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Effects of Mixed Metal Oxide Catalysts on the Synthesis of Cyclic Carbonates from Epoxides under Atmospheric CO_2 Pressure

Blanca Ivonne Vergara-Arenas, Rachel L. Nicholls, Guillermo E. Negrón-Silva, Leticia Lomas-Romero, José Antonio Morales-Sern,* and Bao N. Nguyen*

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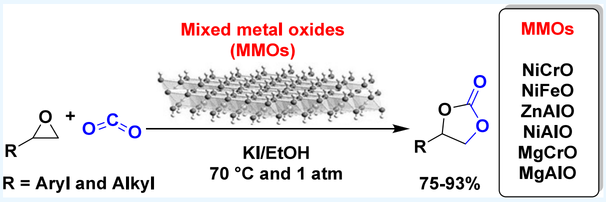
ABSTRACT: One use of CO_2 as a starting material in organic transformations is in the synthesis of cyclic carbonates and polycarbonates. Due to the low reactivity of CO_2, this transformation must be carried out in the presence of an efficient catalyst. Although several catalytic systems have been developed in the past 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 in the synthesis of cyclic carbonates from CO_2 (1 atm) and epoxides at 70 °C. Using these materials as catalysts represents significant benefits since they are very stable, cost-effective, and can be reused in several reaction cycles.



1. INTRODUCTION

High CO_2 emissions from anthropogenic activities directly impact global warming and climate change.[1] The socioeconomic challenge of sustaining current economic growth while avoiding global climate disruption remains unresolved.[2−5] One of the main strategies to reduce CO_2 emissions and stabilize its concentration in the atmosphere is carbon capture and storage (CCS).[6] However, simply capturing and storing CO_2 only postpones the problem, while reducing our supply of carbon feedstock. An alternative is carbon capture and utilization (CCU),[7] which treats CO_2 as a valuable feedstock. CO_2, as a starting material, is a thermodynamically and chemically stable molecule under standard conditions, but it can react with other chemical feedstocks under specific conditions (pressure, temperature, catalysis, etc.) to produce fuels (methane,[8−11] methanol,[12−15] and ethanol[16,17]), polymers,[18,19] and value-added commodity chemicals.[20]

From an organic synthesis perspective, CO_2 is an ideal, inexpensive, and abundant one-carbon building block (C1)[21−24] for producing formic acid, acetic acid, higher alcohols, salicylic acid, urea, carbamates, carbonates, polycarbonates, and polycarbamates. Among these compounds, cyclic carbonates stand out due to their commercial value,[25] making them an important and challenging industrial synthetic target.[26] The growth of the global cyclic carbonates market is driven by the diversification of their applications, including solvents,[24−29] electrolytes for lithium-ion batteries,[30−32] lubricants,[33] plasticizers,[34] surface coatings,[35] cleaners,[36] and intermediates in the production of fine chemicals[37,38] and polymers.[39−41]

Cyclic carbonates are mostly produced by the cycloaddition of CO_2 to epoxides in the presence of a wide range of catalysts,[42] including hydrogen-bond catalysts,[43−48] ionic liquids,[49−51] quaternary ammonium salt,[52−54] organic polymers,[55−58] MOFs,[59−62] porous materials,[63−67] layered double hydroxide (LDH),[68−71] and metal-based catalysts.[72,73]

Considering that the use of mild reactions conditions one of principal challenges in the synthesis of cyclic carbonates,[74] we propose in this study the use of mixed metal oxides (MMOs) as catalysts in cycloaddition reactions (Scheme 1). The aim is to carry out the catalytic process under atmospheric CO_2 pressure and moderate temperature.[75−78] MMOs are materials[79−81] that can be obtained by calcination at 500−600 °C from the corresponding LDH,[82−87] which is a brucite-type octahedral layer with the general formula $[\mathrm{M}^{2+}{}_{1-x}\mathrm{M}^{3+}{}_{x}(\mathrm{OH})_2]^{x+}[{}^{\mathrm{A}n-x/n}m\mathrm{H_2O}]^{x-}$, 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. This results in a compact structure where the oxide ions form a coordination sphere around the metal ions.[88−90] From a catalytic perspective, MMOs are very efficient materials due to their porosity, relatively large specific surface area, reactive sites, and high thermal stability.[91−97] Meanwhile, the use of MMOs as catalysts in the synthesis of cyclic carbonates from CO_2 has been limited to the use of

