MIL-101(Cr) for CO$_2$ Conversion into Cyclic Carbonates, Under Solvent and Co-Catalyst Free Mild Reaction Conditions

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Abstract: Mild reaction conditions (nearly room temperature and atmospheric CO$_2$ pressure) for the cycloaddition of CO$_2$ with epoxides to produce cyclic carbonates were investigated applying MIL-101(Cr) as a catalyst. The MIL-101 catalyst contains strong acid sites, which promote the ring-opening of the epoxide substrate. Moreover, the high surface area, enabling the adsorption of more CO$_2$ (substrate), combined with a large pore size of the catalyst is essential for the catalytic performance. Additionally, epoxide substrates bearing electron-withdrawing substituents or having a low boiling point demonstrated an excellent conversion towards the cyclic carbonates. MIL-101(Cr) for the cycloaddition of carbon dioxide with epoxides is demonstrated to be a robust and stable catalyst able to be re-used at least five times without loss in activity.

1. Introduction

Nowadays, only 40% of the total amount of carbon dioxide (CO$_2$) generated from human activities is being absorbed by the natural carbon exchange. The remaining amount stays in the atmosphere increasing CO$_2$ level and is thus the main cause of global warming [1,2]. So far, several technologies have been developed to reduce the CO$_2$ emission in the atmosphere, namely adsorption or capture. However, CO$_2$ capture and the carbon control sequestration may cause CO$_2$ leakage and thus affect the acidification of natural water resources. It would be a great solution, in the context of economic and environmental benefit, to convert CO$_2$ into useful products instead of CO$_2$ capture or storage. In this regard, the coupling reaction of CO$_2$ with epoxides to produce cyclic carbonates that are further useful in the production of polycarbonate is currently perceived as being friendlier than the industrial production of polycarbonates from bisphenol A, which requires the highly toxic reagent phosgene [3–5]. A catalyst needed for in the cycloaddition of CO$_2$ into epoxides due to the inactivity of CO$_2$ [6,7]. Also, the critical reaction conditions, such as high temperature and pressure of CO$_2$, are required to proceed with the reaction. It is thus essential to explore new catalysts which are useful in the catalytic performance under milder reaction conditions (low temperature and CO$_2$ pressure) [8].

Homogeneous catalysts, including monometallic and bimetallic complexes, have been developed as efficient homogeneous catalysts for the coupling reaction of CO_2 and epoxides [9–12]. Ambient conditions were recently investigated [13]. However, the difficulty of separation and the recovery of the homogeneous catalyst from the reaction mixtures limited their widespread application. Heterogeneous catalysts for epoxide-CO_2 coupling have drawn much attention due to their high activity, large-scale production and selective product formation [6,14–16]. Although heterogeneous catalysts have been reported as effective catalysts for CO_2 cycloaddition, some of them like conventional zeolites, metal oxides require a co-catalyst and critical reaction conditions. The extra co-catalyst and critical conditions are not cost-effective, time-consuming and may lead to the deterioration of the catalyst structure [13].

Metal-organic frameworks (MOFs) are well-known as a new class of catalysts with unique and outstanding properties such as large surface area, well-ordered porous structures and chemical flexibility [14,16–19]. The flexible structure design via different metals (nodes or clusters) bridged by varieties of organic ligands (linkers) has attracted much attention in a broad range of potential applications, including gas adsorption and catalysis. The MILs (Materials of Institute Lavoisier), such as MIL-101, MIL-100 or MIL-53, have shown considerable attractiveness among the MOF materials [20–23]. MIL-101(Cr) is a porous polycarboxylates consisting of trivalent chromium ions cross-linked with 1,4-benzene dicarboxylate anions. Férey and co-workers were the first to report the synthesis of MIL-101(Cr) by a hydrothermal method [20]. MIL-101(Cr) presents a large surface area (Langmuir surface area up to 4290 m^2/g) and high thermal and chemical stability [8,24]. However, the synthesis method, precursors, solvent, synthesis conditions, activation procedure and so forth, play a role in determining porosity and surface properties of MIL-101(Cr). MIL-101(Cr) synthesized according to the method in this work reported surface area of 2014 $m^2 \bullet g^{-1}$ [25]. Moreover, the modified activation procedure could enhance the surface area up to 2553 $m^2 \bullet g^{-1}$, as stated in this work. Besides, several reports are describing a surface area for MIL-101(Cr) between 2000–3000 $m^2 \bullet g^{-1}$ [8,23,24,26,27]. Here, the complicated procedure described by Sun et al. to synthesize and to activate materials was applied to obtain a large surface area [7].

