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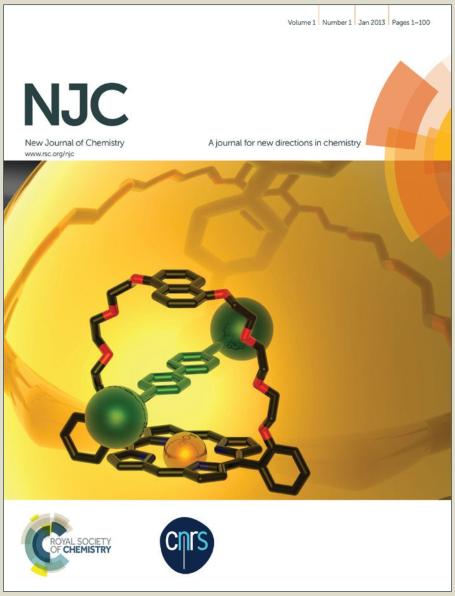

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Zeolitic Imidazole Framework-67 as an Efficient Heterogeneous Catalyst in the Conversion of CO_2 to Cyclic Carbonate

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Zeolitic imidazole framework (ZIF)-67 is an efficient heterogeneous catalyst for the cycloaddition of carbon dioxide with epoxides to make cyclic carbononates. In this work, ZIF-67 was synthesized by a simple and straightforward method at room temperature. The coupling reaction in the presence of ZIF-67 without any co-catalyst or solvent was studied at different conditions. The reaction conversion was more than 99 % and the selectivity toward the chloropropene carbonate was considerably higher (> 99%) than the previously reported ZIF-8. Moreover, ZIF-67 catalyst could be recycled at least four times without noticeable loss of catalytic activity.

Introduction

During the past decades, consumption of fossil fuels has significantly increased the amount of CO_2 in the atmosphere which is one of the main reasons of the global warming. Therefore there is increasing demands to find new strategies to reduce carbon dioxide and prevent future global problems.[1] Utilization of CO_2 as an abundant and inexpensive raw material for synthesizing fine chemicals and fuels is a feasible means to reach this goal.[2] One of the most efficient ways of using CO_2 as a C1 building block is the catalytic coupling of CO_2 into epoxides to form cyclic carbonates.[3] Organic cyclic carbonates are well known as organic intermediates, monomers for polymerization, and aprotic polar solvents that are used widely in chemistry and pharmaceutical industry.[4] Various homogeneous and heterogeneous catalysts have been introduced for this reaction.[3,5] As it is known, the separation and recovery from solution mixture is the main limiting factor for homogeneous catalyst. Hence, development of heterogeneous catalysts for cycloaddition of CO_2 to epoxide that can work efficiently, especially under mild reaction conditions are much desired. Many different heterogeneous catalysts such as zeolites[6], mesoporous oxides,[7] gold nanoparticles supported on resins[8] and functional polymers[9] are previously reported. However, the search for new materials with significant properties as an active catalyst for this reaction continues.

One of the novel classes of materials are metal organic frameworks (MOFs).[10] The hybrid crystalline structure, high surface area[11] (up to 10400 m^2g^{-1}) large pore aperture (98 Å)[12] and low density of MOFs[13] make them potential candidates for different applications such as catalysis.[14] Moreover, the synthetic flexibility of MOFs by controlling the size and functionalization of the organic linkers allows more effective selectivity compared to microporous and mesoporous inorganic materials.[15] There are several examples of designing special MOFs catalysts according to the desired reactions. This purpose was achieved through the synthesis of the MOFs by applying low coordinated metals as nodes or using specific linkers containing adequate chemical functions.[16] However in recent years, some of “saturated” frameworks e.g without any low-coordinated metal species or functionalized linkers have been reported as efficient catalysts.[17] A very good example are ZIFs.

