well characterized. Li-MgO forms active F-centers (crystallographic defect) due to the difference in valence state of lithium (Li⁺) and magnesium (Mg²⁺) and acts as an active site for CO_2 activation. In the synthesis of 4-(chloromethyl)-1,3-dioxolan-2-one from epichlorohydrin, 0.75% (w/w) Li-MgO was the most active catalyst for CO_2 fixation into cyclic carbonate with excellent conversion (~98%) and selectivity (100%), at 130 °C and 3 MPa of CO_2 pressure. The catalyst showed structural stability and was reused for three cycles without loss of activity. The current synthesis protocol is 100% atom-efficient and thus was extended to a variety of substrates. Langmuir- Hinshelwood-Hougen-Watson (LHHW) type of mechanism was proposed and kinetics studied. Both reactants are strongly adsorbed making the overall reaction zero order with an apparent activation energy of 15.14 kcal/mol.

1. Introduction

 CO_2 is a key contributor to global warming due to its increasing concentration in the atmosphere [1] but can be used for a variety of purposes. It is a cheap, abundant, and non-toxic renewable C1 energy resource [2,3]. Nowadays, from the green chemistry point of view utilization of CO_2 into value-added chemicals has achieved significance; for instance, in the synthesis of formic acid, methanol, dimethyl carbonate (DMC), etc. [4,5]. It also been used as a green alternative to phosgene and thionyl chloride [6]. For the past few decades the utilization CO_2 in the synthesis of cyclic carbonate has been extensively studied because the process is 100% atom efficient. Cyclic carbonates have wide applications as solvents or precursors in many fields such as lithium ion battery, pharmaceutical chemistry, biomedical and biodegradable plastic industry, fine chemicals, etc.

 CO_2 has a linear structure with zero dipole moment and is thermally and kinetically a stable molecule [7]. To overcome the stability of CO_2 , there is a need to develop cost-effective catalyst for its activation [8,9]. Several reports are published on the synthesis of cyclic carbonates from coupling of CO_2 and epoxides using different catalysts; for instance, phosphonium based ionic liquid supported on polymer nanoparticle [10], 2-pyridinemethanol [11], magnetically separable ZnBr₂ supported on MCM-41 [12], Pd/C [13], metal porphyrin [14], quaternized chitosan [15] and protonic ionic liquids [16]. Heterogeneous catalysis is always preferred over homogeneous systems because of its well-known attributes. Generally, homogeneous protocols have common drawbacks like non-reusability of catalyst, toxicity and cost of the reagents.

Yamaguchi et al. [17] used Mg-Al hydrotalcite as catalyst for direct utilization of CO₂ into cyclic carbonate using DMF as solvent as well as co-catalyst. Since then various reports are published on the solventless synthesis of cyclic carbonates using heterogeneous catalysts (Table 1) such as nitrogen doped carbon monolith, methyl imidazole (ionic liquid, IL) supported on cellulose [18], IL supported on polystyrene [19], polystyrene supported organometallic catalyst [20], MgO using DMF as solvent [21], and salen complexes with different metals like Zn, Cu, Co and Cr [22–24]. However, there is scope for improving methodology and economic aspect of the processes for synthesis of cyclic carbonates. Table 1 lists various routes of preparation of cyclic carbonates.

Li-MgO was used as a basic catalyst for oxidative coupling of methane [26], synthesis of cyclic carbonates using dimethyl carbonate (DMC) [25], aldol condensation [27] and transesterification reaction [28]. In the case of Li-MgO, the atomic radii size of Li⁺ (~76 pm) and magnesium Mg²⁺ (~72 pm) in their oxide form [29] allow easy

https://doi.org/10.1016/j.mcat.2018.01.012

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Received 4 August 2017; Received in revised form 9 January 2018; Accepted 10 January 2018 2468-8231/ @ 2018 Elsevier B.V. All rights reserved.

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Table 1

Literature review for synthesis of cyclic carbonates.