The metal nodes provide acid or base sites and combined with high porosity; they attract easily gas molecules such as CO_2, which is beneficial for catalytic performance related to the CO_2 addition to generate cyclic carbonates.

In our study, MIL-101(Cr) is synthesized by the hydrothermal method and then applied as a heterogeneous catalyst for the CO_2 addition to various epoxides. The MIL-101(Cr) heterogeneous catalyst, which is synthesized straightforwardly, showed an excellent conversion of epoxides as well as selectivity at 35 °C and ambient pressure (1.5 bar). As the efficiency of the catalyst depends on the reaction conditions, different substrates were investigated. Moreover, the catalyst could be recycled at least five times without noticeable loss of activity. Finally, this catalyst is greener since it fulfills some of the principles of green chemistry, such as no toxic chemicals, solvent-free, low-energy and cost-effective as a heterogeneously catalyzed reaction.

2. Results and Discussion

2.1. MIL-101(Cr) Characterization

Firstly, the synthesized MIL-101(Cr) was characterized to verify the characteristic properties and compared them with previous reports in the literature. The X-ray diffraction (XRD) analysis was performed to identify the crystalline structure of the synthesized MIL-101 (Cr). The sharp and intense diffraction pattern of MIL-101(Cr), Figure 1a was similar to the patterns of reported MIL-101(Cr) [21,23,28]. The textural morphology and the crystal size of the synthesized material were analyzed using scanning electron microscopy (SEM). The SEM analysis revealed a dense nano-crystal structure of MIL-101(Cr) with an average crystal size of 200 nm, Figure 1b. The porosity property of the synthesized material was evaluated by nitrogen adsorption at 77 K. A large uptake of N_2 in the micropores was observed classifying the materials as an isotherm of *Type I*, Figure 1c. High surface

areas of 2553 m^2/g and 2785 m^2/g for BET and Langmuir surface area, respectively, were obtained for the synthesized MIL-101(Cr), although slightly lower than the highest reported surface area of MIL-101(Cr) [21]. A pore volume of 1.089 cm^2/g and a micropore width of 1.691 nm were indicative of the porous properties of the synthesized material. Next, CO_2 adsorption of the synthesized material was measured, as this is one of the substrate molecules in the CO_2 addition reaction. An excellent CO_2 uptake up to 70 cm^3/g at 273 K and 1 bar of CO_2 pressure was disclosed for the synthesized MIL-101(Cr), Figure 1d. Besides, the obtained CO2 adsorption capacity is comparable to values reported in the literature, as is the surface area [26].
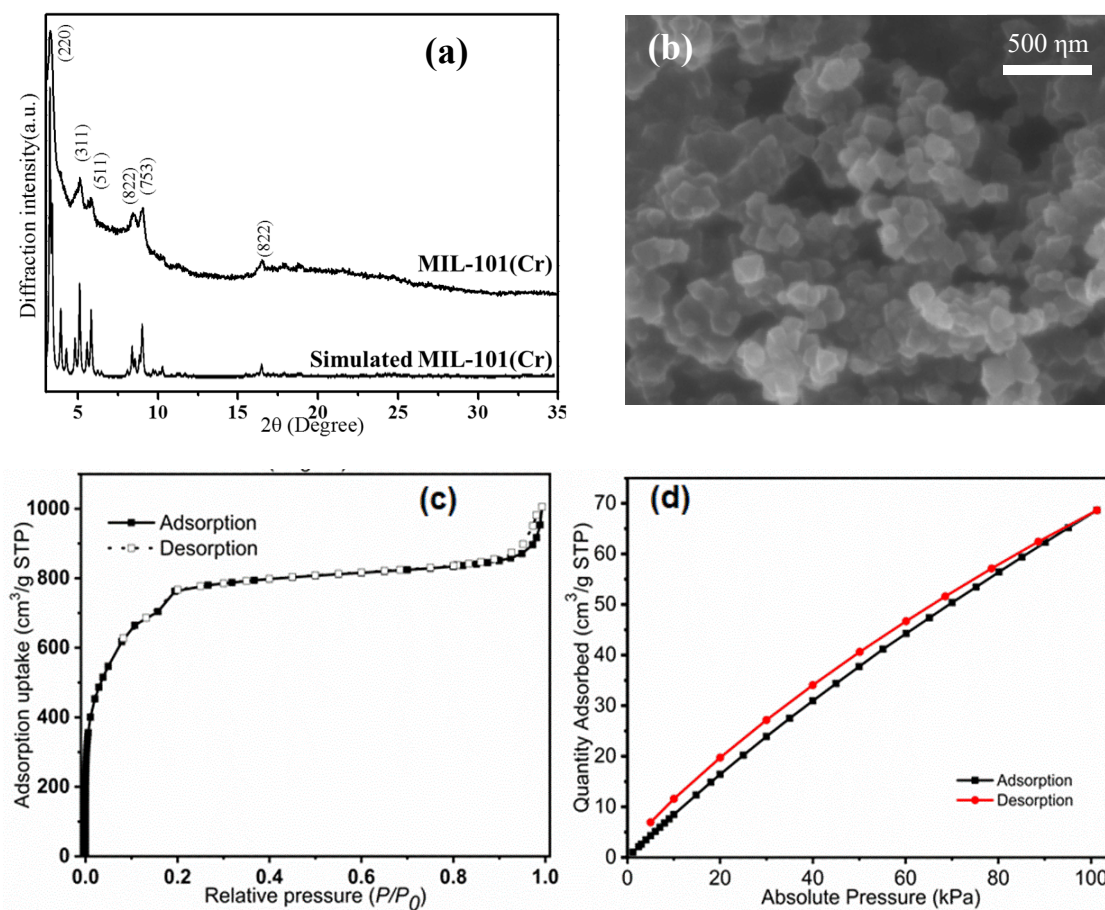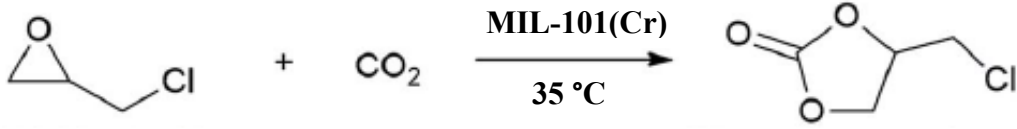