Zeolite imidazolate frameworks based on imidazole linker and metallic nodes are a subclass of MOFs. The major advantage of these crystalline materials is their ability to show properties of both zeolites and MOFs[18] such as uniform micropores, large surface area, accessible pore volumes and exceptional thermal and chemical stabilities.[19] In this work, ZIF-67 synthesized by a simple and straightforward room temperature technique, was introduced as an active heterogeneous catalyst for the cycloaddition of CO_2 to epoxides. The catalyst showed very high activity and selectivity under almost mild reaction conditions without any co-catalyst or solvent. [Figure 1]

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Moreover, ZIF-67 as a green catalyst could be recycled at least four times without noticeable decrease in activity and selectivity. The results compared to the previously reported MOFs for the same reaction.

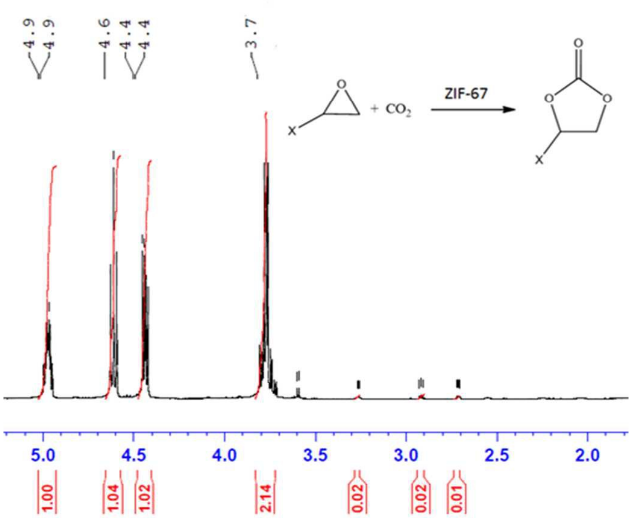


Figure 1. Synthesis of functional organic carbonates from CO_2 and epoxides (X = CH_3, $PhOCH_2$, $ClCH_2$, Ph). ^{1}H-NMR ($CDCl_3$) spectrum of the crude mixture after reaction of epichlorohydrin and CO_2 to synthesize chloropropene carbonate entry 4 in Table 1.

Results and Discussion

Catalyst Characterization

ZIF-67 was prepared according to the reported procedure [20] using 2-methylimidazole and cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$. The textural properties of ZIF-67 were analyzed by X-ray diffraction (XRD), thermal analysis technique (TGA), N_2 adsorption-desorption, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM). The metal content of ZIF-67 samples (before and after reaction) were analyzed by inductively coupled plasma atomic emission analyses (ICP-AES). The XRD pattern of ZIF-67 is displayed in Figure 2 and is in excellent agreement with the previous report.[21] The N_2 adsorption-desorption graph of ZIF-67 (Figure 3) indicates that ZIF-67 has a microporous nature (diameter < 20Å) which is in accordance with the pore size distribution.[21] In addition, the surface area of ZIF-67 was evaluated from BET and Langmuir theoretical calculation and summarized in Table S1 and is corroborated by the related literature.[21] The porosity properties were obtained using the Horvath-Kwazoe (HK) method (Table S1) and the morphology was investigated using SEM, demonstrating the average crystal size is in the 300-500 nm range. (Figure S1). The TGA mass loss curve of ZIF-67 is illustrated in Figure S2. The obtained results (in line with previous reported data[21]) indicate that ZIF-67 is thermally stable at least up to 400 °C. [22a] The FT-IR spectra of the ZIF-67 and 2-methylimidazole exhibit significant difference [Figure S3] and are compatible with the reported literature.[23]

After performing the coupling reaction with ZIF-67, the catalyst was washed with MeOH, dried under vacuum at 150 ^oC and characterized using ICP-AES, XRD, FTIR and SEM. The XRD pattern of the used ZIF-67 shows no significant changes with the fresh sample, Figure-2, suggesting that the crystalline structure is preserved during the reaction. In addition, the C=N and N-H vibration bands in the FT-IR spectra of ZIF-67 (before and after reaction) do not show any noteworthy differences and they are ina good agreement with previous reports.[22b,c] Moreover to confirm the results, ICP-AES and SEM were performed as well. Based on the ICP-AES results, the cobalt content of fresh ZIF-67 and used ZIF-67 only displayed a small variation, 28.17% and 28.1% respectively. Subsequently, the liquid phase (carbonate products) after filteration was analyzed by ICP-AES resulting in 0.2% and proved the structure stability of ZIF-67. Finally, the SEM image after the reaction (Figure S1), proves that ZIF-67 still possess a crystalline morphology. These data cofirm the recyclability of ZIF-67 for four times.