#	Catalyst	Epoxide mmol	CO_2 Pressure MPa	Temp. °C	Time h	Yield%	Sel%	Epoxide per g-cat mol/g	Ref.
1	Metalated porous porphyrin polymer	12.5	0.1	30	24	95	99	0.25	[33]
2	Imidazolium based polymer supported ionic liquid	54	0.8	100	6	91	100	0.11	[34]
3	Bifunctional quaternary phosphonium salt catalyst	0.2	0.1	60	24	85	-	-	[35]
4	Chiral Co(III) complexes	86	5	50	24	80	99	-	[36]
5	Silica grafted ammonium salts	10	4	100	24	95	99	0.016	[37]
6	[Heemim][ZrCl ₅]	10	1	120	3	97	99	0.011	[38]
7	Heteropolyacid-based ionic liquid@SiO ₂	1	1	120	2	96	99	-	[39]
8	Imidazole supported on silica	54	1.5	130	6	100	90	-	[40]
9	Phosphorus ylide	10	0.1	100	6	90	-	0.055	[41]
10	Polystyrene@quaternized ammonium salt	52	2	140	6	96	99	-	[42]
11	Nitrogen@porous carbon monolith	10	5	150	16	84	-	4	[43]
12	Bis-ammonium@ polystyrene	21.5	1.2	130	2.5	98	98.5	-	[19]
13	MgO (DMF solvent)	10	2	135	4	60	-	0.005	[21]
14	Mg-Al HT (DMF solvent)	0.5	1	100	24	90	96	0.008	[44]
15	Li-MgO	127	3	130	4	97	99	0.254	This work

replacement of anion of Mg^{2+} and Li⁺ in the periclase structure of the catalyst [27,30]. The replacement of Mg^{2+} with Li⁺ creates oxygen vacancy or structural defect (F center) in order to maintain crystal neutrality. That F-center acts as active sites of catalyst for CO₂ activation [31,32]. Thus, Li-MgO was considered as the most promising catalyst which needed further insight including its method of synthesis.

In this context, we report a solvent-free synthesis of cyclic carbonate by direct utilization of CO_2 in the presence of Li-MgO. The catalyst was synthesized by simple gel combustion method using glycine as fuel [25]. A variety of loading of Li on MgO was used to determine the most active and selective catalyst vis-à-vis several others. Synthesis of a cyclic carbonate, (4-(chloromethyl)-1,3-dioxolan-2-one) from epichlorohydrin and CO_2 was studied systematically using Li/MgO (Scheme 1). The effect of lithium loading on crystallite size and morphology was studied which will have a direct bearing on conversion and selectivity. Reaction mechanism and kinetics are also presented for the first time.

2. Experimental

2.1. Chemicals

The following chemicals were procured from the reputed firms (Merck, Sigma Aldrich, etc.) and used without further purification: Mg $(NO_3)_2$ LiNO₃, epichlorohydrin, propylene oxide, cyclohexene oxide, glycidol, styrene oxide, ethylene oxide etc.

2.2. Li-MgO preparation

The catalyst was prepared by gel combustion method using glycine as fuel as per our previously published report [25]. The stoichiometric mixtures of precursors like Mg(NO₃)₂·6H₂O, Li(NO₃) and glycine were dissolved in minimum quantity of deionized water (†ESI, Table S1). Then, this homogenized solution was heated at ~100 °C to form a transparent gel which was transferred to muffle furnace at 350 °C for combustion at autoignition temperature of glycine. Combustion was completed in a few seconds; the powdered mass was further calcined at 550 °C for 3 h in air to get pure and nanocrystalline Li-MgO. Rapid hightemperature combustion allow the formation solid defects (F centers) due to the evolution of gases (mainly CO₂, N₂, and H₂O). The



Scheme 1. Synthesis of cyclic carbonate (4-(chloromethyl)-1,3-dioxolan-2-one)

theoretical equation of formation of Li-MgO catalyst (F/O ratio 2) is as follows [28,45]:

9.99 Mg(NO₃)₂.6H₂O + 0.01LiNO_{3(S)} + 20NH₂CH₂COOH_(S) → 9.99MgO + 0.005Li₂O + 40CO_{2(g)} + 20.004 N₂[↑] (g) + 109.94H₂O (g)

2.3. Experimental procedure for cyclization of epichlorohydrin and CO₂

Epichlorohydrin (1a) 127 mmol (10 mL) and catalyst 0.05 g/cm^3 (0.5 g) were taken in 50 mL autoclave (Amar Equipments, Mumbai, India) with pressure and temperature regulators. The reactor was flushed twice with CO₂ to remove air and temperature set at 130 °C; After reaching the temperature the reactor was charged with CO₂ and pressurized to 3 MPa which was maintained throughout the experiment. Reaction progress was monitored by GC. After completion of the reaction, the reactor was cooled down to 10 °C through coolant and slowly depressurized.