Figure 1. Characteristic properties of MIL-101(Cr): (**a**) X-ray diffraction (XRD) spectra of MIL-101(Cr) and simulated MIL-101(Cr), (**b**) crystal morphology via scanning electron microscopy (SEM) analysis, (**c**) Nitrogen isotherm at 77 K and (**d**) CO_2 isotherm at 273 K.

2.2. Catalytic Reaction

MIL-101(Cr) was applied as a heterogeneous catalyst for the CO_2 cycloaddition with an epoxide to produce cyclic carbonates. The catalytic performance was studied under different reaction conditions of temperature, pressure, time and amount of the catalyst. Epichlorohydrin was chosen as the model substrate and later on, other epoxide substrates were applied to demonstrate the potential of the catalyst using the same procedure. MIL-101(Cr) as a catalyst for the CO_2 addition to cyclic carbonates was previously reported. However, high temperature and CO_2 pressure in combination with a co-catalyst next to a few substrates (styrene oxide, propylene oxide) were investigated [26–30]. For example, the results revealed a 97% conversion of styrene oxide at 70 °C under 100 atm of CO_2 pressure within 7 h. Unfortunately, a nearly neglectable conversion (9%) was obtained at low pressure (8 atm) and temperature (25 °C) for a reaction time of 24 h. To enhance the catalytic performance of the catalyst, a solution was found by adding a co-catalyst (tetrabutylammonium bromide, TBAB) in the

reaction mixture. In this way, a catalytic performance of up to 95% conversion of styrene oxide was obtained (conditions: Temperature: 25 °C; pressure: 8 bars of CO_2; reaction time: 48 h). Subsequently, MIL-101(Cr) was investigated for the conversion of propylene oxide under the same reaction conditions and a comparable conversion of 82% was obtained [29,31]. Herein, mild reaction conditions are the focus of the investigation based on robust, high porosity and high CO_2 uptake of the synthesized MIL-101(Cr) as a heterogeneous catalyst. Therefore, to find the optimum reaction conditions, we fixed the reaction temperature at 35 °C and firstly applied 50 mg catalyst with epichlorohydrin (850 mg, 9.2 mmol) under 4 bar of CO_2 pressure (without co-catalyst and solvent). The obtained result revealed a 100% conversion of epichlorohydrin after 48 h (Table 1, entry 2). Also, a full conversion (100%) was retained when the reaction time was reduced to 24 h (Table 1, entry 3). Next, the CO_2 pressure was investigated, starting from high pressure (8 bar) and reduced till close to ambient pressure (1.5 bar). Also, using these conditions, the catalyst showed an excellent performance (99% conversion), although the reaction time was reduced to 24 h and using a CO_2 pressure of 1.5 bar (Table 1, Entries 1, 2, 6 and 7). Interestingly, the difference between conversion and yield (although there is a high selectivity) could be explained by the fact that the product is adsorbed on the MOF and hence, the adsorbed product is not detectable in H-NMR leading to low values of yield. This is in contrast with the recycling experiments where the obtained yields are acceptable. Here the catalysts is recovered via centrifuge and washing. So, all the products are collected and hence an acceptable yield is obtained. The conversion gradually decreased when shorter reaction times were applied (Table 1, Entries 7 and 10–12). A significant drop in conversion was observed when the catalyst loading was reduced from 50 mg to 25 mg (Table 1, entries 7–9). However, it is worth noting that when using a low catalyst loading, the catalyst showed still an appreciable catalytic activity under these mild conditions (35 °C, 1.5 bar) in the absence of solvent and co-catalyst. Though, higher conversions reached by prolonging the reaction time.