Effect of reaction conditions

In order to consider the effect of reaction parameters on the catalytic activity of ZIF-67, different parameters such as temperature, catalyst amount, CO_2 pressure and reaction time were investigated in details for epichlorohydrin. Table 1 shows the conversion and selectivity of carbonate products over side products and unreacted substrates in different controlled reaction conditions. As shown in entry 1, in the absence of the catalyst (ZIF-67) the desired product was not observed in a measurable yield meaning that the presence of catalyst ZIF-67 is crucial for this reaction. Afterwards, the effect of catalyst amount was investigated and the results were summarized in Table 1 (entry 2-4). The reaction was carried out in the presence of different amounts of catalyst (65 mg, 80 mg, 100 mg and 115 mg). It was observed that by increasing the amount of the catalyst, the quantitative conversion increased and the best results were obtained at 100 mg of catalyst combined with 18 mmol of substrate at 100 ^oC, 8 bar and for 8h.

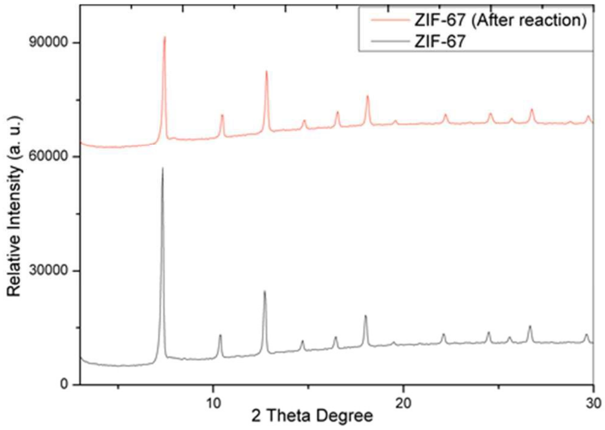
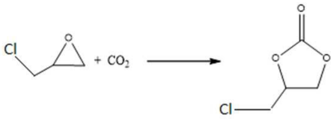


Figure 2. XRD of fresh and reused ZIF-67 catalyst for the cycloaddition of CO_2 with epichlorohydrin.

Table 1. Obtained conversions and selectivities using different reaction conditions:



	Catalyst (mg)	Time (h)	Pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%)	Isolated Yield (%)
1	None	8	8	100	-	-	-
2	ZIF-67 (65)	8	8	100	72	> 99	69
3	ZIF-67 (80)	8	8	100	85	>99	79
4	ZIF-67(100)	8	8	100	> 99	>99	97
5	ZIF-67(100)	8	8	60	29	>99	20
6	ZIF-67(100)	8	8	80	90	>99	89
7	ZIF-67(100)	8	8	95	> 99	>99	99
8	ZIF-67(100)	8	1	95	<3%	-	-
9	ZIF-67(100)	8	4	95	73	>99	72
10	ZIF-67(100)	8	6	95	91	>99	90
11	ZIF-67(100)	8	8	95	>99	>99	95
12	ZIF-67(100)	4	8	100	75	>99	75
13	ZIF-67(100)	6	8	100	90	>99	89
14	ZIF-67(100)	8	8	100	>99	>99	98
15	ZIF-67$^{(First\ use)}$	8	8	100	>99	>99	98
16	ZIF-67$^{(Second)}$	8	8	95	>99	>99	97
17	ZIF-67$^{(Third)}$	8	8	95	>99	>99	98
18	ZIF-67$^{(Forth)}$	8	8	95	>99	>99	98
19	ZIF-8 (100) [a]	4	7	100	100	49	-

Reaction conditions:epichlorohydrin (18 mmol, 1.66 g), a) Ref [23b]