3. Results and discussion

Since 0.75% (w/w) Li-MgO was the most active catalyst for CO_2 fixation into cyclic carbonate, its complete characterization is provided in comparison with other loadings of Li on MgO and pure MgO. To find out if any structural changes had taken placed, reused catalyst was also characterized.

3.1. Catalyst characterization

3.1.1. XRD

XRD patterns of fresh and reused Li-MgO were analyzed in the range of $10-80^{\circ} 2\theta$ using Bruker AXS, D8 discover instrument (USA) with Cu-K α (1.54 Å) radiation. Pure MgO gives sharp peaks at 2θ values 36.8°, 42.8°, 62.2°, 74.3° and 78.6° which correspond to (111), (200), (202), (311), (222) diffraction planes, respectively. Its diffraction pattern matches with periclase cubic type structure of MgO, confirmed by standard JCPDS data card # 45-0946 [46]. Diffraction peaks related to pure MgO were broader than those for Li-MgO samples; the broadening indicates smaller crystallite size [25,31]. Up to 0.5% (w/w) lithium loading has no significant effect in XRD patterns (Fig. 1). It indicates that the material with less than 0.5% lithium loading shows cubic nanocrystalline MgO phase. In Li-MgO catalyst the Li₂CO₃ phase (JCPDS card # 22-1141) was observed at 0.5% of lithium loading ($2\theta = 33^{\circ}$). The increase in crystallinity was proportional to the lithium loading in Li-MgO.



Fig. 1. XRD diffraction patterns of Li- MgO with different loadings.

3.1.2. FT-IR spectra

Fig. 2 shows FT-IR of CO₂ adsorbed species on the surface of 0.75% (w/w) Li-MgO. CO₂ was adsorbed on the surface of the catalyst in three different ways; unidentate, bidentate and bicarbonate [25,27]. The free O^{2-} species of unidentate carbonate shows symmetric O–C–O stretching at 1384 cm⁻¹ and asymmetric stretching at 1504 cm⁻¹.

Lewis-acid–Brönsted base $[M^{2+}O^{2-}]$ type forms bidentate carbonate species. It shows symmetric and asymmetric O–C–O stretching at 1319 and 1621 cm⁻¹ respectively. The surface –OH group forms bicarbonate species. It shows symmetric and asymmetric O–C–O stretching at 1442 and 1638 cm⁻¹, respectively. The band observed at 1087 cm⁻¹ is due to the absorbed CO₂ and the broad spectrum at 645 cm⁻¹ is attributed



Fig. 2. FITR spectrum of 0.75% (w/w) Li-MgO.

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Fig. 3. SEM images of (a) 0.75% (w/w) Li-MgO fresh and (b) reused catalyst 0.75 (w/w) Li-MgO and (c) TEM image of fresh 0.75% (w/w) Li-MgO.

to Mg–O–Mg bending vibrations. The IR spectra of reused catalyst were recorded after third reuse. It does not show a considerable change in nature of IR spectrum thereby proving the stability of catalyst (†ESI Fig. S1).

3.1.3. SEM and TEM

Samples of MgO and 0.75 (w/w) Li-MgO were analyzed by SEM and TEM to observe the morphology of MgO, fresh and reused Li-MgO. The fresh catalyst shows highly porous and uneven distribution of fine particles. The rapid evolution of gases in combustion synthesis results in the formation of pores and voids with uneven distribution. The porous structure of fresh and reused Li-MgO was analyzed by SEM. The morphology had somewhat changed in the reused catalyst with slight agglomeration as compared to the fresh catalyst (Fig. 3).

3.1.4. BET surface area

MgO and 0.75 (w/w) Li-MgO show type IV adsorption isotherm that indicates the formation of mesoporous material and H3 type hysteresis loop that suggests slit-shaped pores or plate-like particles (†ESI Fig. S2). Surface area Li-MgO catalysts decrease with increase in lithium loading (Table 2). The reused catalyst 0.75 (w/w) Li-MgO shows no significant change in BET surface area.