Table 1. The optimization of reaction conditions using MIL-101(Cr) as a heterogeneous catalyst [1] (temperature: 35 °C).

Entry.	Catalyst (mg, mmol)	Time (h)	Pressure (bar)	Conversion (%)	Selectivity (%)	Yield [9] (%)
1	50, 0.08	48	8	100	99	65
2	50, 0.08	48	4	100	99	62
3	50, 0.08	24	4	99	99	68
4	50, 0.08	6	4	53	99	43
5	50, 0.08	7	8	63	99	49
6	50, 0.08	48	1.5	100	99	70
7	50, 0.08	24	1.5	99	99	90
8	35, 0.06	24	1.5	65	99	52
9	25, 0.04	24	1.5	61	99	50
10	50, 0.08	12	1.5	52	99	42
11	50, 0.08	18	1.5	78	99	67
12	50, 0.08	22	1.5	88	99	70
13 [2]	Blank	24	1.5	-	-	0
14 [3]	$Cr(NO_3)_2 \cdot 9H_2O$	24	1.5	-	-	0
15 [4]	BDC	24	1.5	-	-	0
16 [5]	50, 0.08	24	1.5	99	99	90
17 [6]	50, 0.08	24	1.5	99	99	89
18 [7]	50, 0.08	24	1.5	99	99	89
19 [8]	50, 0.08	24	1.5	99	99	88

[1] Epichlorohydrin 9.2mmol, [2] Blank means no catalyst present in reaction, [3] $Cr(NO_3)_2 \cdot 9H_2O$ 0.125 mmol, [4] 1-benzene 1,4-dicarboxylate (BDC) 0.3 mmol, [5] second cycle, [6] third cycle, [7] fourth cycle, [8] fifth cycle, [9] Yields (isolated) were determined by ^{1}H NMR and using 1,3,5,-trioxane as the internal standard.

The robustness and stability of this heterogeneous catalyst (MIL-101(Cr)) were proven via catalyst recyclability experiments. The recycled catalyst retained its catalytic properties, both conversion and selectivity, under these optimal mild reaction conditions (Table 1 entries 16–19, Figure S2). It was demonstrated that the catalytic performance remained for at least 5 recycle times. To find out more about the morphology and physical properties of the recycled catalyst, the recycled catalyst (MIL-101(Cr)) was characterized using XRD and compared with the fresh catalyst. The analysis revealed no observable changes in the crystal pattern of the recycled catalyst compared with the fresh catalyst (Figure S3). However, the surface area of the recycled catalyst was reduced in comparison with the fresh catalyst. This reduction in the surface area could be due to the trapping of reactants or product molecules in the pores of used MIL-101(Cr) (Figure S4). Although a smaller surface area was observed for the recycled catalyst, this reduced surface area did not change the catalytic performance of the MIL-101(Cr) catalyst under these mild reaction conditions since the conversion was retained.

Several MOFs were successfully applied to catalyze the addition reaction of CO_2 with epoxide into cyclocarbonates. The activities of these MOFs are related to the nature of the metal center and ligand present in the framework. The presence of acidic sites in some well-known MOFs such as MOF-5, HKUST-1, UiO-66 and so forth disclosed to be the active sites to catalyze this reaction [32–34]. However, a co-catalyst and solvent are required to participate in the reaction as basic sites. Consequently, amino-bearing ligands and nitrogen-containing ligands to construct MOFs, for example, UiO-66-NH_2, Zn-DABCO were reported also exhibiting a catalytic activity comparable to their parent MOFs [7,31,35]. Additionally, binary MOFs such as UiO-66@HKUST-1 and Co@MOF-5 were described as a bimetallic catalyst for the cycloaddition reaction of carbon dioxide with epoxides. Nevertheless, in all reported cases, a co-catalyst, for example, TBAB, was still required to achieve a satisfactory performance [5,36]. On the other hand, zeolitic imidazole frameworks (ZIFs), a subfamily of MOFs, have attracted much attention concerning their properties and applications. For the cycloaddition reaction of CO_2 with epoxides, ZIFs are applied as heterogeneous catalysts exhibiting an excellent catalytic activity in the absence of co-catalyst and solvent-free. The defect structures at the ZIF surface were claimed to bear the active sites for this catalytic reaction [17,31]. Recently, the material obtained after pyrolysis of ZIFs was also reported to be an active heterogeneous catalyst for the cycloaddition of carbon dioxide with epoxides and demonstrated to be advantageous as a robust heterogeneous catalyst [37,38]. Later, the post-synthesis modified ZIF-90 with pyridinium-based ionic liquid (IL) to generate IL-ZIF-90 was developed [39]. The highly porous catalyst (IL-ZIF-90) showed an excellent CO_2 transforming capability. An overview of catalytic activities of reported MOFs with their reaction conditions for the cycloaddition of carbon dioxide with epoxides is summarized in Table 2.