The effects of reaction temperature on the conversion and selectivity of the carbonate are summarized in Table 1 and the ^{1}H-NMR spectra are illustrated in Figure S4. Continuesly, the results indicated that the conversion of substrate to chloropropene carbonate increased from 29 % to more than 99 % when the temperature changed from 60 °C to 95 °C (entry 5-7) which clarify the effect of heating on this reaction. Further increasing of temperature (110 °C) did not have any effect on the conversion and did not report in the Table 1. It should be noted that at higher temperature more than 100 °C (e.g. 110 °C), the reaction can complete in a shorter time however, the distinctive crystalline structure of ZIF-67 and thus active sites, gradually started to collapse. Therefore, to be able to recycle the catalyst (ZIF-67) for several uses, working at lower temperature is desired.

With these results in mind, the effect of CO_2 pressure on the catalytic activity of ZIF-67 was investigated. The temperature and the amount of catalyst were fixed on the optimum results of previous experiments. First the experiment performed at ambient pressure and just traces of desired carbonate were obtained (entry 8). Afterwards, the conversion of epichlorohydrin raised from 73 % to more than 99 % as the pressure enhanced from 4 bar to 8 bar (entry 9-11) (Figure S5). This could be the result of higher concentration of CO_2 and also of the presence of the epoxide in two phases. Song *et al.*[5e] reported that there are two phases for this reaction, a vapour phase and a liquid phase. Therefore as the reaction mainly occurred in the liquid phase (due to the presence of catalyst inside liquid phase), the higher pressure of CO_2 will increase the solubility of CO_2 in epichlorohydrin and consequently result in higher conversion of substrate. However, a higher pressure (10 bar) did no longer affect the conversion.

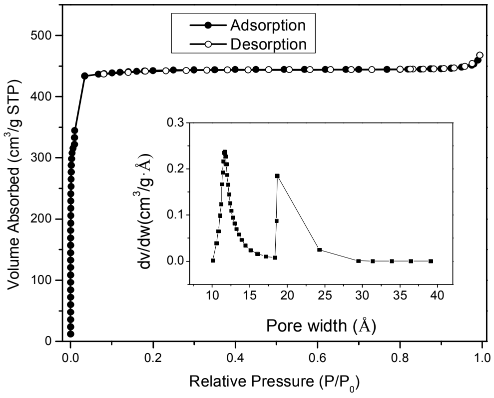
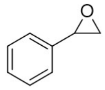
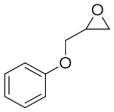
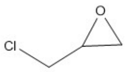
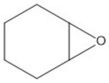


Figure 3. The N_2 adsorption-desorption graph of ZIF-67.

The reaction time was determined by withdrawing aliquots from the reaction mixture at different time intervals (entry 12-14) which were further diluted, filtered and analyzed by ^{1}H-NMR. It was observed that after 4h, the conversion of substrate to chloropropene carbonate reached up to 75 %. Continuing the reaction for two extra hours increased the conversion to 92 %. The reaction was further continued for another two hours (8h in total) resulting in >99% conversion without any sign of side products and any collapse in crystalline structure of ZIF-67. (Figure S6). Whereas the ZIF-8 crystalline structure collapsed even in shorter time and lower temperature.[23b] It should be mentioned that the selectivity of chloropropene over side products in all measurements always is almost 100% which is clearly much higher than the selectivity obtained using ZIF-8 [23b] for the same reaction.

Regarding to these results, the reusability test for ZIF-67 was performed using epichlorohydrin as a substrate (Table 1, entry 15-18). After each cycle, the catalyst was collected using centrifugation, washed three times with methanol and dried at 80 °C for 4 h under vacuum. (Figure S7). Along with that, leaching test for the reaction solution after filteration was analyzed using ICP-AES and showed the Co content was around 0.2%, while for ZIF-8, after 4 h reaction, the crystalin structure gradually collapsed. The ZIF-67 can be used for at least four times without loss of its catalytic activity. Consequently, due to the importance of epoxides in industry, different examples have been applied for this reaction. The results are summarized in the Table 2. As it is shown, the reaction conditions slightly differ for various epoxides, however high yields were obtained in all cases. ^{1}H-NMR spectra are depicted in supporting information. Their difference in the time of reaction can be because of the size of molecules; bigger molecules are more time consuming to go through the pores of ZIF.