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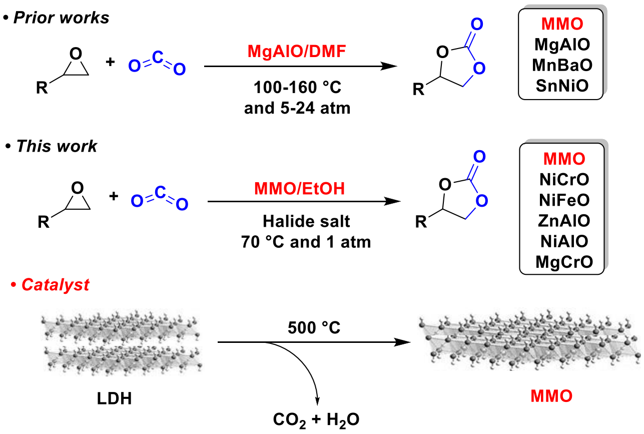
Scheme 1. Synthesis of Cyclic Carbonates



Mg–Al (100 °C and pressure 5 atm)[98] and MnBaO and SnNiO (160 °C and pressure 24.6 atm)[99] mixed metal oxides. The use of other metals in MMOs has not been explored to date (Scheme 1).

2. RESULTS AND DISCUSSION

2.1. Material Synthesis. The MMOs used in this study were obtained by calcination of the corresponding LDH, which were synthesized by the coprecipitation technique and microwave-hydrothermal crystallization. The structures of the LDHs were confirmed by X-ray diffraction. Figure 1a shows the diffractograms for LDH M^{2+}/M^{3+} (Mg^{2+}, Ni^{2+} and Zn^{2+}/Fe^{3+}, 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.[83,100,101] Then, the LDH was calcined at 550 °C for 6 h to obtain the respective MMOs with a periclase-like structure. The plane reflections observed in the diffractograms at (1 1 1), (2 0 2), and (2 2 0) are typical of MMOs (Figure 1b).[102−104]

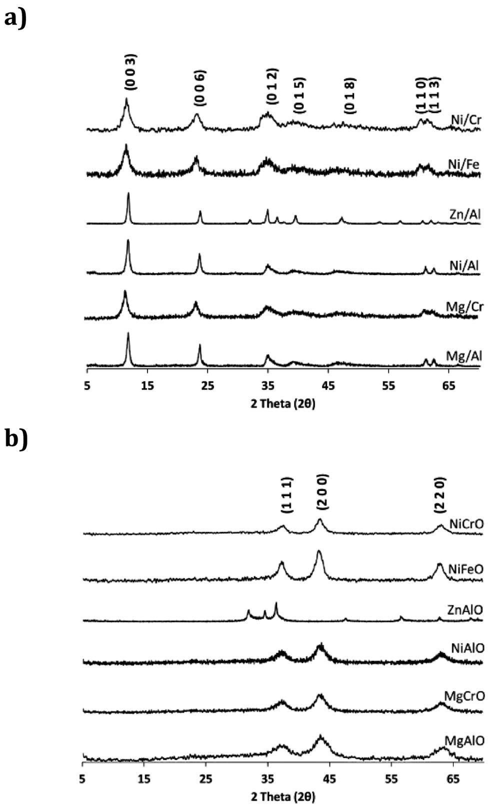


Figure 1. XRD patterns of (a) LDH and (b) MMO.

The adsorption of N_2 (using the BET method)[85] was employed to quantify the specific surface area (SBET) and pore size of the materials (Table 1). The LDH samples exhibited lower porosity and a greater surface area than did the MMO samples.