3.1.5. Basicity by CO₂-TPD

Basicity of pure MgO and Li-MgO samples were analyzed for CO₂-TPD. It gives an idea about strength and nature of basic sites of the catalyst. It shows that total number of basic sites Li-MgO were more than that of pure MgO. The number of basic sites increase with increase in lithium loading but at the same time, the surface area decreases. Thus, total number of accessible basic sites also decrease (Table 2). The basicity of fresh and reused catalyst remains nearly the same.

3.2. Effect of lithium loading

When lithium is doped in MgO matrix, there is the formation of structural defects [50]. Lithium (Li⁺) which replaces magnesium (Mg²⁺) results in the formation of F-centers localized into the crystal lattice. F-center is formed in the crystal lattice due to almost similar sizes of Li⁺ (~76 pm) and Mg²⁺ (~72 pm) ionic radii with different

Table 2

BET analysis and total basicity of pure MgO and lithium promoted magnesia.

Lithium Loading % (w/w)	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Total basicity (mmol/g)
0.00	138.2	7.47	0.38	0.38
0.10	119.4	12.81	0.58	0.71
0.25	92.3	11.23	0.51	0.65
0.50	74.2	10.55	0.26	0.61
0.75	52.1	13.09	0.15	0.60
1.00	22.5	11.05	0.12	0.52
Reused 0.75	51.4	12.16	0.14	0.58

valency in their oxide forms. It is stabilized by O⁻ species and so there is formation of [Li⁺O⁻] defect or F center in the crystal lattice [31]. Lithium-doped impurity tries to persist on the surface of the catalyst so as to maintain its low co-ordination number for the stability of crystal [51]. However, with an increase in dopant lithium, there is subsequent increase in the oxygen valency to maintain the neutrality of crystal lattice. The addition of this dopant impurity changes all morphological features of the catalyst such as crystallite size, surface area, pore size, and pore volume. During combustion synthesis, due to the addition of dopant i.e. lithium (Li), the basicity of Li-MgO was enhanced by formation of crystallographic defect (F-center). Thus 0.75 (w/w) Li-MgO showed excellent conversion per unit mass of catalyst, in synthesis of cyclic carbonate. The reaction conditions were as follows; temperature (130 °C), pressure (3 MPa) and reaction time (4 h) (Scheme 1). To study the efficiency of this process, we have calculated the conversion ratio of substrate per gram of catalyst in synthesis of cyclic carbonate, it gives comparatively good conversion in terms of moles (substrate) per gram of catalyst (Table 1).

The activity of various loadings of lithium over MgO was tested for the synthesis of 4-(chloromethyl)-1,3-dioxolan-2-one from epichlorohydrin and CO₂. The XRD data show the formation of Li_2CO_3 phase after 0.75%, (w/w) of lithium loading; up to 0.75% lithium can exchange magnesium in the crystal lattice, thereafter the excess of lithium forms lithium oxide on the surface of the catalyst. It forms Li_2CO_3 phase when it adsorbs atmospheric CO₂. This blocks the pores of catalyst and reduces its surface area. Thus, 0.75% was found to be optimum loading for the synthesis of cyclic carbonate (Fig. 4).

3.3. Effect of CO_2 pressure on cyclization reaction

Cyclization of epichlorohydrin (1a) to 4-(chloromethyl)-1,3-dioxolan-2-one (1b) as given in Scheme 1 was performed in the range of 0.5-5 MPa pressure of CO₂. The increases in CO₂ partial pressure from 0.5 to 3.0 MPa resulted in the significant increase in epichlorohydrin conversion; after 3.0 MPa pressure significant decline in conversion was observed as discussed in previous reports [47,48]. CO₂ (G), organic



Fig. 4. Effect of lithium loading on synthesis of cyclic carbonate. Reaction conditions: epichlorohydrin 127 mmol; catalyst loading 0.02 g/cm³; reaction temperature 130 °C; speed of agitation 1000 rpm; time 4 h.



Fig. 5. Effect of CO₂ pressure on conversion of epichlorohydrin.

Reaction conditions: epichlorohydrin 127 mmol; catalyst loading $0.02 \,\text{g/cm}^3$; reaction temperature 130 °C; speed of agitation 1000 rpm; time 4 h.

reactant **1a** and product **1b** (L) and catalyst (S) forms a triphasic G-L-S system; at the high CO_2 pressure the dissolved CO_2 concentration in organic liquid phase is increased. CO_2 is acidic and **1a** basic and therefore, there is a formation of the epoxide- CO_2 bond. The CO_2 concentration on the catalyst sites increases and thus according to the Langmuir-Hinshelwood-Hougen-Watson (LHHW) the rate decreases beyond 3 MPa and hence the conversion (Fig. 5).

