The effects of mixed metal oxide catalysts on the synthesis of cyclic carbonates from epoxides under atmospheric CO_2 pressure

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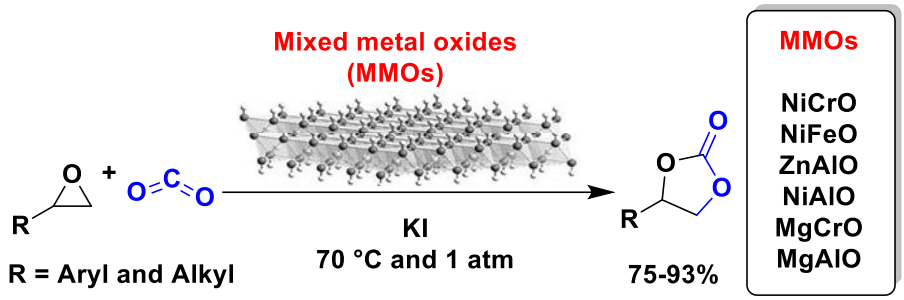
Abstract

One use of CO_2 as a starting material in organic transformations is in the synthesis of cyclic carbonates and polycarbonates. Due to the low reactivity of CO_2, this transformation must be carried out in the presence of an efficient catalyst. Although several catalytic systems have been developed in the last decade, reducing the CO_2 pressure at which the reaction is carried out remains one of the main challenges of the process. In this context, in the present work, we describe the catalytic activity of mixed metal oxides (MMOs) in the synthesis of cyclic carbonates from CO_2 (1 atm) and epoxides at 70 °C. The use of these materials as catalysts represents a great advantage since they are highly stable and economical and can be reused in several reaction cycles.

Keywords: Mixed metal oxides • layered double hydroxide • atmospheric pressure • epoxides• carbon dioxide

Graphical Abstract

Catalytic activity of mixed metal oxides (MMOs) in the synthesis of cyclic carbonates from CO_2 (1 atm) and epoxides at 70 °C.

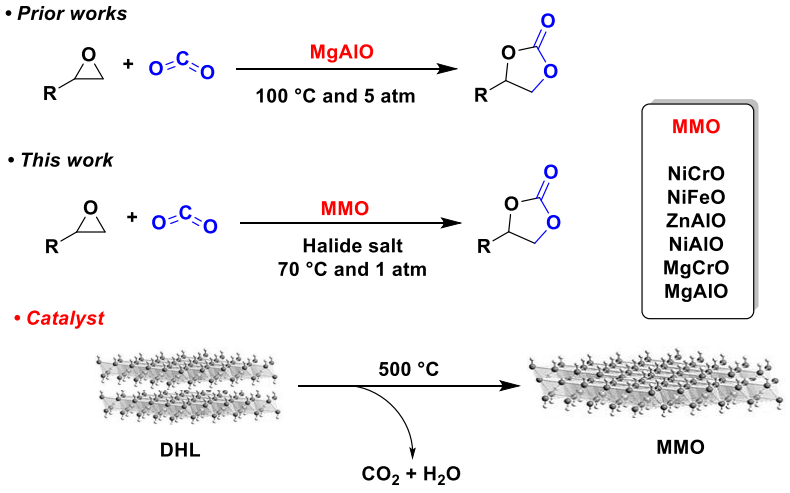


Introduction

Capturing and recycling of CO_2 are among the most important chemical and engineering challenges facing humankind.[1] CO_2 as a starting material is a thermodynamically and chemically stable molecule under standard conditions. However, these materials can react with other chemical feedstocks under certain reaction conditions (pressure, temperature, catalysis, etc.) to produce value-added commodity chemicals.[2] Thus, CO_2 is an ideal C1 building block for organic synthesis because it is inexpensive and abundant and can be considered a waste product.[3]