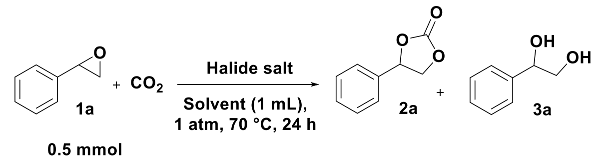
Table 1. Nitrogen Adsorption−Desorption Analysis Parameters of the Materials

entry	material	SBET ($m^2 \cdot g^{-1}$)	pore volume ($cm^3 \cdot g^{-1}$)	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

2.2. Catalytic Activity. To establish the optimal reaction conditions, we first focused on studying the effect of the solvent and halide salt on the reaction conversion 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 KI were used as the halide salts at concentrations of 1 and 100 mol %, with ethanol and acetonitrile as the solvents. Compared with acetonitrile (Table 2, entries 2–8), better conversions were obtained with ethanol (Table 2, entries 10 and 11). In the absence of halide salt, the reaction did not proceed with either solvent (Table 2, entries 1 and 9). With ethanol as the solvent and 10 mol % TBAI or KI, cyclic carbonates were obtained in good conversion (Table 2, entries 2 and 7). The conversion decreased when the reaction was carried out in ethanol and 1–7.5 mol % KI (Table 2, entries 4–6). Maximum conversion is achieved when the reaction is carried out with 1 equiv of halide salt (Table 2, entries 3 and 8). 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.[105−107] In all reactions, phenyl-1,2-ethanediol is the main side product (Table 2). Figure 2 and Figures S7–S14 (Supporting Information) show the complete kinetics of all reactions in ethanol and acetonitrile, as analyzed by gas chromatography (GC).

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 conversions were achieved when the reactions were performed in the presence of KI. In contrast, conversions decreased significantly in the absence of KI for

Table 2. Reaction Conditions Investigated for the Synthesis of Cyclic Carbonates[a]



				conversion %[b]		
entry	solvent	halide	halide salt loading (mol %)	1a	2a	3a
1	EtOH			95	1	4
2	EtOH	TBAI	10	35	62	3
3	EtOH	TBAI	100	23	75	2
4	EtOH	KI	1	69	30	1
5	EtOH	KI	5	53	45	2
6	EtOH	KI	7.5[c]	37	60	3
7	EtOH	KI	10	29	68	3
8	EtOH	KI	100	21	76	3
9	MeCN			95	0	2
10	MeCN	TBAI	10	87	8	3
11	MeCN	KI	10	72	25	1

[a]Reaction conditions: epoxide **1a** (1 mmol), halide salt (0.01 or 1 mmol), solvent (1 mL), CO_2 (1 atm), 24 h and 70 °C. [b]Conversions relative to the epoxide starting material calculated by GC relative to the biphenyl internal standard. [c]7.5 mmol % is equivalent to 10% weight loading.

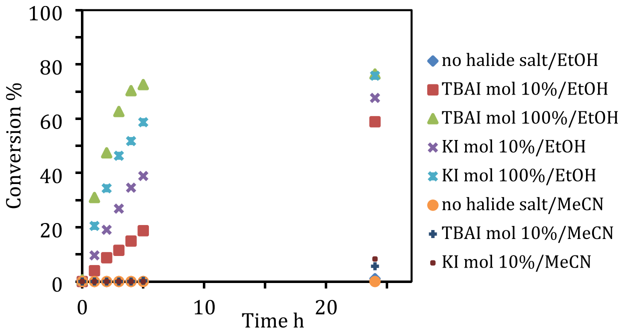
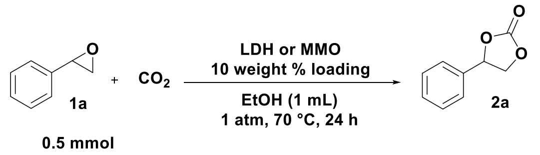


Figure 2. Kinetics of the reaction analyzed by GC.