Table 2. Comparison of catalytic performance of reported metal-organic frameworks (MOFs).

Catalyst	Substrate	Temp. (°C)	Time (h)	Pressure (bar)	Conversion (%)	Selectivity (%)	Ref.
MIL-101	EPH	35	24	1.5	99	99	This work
ZIF-8	EPH	100	4	7	98	33.4	[19]
Zn-DABCO	EPH	100	12	8	>99	99	[7]
Zn-MOF	EPH	100	16	1	100	99	[40]
F-IRMOF(Zn)	EPH	140	1.5	20	80	-	[41]
BIT-3(Zn)	EPH	160	8	30	100	91	[42]
HKUST-1	EPH	60	8	12	78	>99	[36]
UiO-66	EPH	60	8	12	67	>99	[36]
UiO/CuBTC	EPH	60	8	12	91	>99	[36]
(I⁻)Meim-UiO-66	EPH	120	24	1	100	93	[43]
UiO-67(Zr/V)	EPH	100	2	16	64	96	[44]
UiO-67-IL [a]	EPH	90	3	1	99	-	[45]
VPI-100(Zr/Cu) [a]	EPH	90	6	10	99	-	[46]
VPI-100(Hf/Cu) [a]	EPH	90	6	1.5	97	-	[47]
MIL-101-IL	EPH	120	2	20	98	99	[30]
MIL-101	SO	35	24	1.5	29	>99	This work
	SO[b]	60	18	80	50	100	[40]
	SO	120	14	20	63	-	[48]
MIL−101(Cr)−TSIL [a]	SO	110	6	20	95	98	[26]

Table 2. *Cont.*

Catalyst	Substrate	Temp. (°C)	Time (h)	Pressure (bar)	Conversion (%)	Selectivity (%)	Ref.
Co-POM @MIL-101 [a]	SO	110	2	20	88	88	[27]
MOF-5	SO	120	14	20	Inactive	-	[48]
UiO-66-NH$_2$	SO	120	14	20	95	-	[48]
(I⁻)Meim-UiO-66	SO	120	24	1	46	71	[43]
MOF-74(Mg)	SO	120	14	20	94	-	[48]
HKUST-1	SO	120	14	20	48	-	[48]
IRMOF-3	SO	120	14	20	33	-	[48]
MIL-101[a]	PO	100	14	5	80	-	[28]
MIL-101-IL	PO	120	24	1	89	99	[30]

(EPH = epichlorohydrin; SO = styrene oxide; PO = Propylene oxide; [a] Co-catalyst = tetrabutylammonium bromide; [b] required solvent