One of those value-added products obtained from CO_2 is cyclic carbonates, which can be used industrially as a polar aprotic solvent,[4] as an electrolyte for lithium-ion batteries,[5] and as intermediates in the manufacture of fine chemicals[6] and polymers.[7] Cyclic carbonates are mostly produced by the cycloaddition of CO2 to epoxides in the presence of a wide range of catalysts,[8] including hydrogen-bond catalysts,[9] ionic liquids,[10] quaternary ammonium salt,[11] organic polymers,[12] MOFs,[13] porous materials,[14] layered double hydroxide (LDH)[15] and metal-based catalysts.[16]

Considering that the use of mild reaction conditions remains the principal challenge, we propose the use of mixed metal oxides (MMOs) as catalysts in cycloaddition reactions, with the objective of being able to carry out the catalytic process under atmospheric CO_2 pressure and moderate temperature.[17]



Scheme 1. Synthesis of cyclic carbonate

MMOs are materials[18] that can be obtained by calcination at 500-600 °C from the corresponding LDH,[19] which is a brucite-type octahedral layer with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-x/n}\cdot mH_2O]^{x-}$, where the excess positive charge, originating from the M^{2+} to M^{3+} substitution, is compensated for by carbonate anions in the interlayer space. This structure is transformed into an MMO through dehydration, dihydroxylation and

decarbonization of the interlayer component, giving rise to a compact structure where the oxide ions form a coordination sphere around the metal ions.[20] From the point of view of catalysis, they are very efficient materials due to their porosity, relatively large specific surface area, reactive sites, and high thermal stability.[21] While the use of MMOs as catalysts in the synthesis of cyclic carbonates from CO_2 has been limited to the use of Mg-Al mixed metal oxides (100 °C and pressure 5 atm),[22] the use of other metals in MMOs has not been explored to date.

Results and Discussion

Material synthesis

The MMOs used in the present study were obtained by calcination of the corresponding LDH, which in turn were synthesized by the co-precipitation technique and microwave-hydrothermal crystallization. The structures of the DLHs were confirmed by X-ray diffraction. Figure 1a shows the diffractograms for LDH M^{2+}/M^{3+} (Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Al^{3+} and Cr^{3+}), in which LDH exhibited M^{2+}/M^{3+} reflections associated with the layered double hydroxide crystal structure. Planes can be observed at (0 0 3), (0 0 6), (0 1 2), (0 1 5), (0 1 8), (1 1 0) and (1 1 3). These values are the same as those described in the literature for these materials.[23] Then, the LDH was calcined at 550 °C for 6 hours, and the respective MMOs with a periclase-like structure were obtained. The plane reflections observed in the diffractograms at (1 1 1), (2 0 2) and (2 2 0) are typical of MMOs (Fig. 1b).[24]