Table 2. Various epoxides catalyzed by ZIF-67 in the absence of any solvent or co-catalyst.

Epoxides	Time	T °C	Conversion
	8 h	100	96 %
	15 h	100	92 %
	14h	100	93 %
	8h	100	99 %
	28h	130	90 %^{a}

^{a}; the CO_2 pressure is 10 bar.

Table 3. Comparison of ZIF-67 with other MOFs and ZIF-catalyst for cycloaddition of CO_2 to epoxide.

Catalyst	Pressure bar	Temperature (°C)	Conversion (%)	Selectivity (%)
ZIF-8 ^{a}	7	100	98-	33
ZIF-68^b	10	120	93	99
ZIF-90^c	11.7	120	43	-
F-ZIF-90^c	11.7	120	96.6	>99
ZIF-67^d	8	95	>99	>99
MOF-5^e	60	50	97.6	-
UIO-66^f	20	100	94	
UIO-66-NH_2^{f}	20	100	95	>99
MIL-101^f	20	100	63	-
Co-MOF-74^g	20	100	96	>99

(a) reaction conditions: substrate: epichlorohydrin for 4h. (b) substrate: styrene oxide for 12 h. (c) substrate: epichlorohydrin for 6 h. d; this work. (e) substrate: styrene oxide, co-catalyst; *n*-Bu_4NBr and co-solvent for 4 h. (f) substrate: styrene oxide, co-solvent, 4h. (g) substrate: styrene oxide, co-solvent, 4h.

Concerning these results, the efficiency of ZIF-67 as a catalyst was compared with some of reported MOFs or ZIFs for cycloaddition of CO_2 to epoxides. Several MOFs are reported for this reaction of which some of the most active ones are collected in Table 3. Obviously, MOF-5[5e] exhibited a high conversion at low temperature for this coupling reaction, however the presence of quaternary ammonium salts as a co-catalysts are required. Moreover, the reported applied CO_2 presure is as high as 60 bar. Other MOFs demonstrating high conversions for CO_2 cycloaddition reaction are UIO-66-NH_2[24a] and Co-MOF-74[24b]. MIL-101[24a] and UIO-66[24a] present slightly lower activity than ZIF-67. However, all these catalysts still need co-solvents to perform the reaction and also high pressure is compulsory. Besides those, some other Zn-based ZIFs were reported in literature. As it is illustrated in the Table 3, ZIF-8 is a potent catalyst with high activity. However, as mentioned above, ZIF-8 demonstrated much lower selectivity to chloropropene carbonate in comparison with ZIF-67. Furthermore, ZIF-8 cannot be recycled since it gradually degradates during the cycloaddition reaction. In literature, the higher activity and selectivity of ZIF-67 compared to ZIF-8 is attributed to the strength of acid-base sites.[21] In order to study the acid-base properties, CO_2-NH_3 TPD of both ZIF-8 and ZIF-67 were applied (Figure S8) (Table S2) and calculations reported in supporting information. The obtained data are in a good agreement with the related publications. [21] It is obvious that the acid-base properties of ZIF-67 and ZIF-8 are very close. Hence, that cannot be the only affecting factor in the cycloaddition reaction, most likely due to the role of CO_2 gas as one of the substrates. Some other parameters such as the amount of CO_2 adsorption on the surface of catalyst, defects on the structure, size and volume of pores, may affect the reactivity and selectivity to desired carbonate products. Further investigation is under way to clarify the details of affecting parameters.

