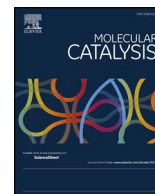




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# Solventless synthesis of cyclic carbonates by direct utilization of CO<sub>2</sub> using nanocrystalline lithium promoted magnesia

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## ABSTRACT

Cyclic carbonates are industrially important chemicals. In this work, an efficient synthesis of cyclic carbonate was achieved by cyclization of epoxide with CO<sub>2</sub> 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<sup>+</sup>) and magnesium (Mg<sup>2+</sup>) and acts as an active site for CO<sub>2</sub> 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<sub>2</sub> fixation into cyclic carbonate with excellent conversion (~98%) and selectivity (100%), at 130 °C and 3 MPa of CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> has a linear structure with zero dipole moment and is thermally and kinetically a stable molecule [7]. To overcome the stability of CO<sub>2</sub>, 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<sub>2</sub> and epoxides using different catalysts; for instance, phosphonium based ionic liquid supported on polymer nanoparticle [10], 2-pyridinemethanol [11], magnetically separable ZnBr<sub>2</sub>

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 CO<sub>2</sub> 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<sup>+</sup> (~76 pm) and magnesium Mg<sup>2+</sup> (~72 pm) in their oxide form [29] allow easy

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**Table 1**  
Literature review for synthesis of cyclic carbonates.

#	Catalyst	Epoxide mmol	CO <sub>2</sub> 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 <sub>5</sub> ]	10	1	120	3	97	99	0.011	[38]
7	Heteropolyacid-based ionic liquid@SiO <sub>2</sub>	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<sup>2+</sup> and Li<sup>+</sup> in the periclase structure of the catalyst [27,30]. The replacement of Mg<sup>2+</sup> with Li<sup>+</sup> creates oxygen vacancy or structural defect (F center) in order to maintain crystal neutrality. That F-center acts as active sites of catalyst for CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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.

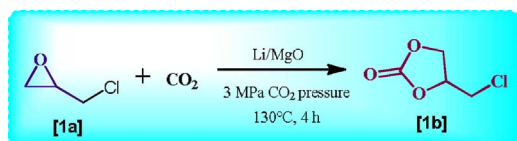
## 2. Experimental

### 2.1. Chemicals

The following chemicals were procured from the reputed firms (Merck, Sigma Aldrich, etc.) and used without further purification: Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, LiNO<sub>3</sub>, epichlorohydrin, propylene oxide, cyclohexene oxide, glycidol, styrene oxide, ethylene oxide etc.

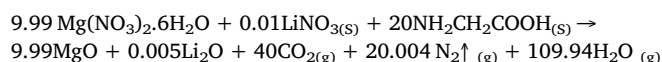
### 2.2. Li-MgO preparation

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(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Li(NO<sub>3</sub>) 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 high-temperature combustion allow the formation solid defects (F centers) due to the evolution of gases (mainly CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O). 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]:



### 2.3. Experimental procedure for cyclization of epichlorohydrin and CO<sub>2</sub>

Epichlorohydrin (**1a**) 127 mmol (10 mL) and catalyst 0.05 g/cm<sup>3</sup> (0.5 g) were taken in 50 mL autoclave (Amar Equipments, Mumbai, India) with pressure and temperature regulators. The reactor was flushed twice with CO<sub>2</sub> to remove air and temperature set at 130 °C; After reaching the temperature the reactor was charged with CO<sub>2</sub> 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<sub>2</sub> 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 place, 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° 2θ using Bruker AXS, D8 discover instrument (USA) with Cu-Kα (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 Li<sub>2</sub>CO<sub>3</sub> phase (JCPDS card # 22-1141) was observed at 0.5% of lithium loading (2θ = 33°). The increase in crystallinity was proportional to the lithium loading in Li-MgO.

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