The direct comparison of MIL-101(Cr) with other MOF catalysts reveals that MIL-101(Cr) exhibits the highest catalytic activity under mild reaction conditions. According to previous reports, based on the theoretical calculations (DFT) of the catalytic mechanism, the ring-opening process of the epoxide is the rate-limiting step of this reaction [49]. Also, it was observed that the Lewis acid sites played a main role in the ring-opening process by binding the oxygen atom of the epoxide [50]. A well-known technique to analyze the amount of acid and basic sites on MOFs is temperature program desorption (TPD), which makes use of gas probe molecules (NH$_3$ and CO$_2$ to determine the acid and basic amounts, respectively) [48]. Using TPD, Kim et al. determined, based on the integration of NH$_3$-TPD signals, the acid sites of several MOFs and reported that MIL-101 contained the highest amount of acid sites in comparison with the other MOFs (Figure 2) and especially strong acid site (593–673 K) [48]. The presence of this high amount of strong acid sites in MIL-101(Cr) can be applied to elucidate the high catalytic performance of MIL-101 for the cycloaddition of carbon dioxide with epoxides in comparison with other reported MOFs. Recently, it was reported that the defect structure in MOFs plays an active role as active sites in a catalyst [51]. Herein, the defect structures present in MIL-101(Cr) could participate as well and result in an excellent catalytic performance under mild conditions. However, to fully prove the role of the defects, a study of the defect sites in this MIL-101(Cr) based-catalyst compared with the reported MIL-101(Cr) using different characterization and analysis techniques is required. Still, in this report, the focus was mainly directed on the mild reaction conditions.
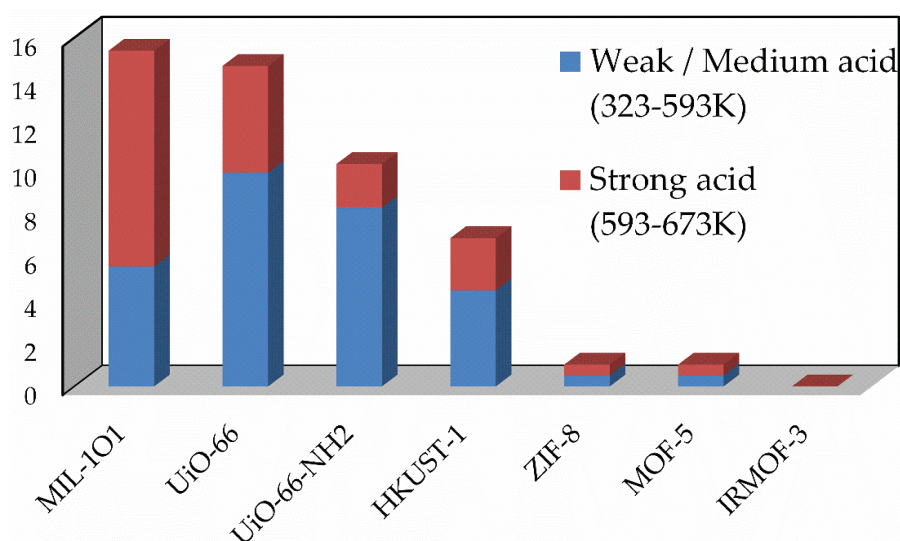

Figure 2. Amounts of acid sites of different MOFs obtained NH$_3$- temperature program desorption (TPD) reported by Kim et al. [48]

2.3. Substrate Scope

The cycloaddition reaction of CO_2 applying different substrates catalyzed by MIL-101 (Cr) was also investigated. The obtained results are summarized in Figure 3 and demonstrate that MIL-101 (Cr) can convert the substrates to their corresponding products under mild reaction conditions. Epibromohydrin and propylene oxide (>99%) were converted fully to their corresponding cyclic carbonates, while phenyl glycidyl ether and styrene oxide display a lower conversion of 25% and 29%, respectively. In this series of epoxides, epoxides having a lower boiling point, for example, propylene oxide (34 °C), epibromohydrin (134 °C) and epichlorohydrin (118 °C) are fully converted to their cyclic carbonates. These results are in line with previous investigation by Taherimehr and co-workers, who also achieved excellent conversion for epoxide substrates with a lower boiling point [52]. In comparison, epoxides having a higher boiling point, for example, phenyl glycidyl ether (245 °C) and styrene oxide (194 °C), are only partially transformed. The allyl glycidyl ether and butyl glycidyl ether with intermediate boiling points (154 °C and 256 °C, respectively), gave an intermediate conversion. Under the investigated conditions, CO_2 mainly remains in the gas phase, while the epoxide substrate having a relatively low boiling point tends to shift into the gas phase. This could be advantageous for good interphase contact between the different components (epoxides, CO_2 and catalytic sites) and thus resulting in achieving a good conversion. Also, substrates containing electron-withdrawing substituents exhibit a higher conversion via enhanced easiness of the ring-opening of the epoxide allowing the nucleophilic attack followed by carbonate formation [31]. The epoxide properties affecting the catalytic performance under mild conditions were illustrated using different MOFs as a catalyst. For instance, using MOF-5 as the catalyst, the following substrate conversion trend was reported—epichlorohydrin > styrene oxide > phenyl glycidyl ether at 50 °C, 0.1 MPa of CO_2 pressure and co-catalyst (n-Bu_4NBr, 2.5 mol %). Whereas, raising the CO_2 pressure to 6 MPa revealed an increase of the conversion of phenyl glycidyl ether, even higher than the styrene oxide conversion (under similar conditions). A same result was also reported for Zn-DABCO at high pressure (8 bars).
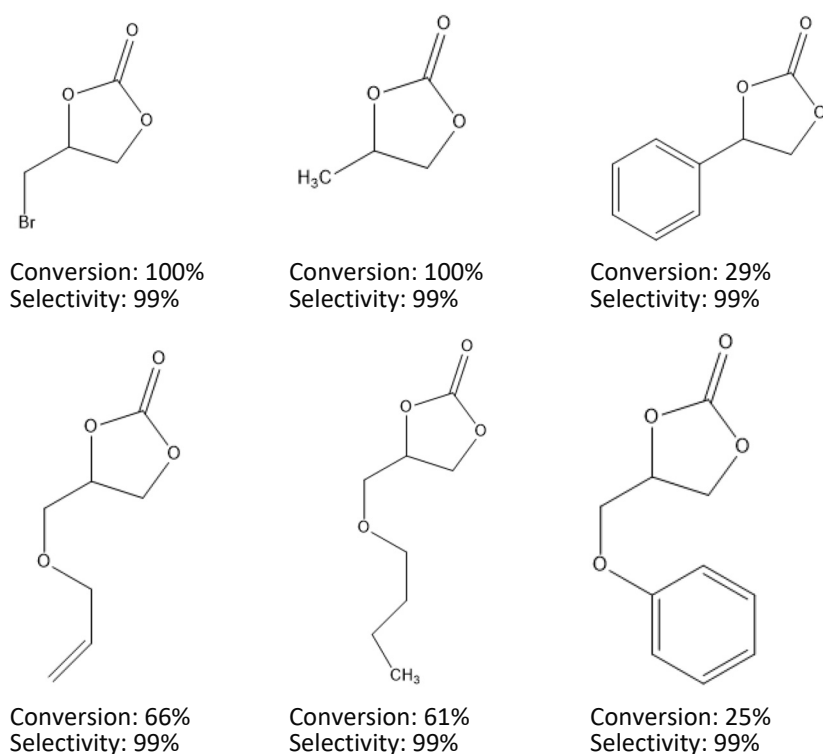