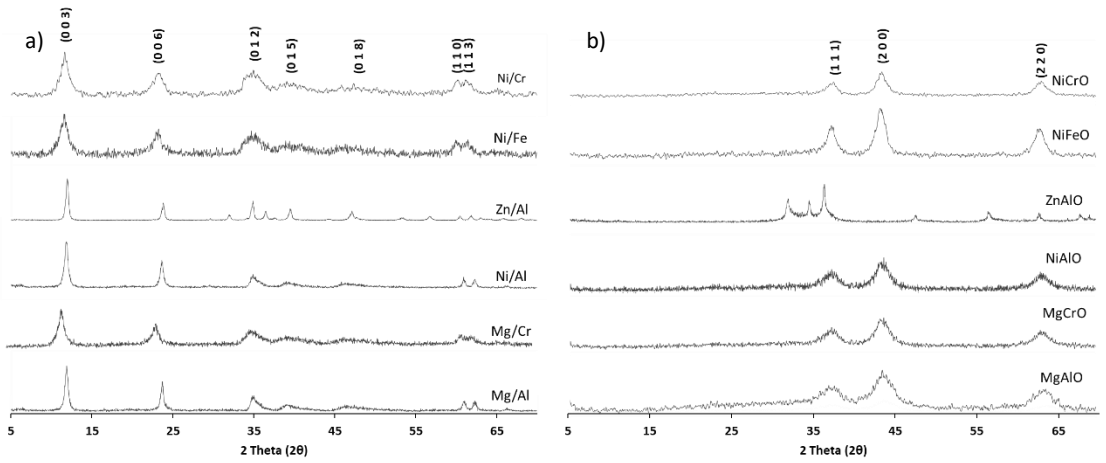


Fig. 1. X-ray diffraction patterns of a) LDH and b) MMO

The adsorption of N_2 (the BET method) was used to quantify the surface area and pore size of the materials (Table 1). The LDH samples exhibited lower porosity and a greater surface area than did the MMO samples.

Table 1. Nitrogen adsorption–desorption analysis parameters of the materials

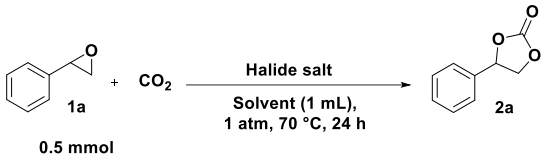
Entry	Material	Parameters		
		S_{BET} ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g$)$^-$	Pore size (Å)
	LDH			
1	Ni/Cr	97	0.28	36.6
2	Ni/Fe	60	0.3	196
3	Zn/Al	55	0.52	186
4	Ni/Al	70	0.19	92
5	Mg/Cr	96	0.22	77
6	Mg/Al	105	0.53	150
	MMO			
7	NiCrO	39	0.41	420
8	NiFeO	121	0.41	134
9	ZnAlO	34	0.25	149
10	NiAlO	154	0.75	150
11	MgCrO	290	0.916	55
12	MgAlO	222	0.74	177

Catalytic activity

To establish the optimal reaction conditions, we first focused on studying the effect of the solvent and halide salt on the reaction yield and in the absence of MMOs. Thus, the reaction of CO_2 with styrene oxide **1a** to give the corresponding cyclic carbonate **2a** was investigated. Tetrabutylammonium iodide (TBAI) and potassium iodide were used as the halide salts at concentrations of 10 and 100 mol%, respectively, and ethanol and acetonitrile were used as the solvents. Better yields were obtained with ethanol (Table 2, entries 2-5) than with acetonitrile (Table 2, entries 7 and 8). With no halide salt present, the reaction did not proceed with either solvent (Table 2, entries 1 and 6). With ethanol as the solvent and 10 mol% TBAI or KI, cyclic carbonates were obtained in good yields (Table 2, entries 2 and 4). The yield decreased when the reaction was carried out in acetonitrile and 10 mol% TBAI or KI (Table 2, entries 7 and 8). The maximum yield is achieved when the reaction is carried out with one equivalent of halide salt (Table 2, entries 3 and 5). The use of TBAI or KI is decisive for the opening of the epoxide and the formation of halohydrin anion, which is a key intermediate in the catalytic process as previously demonstrated.[25] The complete kinetics of the reactions are shown in the SI.

The next step of this work was to study the effect of LDH and MMO as catalysts in the catalytic process. As shown in Table 3, the highest yields were obtained when the reactions were carried out in the presence of KI. In contrast, the yields decrease notably in the absence of KI for both materials. In comparative terms, between LDH and MMO, we observed that the calcined materials were more efficient during the catalytic process, as indicated by the difference in MMO MgCrO and NiAlO, for which 93% and 90% conversion, respectively, were achieved after 24 hours of reaction (Table 3, entries 5 and 4). Figure 2 shows the reaction kinetics of the process catalysed by MgCrO and NiAlO. In both cases, the maximum yield is reached after 24 h of reaction.