Table 3. Synthesis of Cyclic Carbonate 2a in the Presence of LDH or MMO[a]



		2a conversion %[b]			2a conversion %[b]	
entry	LDH	KI 0%	KI 10%	MMO	KI 0%	KI 10%
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	15	82

[a]Reaction conditions: epoxide **1a** (1 mmol), LDH or MMO (weight 10% loading), KI (0.1), EtOH (1 mL), CO_2 (1 atm), 24 h and 70 °C. [b]Conversions relative to the epoxide starting material calculated by GC relative to the biphenyl internal standard.

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, which achieved 93 and 90% conversion, respectively, after 24 h of reaction (Table 3, entries 5 and 4). Figure 3 shows the reaction kinetics of the process catalyzed by MgCrO and NiAlO. In both cases, the maximum conversion is reached after 24 h of reaction.

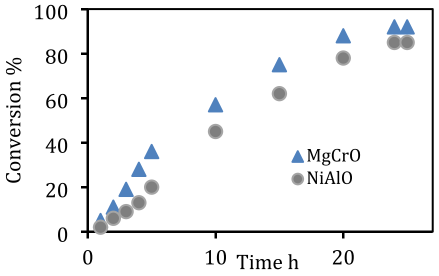


Figure 3. Reaction kinetics to obtain **2a** in the presence of MgCrO and NiAlO.

The efficiency of the MgCrO catalysts is compared with results previously in the literature for the synthesis of **2a** in the presence of others MMOs as catalysts.[98,99] As shown in Table 4, similar conversions were obtained when the reaction was carried out in the presence of MgAlO,[98] MnBaO, or SnNiO.[99] However, the main differences lie in the pressure and temperature at which the cycloaddition reaction takes place. In this case, we achieved a high conversion at atmospheric pressure, thus demonstrating that our catalytic system is efficient under mild reaction conditions.

Table 4. Comparison in the Efficiency of the MgCrO Catalysts and Previous MMOs Used in the CO_2 Cycloaddition to Styrene Oxide 1a

	MMOs as catalyst			
parameter	MgCrO	MgAlO[a]	MnBaO[b]	SnNiO[b]
cocatalyst	KI			
solvent	EtOH	DMF	DMF	DMF
pressure (atm)	1	5	24.6	24.6
temperature (°C)	70	100	160	160
conversion (%)	93	92	90	87
reference	this work	[75]	[76]	[76]

[a]Synthesized from Mg/Al LDH.[98] [b]Synthesized by the coprecipitation method.[99]

Table 5 shows a comparison of the catalytic activity based on the turnover number (TON) and turnover frequency

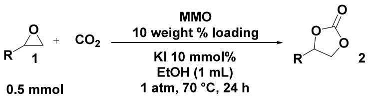
Table 5. Comparison of Catalytic Activity of Selected Heterogenous Catalysts for the Reaction of CO_2 with Styrene Oxide 1a under Mild Conditions

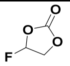
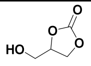
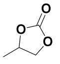
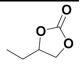
catalyst	CO_2 (atm)	T (°C)	TON	TOF	ref
LDH Mg/Cr	1	70	69.3	2.89	this work
MMO MgCrO	1	70	13.4	0.56	this work
polyurethane PU-BTP	1	60	5.2	0.60	[108]
polyurethane SG-Au-BPT	1	60	10.0	1.10	[108]
MOF Eu(BTB)(phen)	1	70	27.9	2.30	[109]

(TOF) of the MgCrO catalysts and other reported heterogeneous catalysts. For this comparison, we selected heterogeneous catalysts that were used under mild reaction conditions (CO_2 1 atm and 70 °C), similar to those employed in the present work. The values obtained for our catalyst were comparable to those obtained with polyurethane base catalysts PU-BTP and SG-Au-BPT,[108] as well as those obtained when the reaction is performed in the presence of an Eu-MOF as a catalyst.[109] TON and TOF for all catalysts, including library and recycled materials, are shown in Tables S3−S5 (Supporting Information).

With these results in hand, we focused on studying the reaction trend with other epoxides. Table 6 shows the results of the cycloaddition reactions of CO_2 to the epoxides corresponding to cyclic carbonates **2b**−**2d**. The six different MMOs were evaluated, confirming that MgCrO and NiAlO are the most effective catalysts for achieving high yields (Table 6).