3.4. Catalyst loading

In the absence of external mass transfer resistance, the conversion of **1a** was proportional to catalyst loading which was studied in the range of 0.01–0.10 g/cm³. Increase in catalyst loading proportionally increases the number of active sites (Fig. 6). The initial rate of reaction of epichlorohydrin increases linearly with catalyst loading.

3.5. Effect of temperature

Effect of temperature for cyclization of epichlorohydrin (1a) with CO_2 was studied in the range of 110–140 °C. From Fig. 7 it clearly indicates that temperature plays a crucial role in the conversion of 1a–1b. From 110–130 °C the conversion increases according to temperature but thereafter decrease from 1a–1b. Using this experimental data, we have developed the kinetic model for this reaction.

This reaction shows the Langmuir–Hinshelwood–Hougen–Watson (LHHW) type mechanism and zero order reaction kinetics. By plotting Arrhenius plot, we have calculated the apparent activation energy (15.14 kcal/mol). The detailed kinetic study is provided in ESI[†].



Fig. 6. Effect of catalyst loading on epichlorohydrin.

Reaction conditions: epichlorohydrin 127 mmol; CO₂ pressure 3 MPa; reaction temperature 130 $^\circ$ C; speed of agitation 1000 rpm; time 4 h.



Fig. 7. Effect of temperature on conversion of epichlorohydrin. Reaction conditions: epichlorohydrin 127 mmol; CO₂ pressure 3 MPa; speed of agitation 1000 rpm; time 4 h.

3.6. Catalyst reusability study

After completion of the reaction, the catalyst was separated by filtration, washed with methanol for 2–3 times to remove adsorbed organic molecules like **1a** and **1b** from the surface of the catalyst. It was then refluxed in MeOH at 60 °C for 2 h, filtered and dried at 100 °C for 6 h. The reusability of catalyst was studied up to three cycles at optimized reaction conditions. It was found that 0.75% Li-MgO catalyst was robust, recyclable and did not show any significant change even after the third cycle (Fig. 8).

3.7. Possible reaction mechanism

Based on previously published reports [47,49,52,53] and our experimental outcomes, we propose a possible reaction mechanism for fixation of CO₂ with **1a** to form **1b**. CO₂ has mild acidity which gets adsorbed on $[\text{Li}^+\text{O}^-]$ (strongly basic) site of the catalyst and **1a** is adsorbed on Lewis acidic sites of catalyst (Mg²⁺ or Li⁺) (located adjustment on the surface of catalyst) as in intermediate (**I**) (Scheme 2). After adsorption of CO₂ and **1a** on the surface of the catalyst, the linear structure of CO₂ gets disturbed and partial charge separation takes place. The activated species of CO₂ leads to nucleophilic attack on sterically less hindered carbon of **1a** and opens the ring to form an intermediate **II**. The intermediate **II** further undergoes chemical rearrangement to form a CO₂ incorporated product and the cyclic carbonate (**1b**) is formed. After formation of the product, it gets desorbed from the catalyst site (as intermediate **II**). This catalytic cycle occurs continuously to get cyclic carbonate as the product.

3.8. Reaction kinetics

In the absence of both external mass transfer and intra-paticle diffusion resistances, the reaction is kinetically controlled [56–59]. Langmuir–Hinshelwood–Hougen–Watson (LHHW) mechanism was used to derive a model for the synthesis of cyclic carbonate. It was



Fig. 8. Reusability of Li-MgO in synthesis of cyclic carbonate.

observed that CO_2 and epichlorohydrin adsorb on strong basic sites and weak Lewis acidic sites of the catalyst, respectively.

Assuming that, the catalyst having two different sites (S $_1$ and S $_2$) for adsorption of CO $_2$ and epichlorohydrin.