Figure 3. Variety of cyclic carbonates produced by MIL-101(Cr) as catalyst. (Reaction conditions: Catalyst: 50 mg, 0.08 mmol; epoxide substrates: 9.2 mmol; temp. 35 °C; pressure: 1.5 bar of CO_2; no solvent; no co-catalyst).

2.4. Catalytic Mechanism

The carbon dioxide coupling mechanism with epoxides to generate cyclic carbonates is depending on the type of the catalyst used. For example, in case the catalyst contains both Lewis acid and basic sites, it is accepted that the acidic site activates the epoxide. In contrast, the basic site activates the carbon dioxide [53]. On the other hand, the co-catalyst is the source of the basic site for the reaction when the catalyst provides the Lewis acidic site only. A mechanism for the reaction of epoxide and CO_2 catalyzed by catalysts with Lewis acidic sites only in the absence of co-catalyst was also proposed [48]. Carbon dioxide can act as nucleophile or electrophile in the reaction. Here, the first step of the mechanism is the electrophilic activation of the epoxide ring by the Lewis acidic site of the MIL-101(Cr) catalyst resulting in the ring-opening of the epoxide. Next, a nucleophilic attack from the oxygen atom of CO_2 occurs and binds with the carbon of the epoxide to form intermediate metal species. Finally, the ring-closing occurs where the oxygen anion of the open ring interacts with the carbon atom of the carbon dioxide and extrudes the cyclic carbonate, as shown in Figure 4. Also, high surface features and a large pore volume of the catalyst for example, MOFs, promote the coordination sites required for the epoxide binding, which plays a crucial role in the overall catalytic performance of the cycloaddition of CO_2 to generate the cyclic carbonate product.
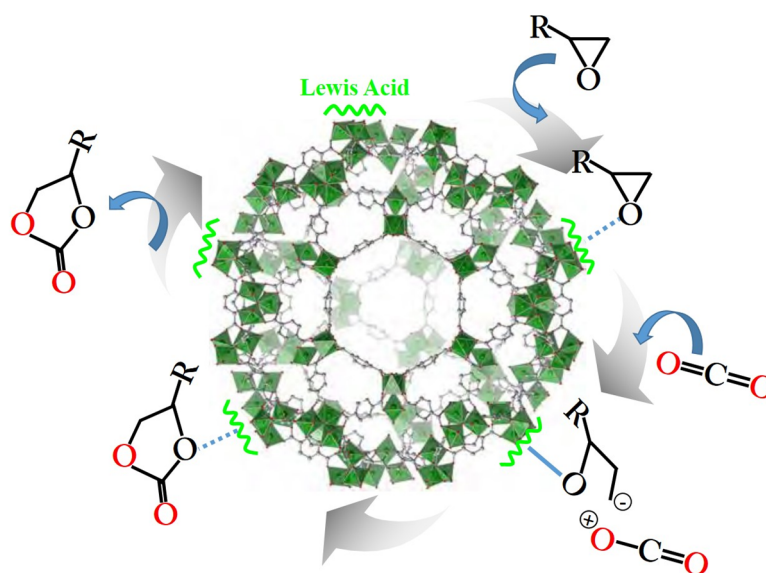

Figure 4. Mechanism of the CO_2 cycloaddition into epoxide producing the cyclic carbonates using MIL-101(Cr) as catalyst.