Table 6. Scope of the MMO-Catalyzed Cycloaddition Reaction[a]



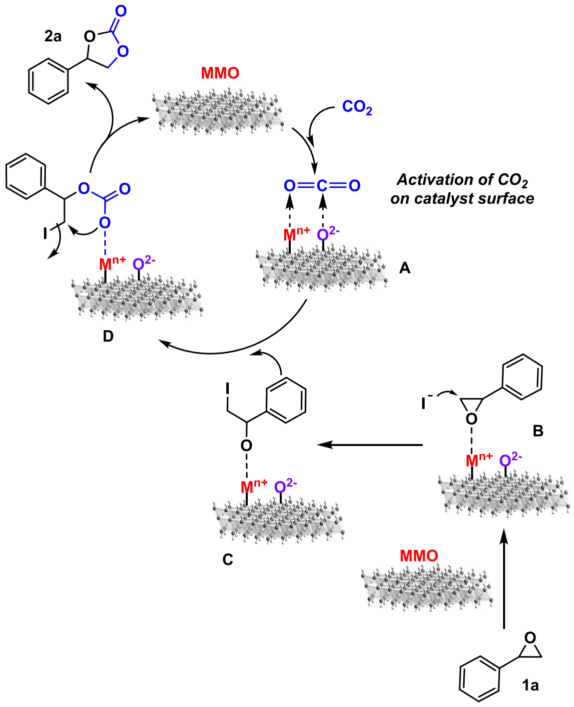
Entry	MMO	Cyclic carbonate and yields (%)[b]			
		 2b	 2c	 2d	 2e
1	NiCrO	85	82	84	85
2	NiFeO	80	78	75	76
	ZnAlO	85	81	80	82
4	NiAlO	88	91	90	90
5	MgCrO	92	90	91	93
6	MgAlO	82	80	78	80

[a]Reaction conditions: epoxide **1** (1 mmol), MMO (weight 10% loading), KI (0.1), EtOH (1 mL), CO_2 (1 atm), 24 h and 70 °C. [b]Yields of the isolated product after chromatographic purification.

Scheme 2 shows a proposed mechanism for the cycloaddition reaction using MMO and KI as catalysts. The reaction begins with the activation of CO_2 on the MMO surface (acid−base sites)[110] by the metals,[111] leading to the formation of intermediate **A**. Meanwhile, metals on the MMO surface act as Lewis acid sites, facilitating the activation of epoxide **1a** via intermediate **B**. Subsequently, the ring of intermediate **B** is opened by a nucleophilic attack on the less sterically hindered carbon by KI, producing intermediate **C**.[101−107,112] Alkylcarbonate **D** is formed after a reaction between **B** and **C**. Finally, intermediate **D** is the direct precursor of cyclic carbonate **2a**.

2.3. Reuse of the MgCrO-Mixed Oxide. To evaluate the recyclability of MgCrO in the synthesis of **2a**, two reactivation processes were applied to the material. In the first process, after separation of 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, with the reactions still proceeding with a high yield (**2a** 90%). MgCrO can be recycled at least three times without significant losses in the catalytic activity (Figure 4). This result contrasts with that observed when the MMO was only dry at 100 °C, where the conversion decreased significantly due to 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 (Figure 4, red column, yield 87%).

Scheme 2. Proposed Mechanism for the Cycloaddition of CO_2 and Epoxides Employing MMO and KI as Catalysts



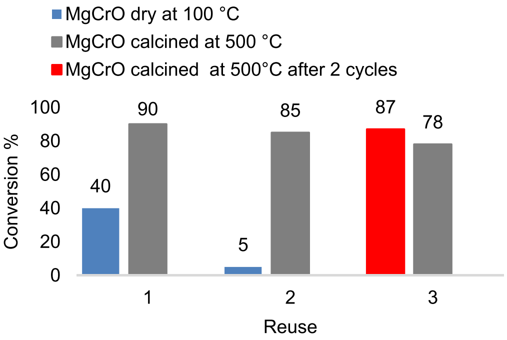


Figure 4. Reuse of MgCrO in the catalytic reaction to obtain **2a**. The catalyst was dried or calcined after each use.