Considering the reaction,

$$A(epichlorohydrin) + B(CO_2) \xrightarrow{\text{Li/MgO}} C(cyclic carbonate)$$
(1)

Adsorption of epichlorohydrin (A) and CO_2 (B) was on catalytic site S_1 and S_2 respectively;

$$A + S_1 \stackrel{K_A}{\rightleftharpoons} AS_1 \tag{2}$$

$$B + S_2 \stackrel{AB}{\rightleftharpoons} BS_2 \tag{3}$$

Then surface reaction takes place between adsorbed CO_2 and epichlorohydrin

$$AS_1 + BS_2 \stackrel{^{\wedge}}{\rightleftharpoons} CS_1 + S_2 \tag{4}$$

After reaction completion, product gets desorbed from catalyst site;

$$CS_1 \underset{K_{D'}}{\overset{K_D}{\rightleftharpoons}} C + S_1$$
(5)

The total concentration of total catalyst sites C_T expressed as;

 $C_{T} = C_{T_{1}} + C_{T_{2}}$ (6)

But, $C_{T_1} = C_{S_1} + C_{AS_1} + C_{CS_1}$ (7)

$$C_{T_2} = C_{S_2} + C_{BS_2}$$
 (8)

From Eqs. (7) and (8);

ŀ

$$C_{T_{1}} = C_{S_{1}} + K_{A}C_{A}C_{S_{1}} + K_{C}C_{C}C_{S_{1}}$$
(9)

$$C_{T_2} = C_{S_2} + K_B C_B C_{S_2}$$
(10)

It was assumed that at equilibrium stage, rate of adsorption and desorption is the same, concentration of vacant sites can be written from Eqs. (9) and (10);

$$C_{S_{1}} = \frac{C_{T_{1}}}{K_{A}C_{A}C_{S_{1}} + K_{C}C_{C}C_{S_{1}}}$$
(11)

$$C_{S_2} = \frac{C_{T_2}}{K_B C_B C_{S_2}}$$
(12)

If surface reaction rate is controlling step, then rate of reaction can be written as;

$$-r_A = kC_{AS_1}C_{BS_2} - k'C_{CS_1}C_{S_2}$$
(13)

$$= kK_A C_A C_{S_1} K_B P_B C_{S_2} - k' K_C C_C C_{S_1} C_{S_2}$$
(14)

$$=\frac{(kK_A C_A K_B P_B - k'K_C C_C)C_{T_1}C_{T_2}}{(1 + K_B P_B)(1 + K_A C_A + K_C C_C)}$$
(15)

When reaction is not at equilibrium; the following is obtained where, $w = C_{T1} + C_{T_2}$

$$=\frac{kwK_BP_BK_AC_A}{(1+K_BP_B)(1+K_AC_A)}$$
(16)

When the adsorption of CO₂ and epichlorohydrin is strong on catalyst surface, then $(1 + K_B p_B < < < K_B p_B)$, $(1 + K_A C_A < < < K_A C_A)$, then above equation is written as;

$$-r_A = kw \tag{17}$$

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Scheme 2. Possible mechanism of synthesis of cyclic carbonate.



Fig. 9. Plot of fractional conversion (X_{A}) of epichlorohydrin vs time at different temperatures.

This eqⁿ shows zero order kinetics and can be written in fractional conversion, (X_A) as;

$$\frac{dX_A}{dt} = \frac{kw}{C_{A_0}} \tag{18}$$

$$\frac{dX_A}{dt} = k_1 w \tag{19}$$

Where,

$$k_1 = \frac{k}{C_{A_0}} \tag{20}$$

Integrating above eqⁿ the following is obtained,

$$X_A = kt \tag{21}$$

The plot X_A vs time shows the straight line (Fig. 9) which means that the zero order kinetic model shown in Eq. (21) is correct.

Arrhenius plot was made from the slopes obtained in Fig. 9 and the activation energy of reaction was calculated as 15.14 kcal/mol (Fig. 10).

3.9. Substrate study

Under the optimized reaction conditions the catalyst was found to be applicable to various terminal epoxides to provide the corresponding cyclic carbonates in high yields and selectivity (Table 3). Furthermore, in the case of an internal epoxide (cyclohexene oxide) as the substrate (entry 3), a cyclic carbonate was obtained at lower yield even at longer reaction time (6 h), it may be due to steric hindrance as reported in previous literature [54,55]. The products were characterized by GC–MS, ¹HNMR, and ¹³CNMR (†ESI).

NMR data;

4-Chloro-1,3-dioxolan-2-one (entry 1): ¹H NMR (500 MHz, CDCl₃) δ 4.94 (m, 1H), 4.53 (t, 1H), 4.33 (dd, 1H), 3.67–4.02 (d, 2H); ¹³C NMR:



Fig. 10. Arrhenius plot for cycloaddition of CO2 to epichlorohydrin.