3. Materials and Methods

3.1. Materials

Chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), 1-benzene 1,4-dicarboxylate (BDC), hydrogen fluoride (HF > 40% in H_2O), *N,N*-dimethylformamide (DMF), ethanol, dichloromethane and epoxide substrates (epichlorohydrin (EPH), epibromohydrin, propylene oxide, styrene oxide (SO) and phenyl glycidyl ether) were purchased from Aladdin chemical (AR grand, Shanghai Aladdin Biochemical Technology Co., Ltd., China) and used as received.

3.2. Catalyst Preparation

MIL-101(Cr) was synthesized using the hydrothermal method previously reported with a slight modification in the synthesis procedure [25]. In a typical synthesis, the $Cr(NO_3)_3.9H_2O$ (0.4 g, 1 mmol) and BDC (0.249 g, 1.5 mmol) were dissolved in deionized water (DI, 10 mL) and followed with the addition of HF (10 µL). The mixed suspension was vigorously stirred for 20 min in a Teflon liner

(40 mL) before transferred into the stainless steel autoclave. The autoclave was kept under autogenic pressure at 180 °C for 8 h and then cooled to room temperature. The resulting green solid was separated from the mixture via centrifuge (8500 rpm, 5 min) and washed with DI water and DMF. The solid product was post-treated in water (20 mL) at 80 °C for 1 h and ethanol (20 mL) at 70 °C for 3 h, respectively. After centrifugation, the obtained solid (as-synthesized MIL-101(Cr)) was dried at 120 °C under vacuum overnight before further use and analysis (activated MIL-101(Cr)).

3.3. Catalytic Reaction

The synthesized MIL-101(Cr) catalyst (50 mg) and substrates (9.2 mmol) were charged in a high-pressure reactor (15 mL stainless steel, XINGDA company, Beijing, China) with a magnetic stirrer. The atmosphere in the reactor was exchanged with CO_2 before pressurized to 1.5 bar of CO_2 pressure. The reactor was immersed in a pre-heated oil bath at 35 °C under stirring conditions (300 rpm) for the required period of reaction time. The reactor was cooled to room temperature and 1,3,5-trioxane, as the internal standard (3 mmol) and $CDCl_3$ (1 mL) were added. The reaction mixture was analyzed via ^1H NMR using $CDCl_3$ as a solvent. The catalyst was recovered by the centrifugation and then washed three times with dichloromethane and then dried at 80 °C under vacuum for 12 h for the next reuse. The same reaction conditions were applied to other substrates.

3.4. Catalyst Characterization

The powder X-ray diffraction (XRD) D8 Advanced Diffractometer, Bruker (Germany) (Bragg-Brentano geometry) at 40 kV and 45 Ma with Cu Kα radiation source (λ = 1.54056 Å at 40 kV and 45 Ma) and scanning rate of 2° min^{-1} was used to characterize the crystalline structure of the material. The morphology was observed by SEM (JSM-IT300/JSM-IT300, JEOL, Japan). The gas adsorption-desorption measurement was carried out by Micrometrics instrument (ASAP 2020 Analyzer) using N_2 and CO_2 gases of 99.999% purity. The pore distribution and surface area were analyzed by Brunauer-Emmett-Teller (BET) and Langmuir methods. The linearized BET and Langmuir equations were fitted in the range of $0.003 < P/P_0 < 0.05$.

4. Conclusions

In this study, MIL-101(Cr) was synthesized via the hydrothermal method and applied as a heterogeneous catalyst for the cycloaddition of CO_2 into epoxide. The catalytic activity of the MIL-101(Cr) catalyst was investigated, aiming at mild reaction conditions (reaction temperature, pressure, time, catalyst loading and epoxide substrate). The MIL-101(Cr) demonstrates excellent conversion and selectivity under mild reaction conditions (near room temperature (35 °C) and an atmospheric pressure of CO_2 (1.5 bar)). The epoxides containing an electron-withdrawing group could easily be converted into the cyclic carbonate product under these mild conditions, even in the absence of co-catalyst and solvent. The presence of strong Lewis acids and high porosity in the MIL-101(Cr) is beneficial for CO_2 adsorption and improves the catalytic performance. Besides, MIL-101(Cr) exhibits a non-noticeable loss in the catalytic conversion during at least five cycles. The results demonstrate a highly active, greener and economically viable heterogeneous catalyst for the cyclic carbonate production from epoxide and CO_2 compared to any reported MOFs.

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