To confirm the homogeneity of the catalyst in the reuse reactions, the structures of materials were verified by XRD before use. Figure 5 shows the plane reflections observed in the diffractograms at (1 1 1), (2 0 2), and (2 2 0), which are the same as the original catalyst.

Furthermore, to confirm the structure of the catalyst after use, we compared the original catalyst with the catalyst before reuse using FTIR, SEM, and EDX (Figure 6). The FTIR spectra of original catalyst and catalyst before reuse show bands in the wavenumber range of 500−800 cm^{-1} corresponding to the vibration of metal oxygen bonds in both materials. The absence of the band at 1321 and 1397 cm-1 (CO_3^{2-}) confirms that the calcination proceeded favorably (Figure 6a).

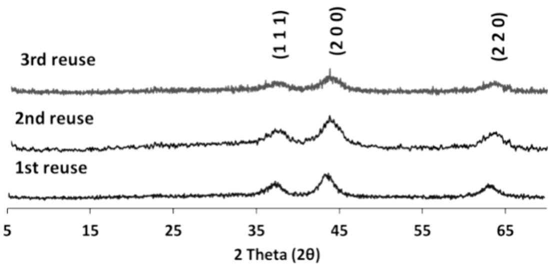
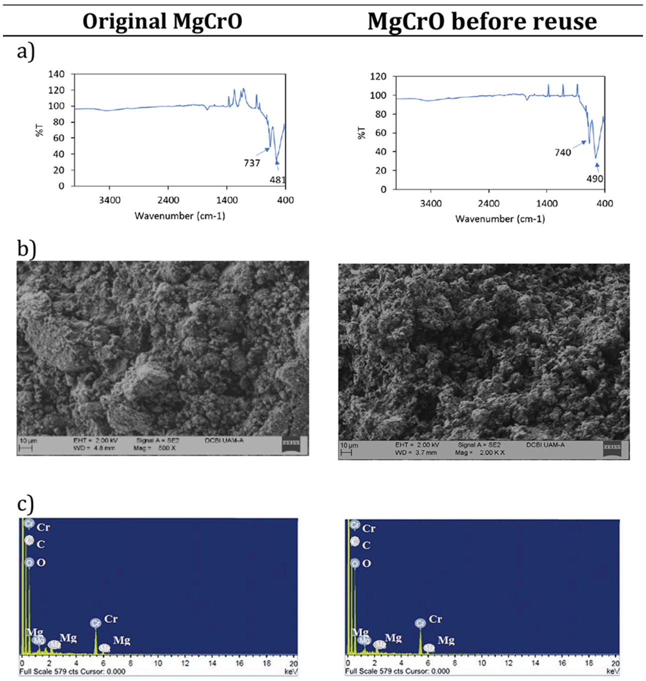


Figure 5. XRD patterns for MgCrO after reactivation at 500 °C.



Element	Weight%
C	0.21
O	49.98
Cr	12.02
Mg	37.79
Total	100.00

Element	Weight%
C	0.14
O	50.10
Cr	11.99
Mg	37.77
Total	100.00

Figure 6. Comparation of the origin catalyst and catalyst before reuse. (a) FTIR, (b) SEM, and (c) EDX.

The SEM images of both materials showed similar agglomerates (Figure 6b). Finally, SEM-EDX analysis revealed the presence of Mg and Cr in both catalysts (Figure 6c). These results confirm that the material remains homogeneous after being used, recovered, and calcined at 500 °C.

3. CONCLUSIONS

In conclusion, our experimental investigation of the reaction of CO_2 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 was decisive for achieving high yields of cycloaddition under atmospheric pressure at 70 °C.