Other ZIF examples applied for the cycloaddition reaction of carbon dioxide are ZIF-90[24c], F-ZIF-90[24c] and ZIF-68[24d] which all were reported recently. These ZIFs do not require co-solvent or co-catalyst, nevertheless still the coupling reaction is performed at higher temperature and pressure compared to ZIF-67. (Table 3) In addition, a non-neglectable advantage of ZIF-67 is that the synthesis is cost-effective without requirement for one or more extra functionalization steps, whereas for ZIF-68, the linker is costly and ZIF-90 shows an acceptable activity and selectivity only after functionalization.

Catalyst mechanism

The mechanism for cycloaddition of CO_2 to epichlorohydrin to give carbonate has been reported[23b] in which the Lewis acid sites catalyze the fixation of CO_2 to epoxide to produce cyclic carbonates and other precursors. It is already known that in ZIF-67 the Lewis acid sites originates from Co(II) and Co(III) species and base moieties derive from nitrogen atoms. In the ZIF structure, both of them can be activated in some ways, for example due to defects or the effect of water and oxygen on the surface of ZIF.[25a] Moreover, the existence of both Lewis acid sites (Co(II) and Co(III) species) and existence of uncoordinated nitrogen atoms, ZIF-67 has polar pore walls which favor the binding and the activation of the polar carbon-oxygen bond of carbon dioxide[23b] (Figure 4). Furthermore, based on the BET measurements (Table S1) ZIF-67 illustrates high capacity for adsorption of carbon dioxide. Chizellet and co-workers[25a] recently investigated that in ZIF-8 both Lewis acid sites (unsaturated coordinative Zn) and Lewis base sites (NH groups of ligand) can catalyze the reaction of Transesterification located on the external surface or structural defects. In other words, just the sites established on the external surface or at defects of ZIF-8 are active. Based on the mechanism and several lines of evidences for ZIF-67,[21] ZIF-9,[25b] and ZIF-8[25a] catalysts in similar reactions, it can be concluded that the cycloaddition of CO_2 to epoxide in presence of ZIF-67 also is catalyzed by the active sites on the external surface.

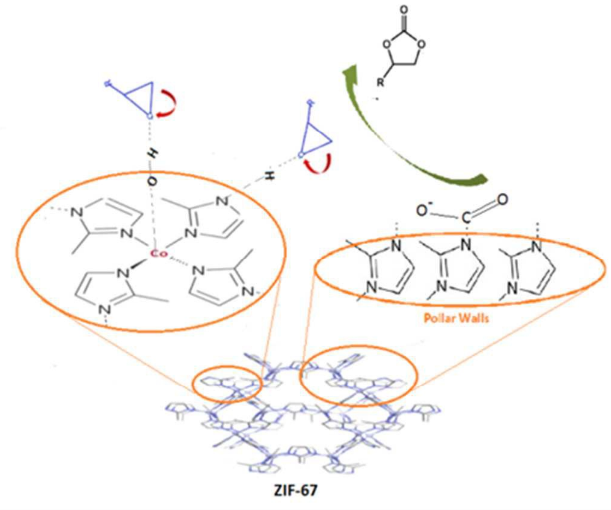


Figure 4. Possible mechanism for cycloaddition of CO_2 to epoxide.

Conclusion

In summary, we found out that ZIF-67 is a very efficient heterogeneous catalyst for synthesizing chloropropene from carbon dioxide and epichlorohydrin in absence of any solvent or co-catalyst. The reaction was studied in different conditions and for various epoxides. It was shown that in all cases the conversions toward the desired products are very high. Moreover, the catalyst could be recycled at least four times without considerable loss in activity or selectivity to the desired carbonate. Moreover, the activity and selectivity of ZIF-67 for cycloaddition of CO_2 to epoxides, compared to some of the most active MOFs and ZIFs catalysts previously reported in the literature. It was shown that, ZIF-67 can be an appropriate cost-effective and environmental frind choise with high reactivity and selectivity for the coupling reaction of CO_2 to epoxides.