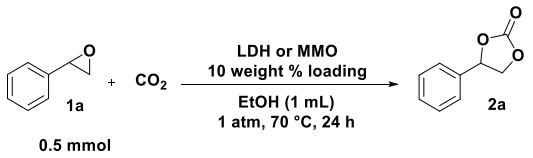
Table 2. Reaction conditions investigated for the synthesis of cyclic carbonates



Entry	Solvent	Halide	Halide salt loading/mol%	Conversion %[a]
1	EtOH	-	-	1
2	EtOH	TBAI	10	62
3	EtOH	TBAI	100	75
4	EtOH	KI	10	68
5	EtOH	KI	100	76
6	MeCN	-	-	0
7	MeCN	TBAI	10	8
8	MeCN	KI	10	25

[a]Conversions relative to the epoxide starting material calculated by GC relative to the biphenyl internal standard.

Table 3. Synthesis of cyclic carbonate **2a** in presence of LDH or MMO



Entry	**LDH**	**2a** conversion %[a]		**MMO**	**2a** conversion %[a]	
		No KI	KI[b]		No KI	KI[b]
1	Ni/Cr	20	78	NiCrO	35	86
2	Ni/Fe	3	75	NiFeO	14	80
3	Zn/Al	8	76	ZnAlO	16	82
4	Ni/Al	42	79	NiAlO	51	90
5	Mg/Cr	53	81	MgCrO	61	93
6	Mg/Al	5	69	MgAlO	5	82

[a]Conversions relative to the epoxide starting material calculated by GC relative to the biphenyl internal standard. [b] 10% mmol.

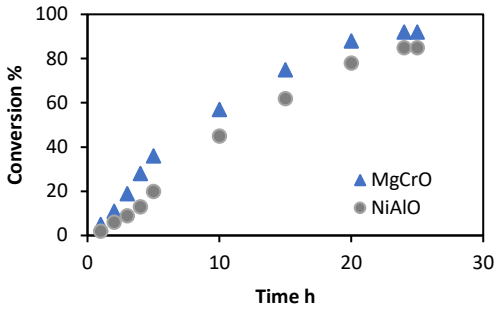
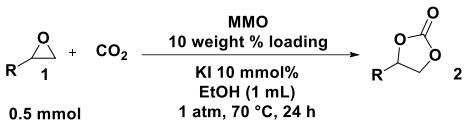
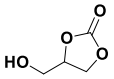


Fig. 2. Reaction kinetics to obtain **2a** in the presence of MgCrO and NiAlO

Table 4. Scope of the MMO-catalysed cycloaddition reaction

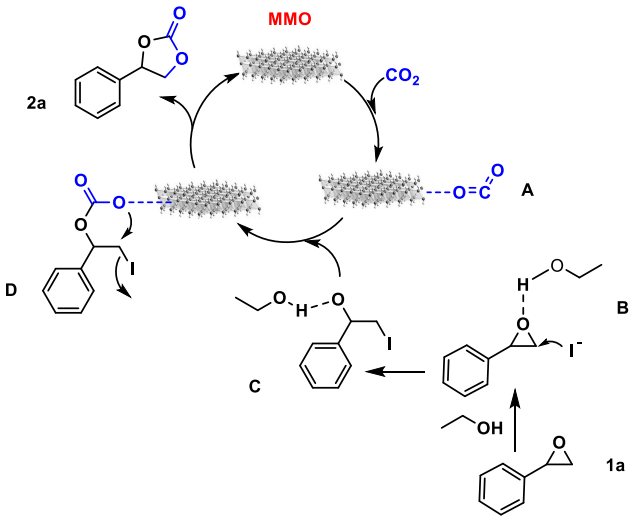


Entry	MMO	Cyclic carbonate and yields (%)[a]			
		 2b	 2c	 2d	 2e
1	NiCrO	85	82	84	85
2	NiFeO	80	78	75	76
3	ZnAlO	85	81	80	82
4	NiAlO	88	91	90	90
5	MgCrO	92	90	91	93
6	MgAlO	82	80	78	80

[a]Yields of the isolated product after chromatographic purification

With these results in hand, we focused on studying the reaction trend with other epoxides. Table 4 shows the results of the CO_2 cycloaddition reactions to the epoxides corresponding to obtain cyclic carbonates **2b**-**2d**. The six different MMOs were evaluated, confirming that MgCrO and NiAlO are the best catalysts for achieving high yields (Table 4).