4. EXPERIMENTAL SECTION

4.1. General Information. Styrene oxide, propylene oxide, 1,2-epoxybutane, glycidol, potassium iodide, sodium carbonate, sodium hydroxide, magnesium nitrate hexahydrate, aluminum nitrate nonahydrate, zinc nitrate hexahydrate, chromium nitrate nonahydrate, nickel nitrate hexahydrate, and iron nitrate nonahydrate were purchased from Sigma-Aldrich. Anhydrous solvents were obtained from a Dow-Grubbs type system (Pure Solv MD, Innovative Technology) and/or Sigma-Aldrich. Flash chromatography was performed using silica gel (40−60 μm) in glass columns. The NMR spectra were obtained using a Bruker Ascend-400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in hertz (Hz). GC/MS data were collected with the Agilent HP6890 series GC system, using an Agilent HP5973 mass selective detector operating in EI mode and an Agilent HP-5MS column (30 m × 0.32 mm × 0.25 μm). Gas chromatography was conducted using an Agilent HP 6890 Series Gas Chromatography system equipped with an FID detector and was employed an Agilent DB-624 column (30 m × 250 μm × 1.4 μm).

Powder X-ray diffraction (XRD) was carried out using a Stoe Stadi-P Cu diffractometer with Cu Kα1 (using 40 kV and 30 mA). The chemical composition of MMOs was recorded using SEM-EDX images, and emission spectra were obtained with a Zeiss SUPRA 55 VP scanning electron microscope at 10 kV, employing a 300× secondary electron detector. The pore sizes, specific pore volume, and specific surface area of the LDH and MMO materials were determined using ASAP 2020 adsorption equipment. The nitrogen adsorption−desorption isotherm was carried out at liquid nitrogen temperature. Specific surface areas were measured using the multipoint Brunauer−Emmett−Teller (BET) method. The corresponding specific pore volume and pore sizes were determined using the BJH method.[62]

4.2. Synthesis of Layered Double Hydroxide. Two solutions are prepared: solution 1: metal(II) nitrate (0.1 mol, 3 equiv) and metal(III) nitrate (0.03 mol, 1 equiv) were dissolved in H_2O (45 mL). Solution 2: sodium carbonate (0.09 mol) and sodium hydroxide (0.35 mol) were dissolved in H_2O (70 mL). Solution 2 was added dropwise (over 2 h) to solution 1, forming a gel. The reaction mixture was heated at 60 °C for 24 h. The suspension was vacuum filtrated and washed with hot H_2O at 70 °C. The solid was dried in an oven for 24 h at 100 °C.[83,113]

4.3. Synthesis of Mixed Metal Oxides. The calcined materials were obtained by heating the as-synthesized LDHs at 550 °C in a tubular furnace under N_2 flow for 6 h, with a heating rate of 120 °C per hour. Black solids stable in air were obtained and characterized by XRD.[114]

4.4. Catalytic Experiments. In a typical experiment, a 50 mL oven-dried Schlenk tube fitted with a stirrer bar and a septum was evacuated and backfilled with CO_2. KI (10 mmol %), biphenyl (0.1 mmol), styrene oxide **1a** (1 mmol), and 2 mL of solvent and/or catalyst were added while stirring at 70 °C for 24 h under 1 atm pressure. The progress of the reaction was analyzed hourly by GC. The MMO was then removed by centrifugation and washed with CH_2Cl_2 (5 × 2 mL). The combined organic extracts were evaporated, yielding the corresponding reaction mixture.

4.5. GC Analysis. GC samples were analyzed using an Agilent HP 6890 Series GC system with an FID detector and an Agilent DB-624 column (30 m × 250 μm × 1.4 μm). The temperature method was carried out as follows: for 1 min, it was kept at 50 °C, ramping up to 250 °C at a rate of 20 °C/min, and hold at 250 °C for 15.5 min, with a gas flow rate of 3.0 mL/min at 10 psi. Calibration curves were carried out to determine product yields using commercial samples with biphenyl as an internal standard (IS). Standard solutions of styrene oxide and biphenyl in acetonitrile were prepared at concentrations of 0.05−0.75 M, and their response was measured in terms of peak area (Table S1 and Figures S2 and S3).