Experimental section

Catalyst preparation

All chemicals were purchased from Aladdin chemical Co. and Sigma-Aldrich and used as received without any further purification unless otherwise noted. ZIF-67 was synthesized at room temperature according to the literature procedure [20] using cobalt nitrate hexahydrate ($Co(NO_3)_2$. $6H_2O$) [Merck, 98.5%] and 2-methylimidazole as a ligand. 1 mmol [0.291 g] of cobalt nitrate was dissolved in 11g of methanol (Sinopharm chem. Co) 99.5%, another solution of 8 mmol [0.66 g] of 2-methyl imidazole (Aladdin 99.8 %) in 11g of methanol was prepared and subsequently added to the cobalt solution. The mixture was stirred vigorously for 24 hours. Afterwards, the precipitates were separated by centrifugation at 7000 rpm and washed with methanol three times. The solid crystals were dried at room temperature under vacuum oven for 12 hours. The catalyst was activated at 200 °C, for 3 h under vacuum before use.

Catalyst reaction

In a typical procedure, 18 mmol of epoxide and 100 mg of ZIF-67 were charged in a 10 ml stainless steel high-pressure reactor (XINGDA company, Beijing, China). Subsequently, the reaction mixture pressurized with CO_2 at 8 bar in 95 ^{o}C. After a certain time, the reactor was cooled down to room temperature and the excess gas was vented out. The catalyst was separated by centrifugation and final product analyzed by ^{1}H-NMR. In the recycle experiments, the catalyst separated by centrifugation and washed three times with methanol. Thereafter, the catalyst was dried under vacuum at 80 ^{o}C for 4 hours before the next use.

Characterization methods

The characterization of Zif-67 was performed by XRD (Brucker D8 advance difractometer, Bragg-Brentano geometry) using Cu Kα radiation source (λ= 1.54056 Å) at 40 kv and 45 Ma. The data collected as a 5o/s scanning speed. Gas adsorption-desorption isotherm and pore size distribution of products were measured by the volumetric method on Micrometrics instrument (ASAP 2020 analyzer). N_2 gas with purity> 99.999 % was applied for the measurements. For degassed the samples, they evacuated at 200 °C under vacuum for 200 min. The micro pore surfaces were analyzed by the Brunaver-Emmett-Teller (BET) and Langmuir method. The linearized BET and Langmuir equation were fit to data within the range $0.003 < P/P0 < 0.05$. The morphology of both ZIF-67 and ZnCo-ZIF-8 were measured with FE-SEM (FEI Nova 600). Thermal analysis technology (TGA) was measured on a Netzsch STA 409 thermal analyzer. Certain amount of compound was placed inside a crucible and heated from room temperature to 800 °C under a flow of nitrogen gas. The acidity and basicity of the samples determined by NH_3-TPD and CO_2-TPD, using AutoChem II 2920 machine. 0.1 g catalyst (ZIF-67) was located inside the machine and pretreated at 250 °C for 3 h. Subsequently the samples were cooled down to room temperature and saturated with dry and pure NH_3 or CO_2 gas. Afterwards, the helium blowed to the sample (20 ml/min) to carry the physical-absorbed CO_2 or NH_3 gas. Desorption process was performed from 30 to 270 °C at a 10 °C/min heating rate. All data was analyzed by a thermal conductivity detector [TCD]. ^{1}H NMR spectra of the reaction products were run on Bruker Avance III 500. FT-IR spectra were recorded on a SCIMITAR FTS 2000 spectrometer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed using Optima 4300DV, PerkinElmer wavelength coverage: 165-782nm.

Acknowledgements

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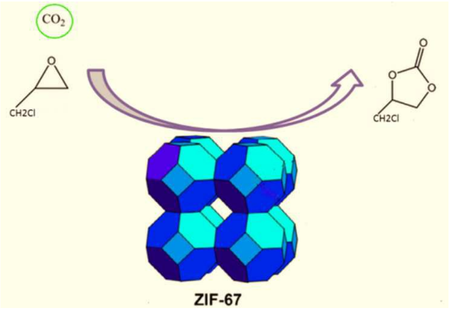
Table of contents:



ZIF-67 acts as a very efficient catalyst for the cycloaddition of CO_2 to epoxides synthesising cyclic carbonates with high selectivity, without any need of solvent or co-catalyst.