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Table 3

substrate scope for synthesis of cyclic carbonate using 0.75 (w/w) Li-MgO.



Reaction conditions: Epichlorohydrin 127 mmol; CO_2 pressure 3 MPa; catalyst loading 0.1 g/cm³; reaction temperature 130 °C; reaction time 4 h.

δ 44.1, 67.5, 73.5, 154.5.

4-Phenyl-1,3-dioxolan-2-one (entry 2): ¹H NMR (500 MHz, CDCl₃) δ 7.52–7.40 (m, 3H), 7.40–7.32 (m, 2H), 5.69 (dd, J = 8.5 and 8.0 Hz, 1H), 4.81 (dd, J = 8.5 and J = 8.5 Hz, 1H), 4.35 (dd, J = 8.5 and J = 8.0 Hz, 1H); ¹³CNMR: 70.9, 78.1, 126.2, 129.4, 130.2, 137.4, 155.2.

Hexahydrobenzo [d] [1,3] dioxol-2-one (entry 3):¹HNMR (500 MHz, CDCl₃) 4.65 (t, 1H, J = 3.6 Hz), 1.83–1.91 (m, 4H), 1.61–1.66 (m, 2H), 1.38–1.48 (m, 2H). ¹³C NMR δ = 155.8, 76.1, 26.2, 19.3.

4-Methyl-1,3-dioxolan-2-one (entry 4): ¹H NMR (500 MHz, CDCl₃) δ 4.94 (m, 1H), 4.53 (t, 1H), 4.08 (dd, 1H), 1.47 (d, 3H); ¹³C NMR δ 19.2, 70.5, 73.9, 155.4.

4-(hydroxymethyl)-1,3-dioxolan-2-one (entry 5): ¹H NMR (500 MHz, DMSO) δ 5.21 (m, 1H), 4.79–4.70 (m, J = 8.7, 6.0, 3.1 Hz, 1H), 4.45 (t, J = 8.4 Hz, 1H), 4.26 (t, 1H), 3.66–3.61 (m, 1H), 3.47 (dd, J = 12.7, 3.4 Hz, 1H). ¹³C NMR: 60.2, 66.1, 77.3, 155.1.

1,3-dioxolan-2-one (entry 6): ¹H NMR (500 MHz, DMSO) δ 4.44 (s, 4H).

4. Conclusions

In summary, Li-MgO catalyzed simple and cost-efficient protocol for the synthesis of cyclic carbonates was developed. For this reaction, we have studied the effect of different lithium loading on cyclization of epichlorohydrin and CO₂ to form cyclic carbonates. The synthesis of cyclic carbonates is 100% atom efficient method. Li-MgO has weak Lewis acidity due to Li⁺ and Mg²⁺ and strong basicity due to the structural defect in the structure formed by Li-impurity. It was found that 0.75 (w/w) Li-MgO was the best and reusable catalyst for cycloaddition of CO₂ to epichlorohydrin to synthesize 4-(chloromethyl)-1,3-dioxolan-2-one under solvent free conditions with excellent conversion (~98%) and selectivity (100%), at 130 °C and 3 MPa of CO₂ pressure. The catalyst showed structural stability and was reused for three cycles without loss of activity. The current synthesis protocol is 100% atom-efficient and thus was extended to a variety of substrates. Cycloaddition of CO₂ to epichlorohydrin follows the LHHW type of

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model with both species getting strongly adsorbed leading to zero order reaction, with an apparent activation energy 15.14 kcal/mol.

Acknowledgements

This work was performed within the collaborative project "Sustainable Catalytic Syntheses of Chemicals using Carbon Dioxide as Feedstock (GreenCatCO₂)" supported by Department of Science and Technology (DST), Government of India, and the Academy of Finland to Professors Ganapati D. Yadav and Riitta Keiski. Kalidas B. Rasal would like to thank the Academy of Finland (Project nos. 129173 (SUSE) and 140122 (GreenCatCO₂)) and the Finnish funding agency for technology and innovation, Tekes (Project no. 40313/09 (Fermet)) for financial support. Ganapati D. Yadav also thanks DST for J.C. Bose National Fellowship and received support from R.T. Mody Distinguished Professor Endowment.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.01.012.

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