4.6. Characterization Data. *4.6.1. 2a.* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41−7.45 (m, ArH, 3H), 7.34−7.37 (m, ArH, 2H), 5.67 (t, *J* = 7.9 Hz, 1H), 4.79 (dd, *J* = 8.1, 8.6 Hz, 1H), 4.33 (dd, *J* = 7.8, 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.7 ($O-CO_2$), 135.8 (Cipso), 129.7 (2×ArCH), 129.2 (ArCH), 125.8 (2×ArCH), 77.9 (CH), 71.1 ($O-CH_2$).[115]

4.6.2. 2b. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.40 (ddd, J_{HH} = 0.88, 4.08 Hz, J_{HF} = 65.8 Hz, 1H, CHF), 4.65 (ddd, J_{HH} = 4.0, 10.8 Hz, J_{FH} = 33.0 Hz, 1H), 4.56 (ddd, J_{HH} = 0.88, 10.8 Hz, J_{FH} = 21.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.2 ($O-CO_2$), 104.5 (d, CHF), 70.5 (d, CH_2). ^{19}F NMR ($CDCl_3$, 376 MHz): δ − 44.50 (ddd, *J* = 21.0, 33.0, 65 Hz).[116]

4.6.3. 2c. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.82 (dqu, *J* = 3.2, 6.64, 9.9 Hz, 1H), 4.54(dd, *J* = 8.36, 16.72 Hz, 1H), 4.48 (dd, *J* = 2.64, 8.32 Hz, 1H), 4.01 (ddd, *J* = 3.0, 5.7, 18.5 Hz, 1H), 3.74 (ddd, *J* = 3.4, 7.0, 19.8 Hz, 1H), 2.53 (t, *J* = 5.4, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.7 ($O-CO_2$), 76.6 (CH), 66.6 ($O-CH_2$), 61.7 (CH_2).[117]

4.6.4. 2d. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.77 (sextet, *J* = 1.04, 6.24, 13.6, 19.88 Hz, 1H), 4.47 (t, *J* = 7.72 Hz, 1H), 3.93 (dd, *J* = 7.2, 8.48 Hz, 1H), 1.37 (d, *J* = 6.28 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.2 ($O-CO_2$), 73.7 (CH), 70.7 ($O-CH_2$), 19.2 (CH_3).[118]

4.6.5. 2e. ^{1}H NMR (CDCl3, 400 MHz): δ 4.60 (tqu, *J* = 1.0, 5.7, 13.7 Hz, 1H), 4.45 (t, *J* = 7.9 Hz, 1H), 4.00 (dd, *J* = 6.9, 8.4 Hz, 1H), 1.68 (qudd, *J* = 1.84, 7.4, 6.8, 14.1, 21.2 Hz, 2H, CH_2), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.2 ($O-CO_2$), 78.1 (O−CH), 69.1 ($O-CH_2$), 26.7 (CH_2), 8.3 (CH_3).[115]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c07538.

> Synthesis of MMOs; full characterization of MMOs, standard cycloaddition reaction procedure; GC analysis; kinetic studies, MMO efficiency evaluation; reuse of catalysts on the reaction; characterization of cyclic carbonates, NMR spectrum (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

José Antonio Morales-Sern − *Centro de Investigaciones Científicas, Instituto de Química Aplicada, Universidad del Papaloapan, Tuxtepec, Oaxaca 68301, México;* orcid.org/0000-0002-5204-772X; Email: joseantonio.moralesserna@gmail.com

Bao N. Nguyen − *Institute of Process Research and Development, School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.;* orcid.org/0000-0002-0254-025X; Email: b.nguyen@leeds.ac.uk

Authors

Blanca Ivonne Vergara-Arenas − *Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Ciudad de México C. P. 09340, México*

Rachel L. Nicholls − *Institute of Process Research and Development, School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.*

Guillermo E. Negrón-Silva − *Departamento de Ciencias Básicas, Universidad Autónoma Metropolitana-Azcapotzalco, Ciudad de México C. P. 02200, México*

Leticia Lomas-Romero − *Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Ciudad de México C. P. 09340, México*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.4c07538

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.

Notes

The authors declare no competing financial interest.

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