Scheme 2 shows a proposed mechanism for the cycloaddition reaction using ethanol as the solvent and MMO and KI as catalysts. The reaction begins with the activation of CO_2 by MMO to give rise to the formation of intermediate **A**. In parallel, ethanol acts as a Brønsted acid, leading to the activation of the epoxide via intermediate **B**. Then, opening the ring at **B** by nucleophilic attack on the less sterically hindered carbon using IK produces **C**.[25,26] The alkylcarbonate **D** is formed after a reaction between **B** and **C**. Finally, the intermediate **D** is the direct precursor of cyclic carbonate **2a**.



Scheme 2. Proposed mechanism for the cycloaddition of CO_2 to epoxides using MMO and KI as catalysts and ethanol as the solvent.

Reuse of the Cu-Al mixed oxide

To evaluate the recyclability of MgCrO, two reactivation processes were applied to the material. In the first one, after separating the material from the reaction mixture, the material was dried at 100 °C for 24 h. The second process included calcination at 500 °C for 5 h in an O_2 atmosphere. After the first reuse, we observed that the catalyst that was reactivated at a high temperature (500 °C) retained its activity, so the reactions still proceeded in high yield (90%). MgCrO can be recycled at least three times without significant losses in catalytic activity (Fig. 3). This result contrasts with that observed when the MMO was only dry at 100 °C, where the yield decreased significantly as a consequence of the loss of catalytic activity of MgCrO. This significant difference is probably due to the presence of organic material at the catalytic sites, which is eliminated after calcination at 500 °C to recover the catalytic properties of the MMO (Fig. 3, red column, yield 87%).

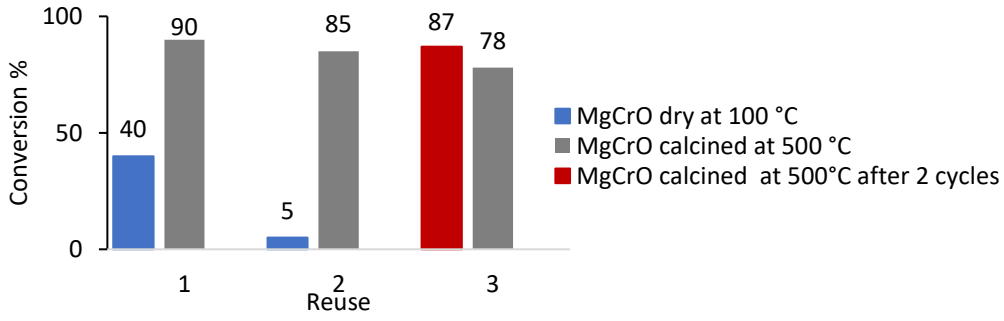


Fig. 3. Reuse of Cu-Al mixed oxide after reactions **1**, **2a** and **3a**.

Conclusions

In conclusion, our experimental investigation of the reaction of CO2 with epoxides to give the corresponding cyclic carbonate showed that mixed metal oxides can be efficient catalysts in the overall process. We demonstrated that MgCrO and NiAlO were the most active MMOs and that the presence of KI or TBAI as catalysts and ethanol as the solvent were decisive for achieving high yields of cycloaddition under atmospheric pressure at 70 °C.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thanks British Council, the Newton Fund and CONACyT for a project grant (Institutional Links FONCICYT-275694). B.N.N. and J.A.M.S are grateful to the Royal Society (UK) for the International Alumni Grant.

Author contributions

J.A.M.S and B.N.N. conceived the project and acquired the funds. B.I.V.A, R.L.N, J.A.M.S and B.N.N. designed the experiments. B.I.V.A, R.L.N., G.E.N.S. and L.L.R conducted the experimental work. J.A.M.S and B.N.N. coordinated the whole project. B.I.V.A, R.L.N, J.A.M.S and B.N.N. wrote the manuscript. All the authors contributed to the discussions.

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