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Application of Covalent Organic Frameworks (COFs) in Cyclic Carbonate Production by a Green Way: An Overwiew †

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Abstract: One of the strategies of solving greenhouse problem is transformation CO_2 to valuable chemicals such as carbamates, cyclic carbonates, oxazolidones and tetramic acids. Among these chemicals, cyclic carbonates can be used in lithium-ion batteries as electrolyte. Cyclic carbonate production via CO_2 cycloaddition is feasible way in terms of thermodynamic and atom economy. However, CO_2 transformation processes require high energy. So, researchers have been studied several catalysts. Covalent Organic Frameworks (COFs) can be achieve success even under humid conditions in cyclic carbonate production via CO_2 cycloaddition. Features of COFs are low density, large surface area, adjustable pore size and structure.

Keywords: CO_2 cycloaddition; cyclic carbonate Production; CO_2 utilization; electrolyte developing for lithium-ion batteries

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1. Introduction

It has been known that global warming happens due to releasing greenhouse gases to the atmosphere. CO_2 is the major gas which causes global warming [1]. CO_2 capturing is possible via separating from exhaust gas mixture which occur because of burning fossil fuels. It is known that the exhaust gas composes of CO_2, nitrogen and some oxygenated compounds (SO_2, NO_2 and O_2). This process is called as post-combustion capture. The process can take place in industrial plants and power stations [2]. Utilization of this capturing CO_2 is an important strategy in terms of economic and environmental aspects. For CO_2 utilization, two routes have been developed by the researchers. These are directly using of CO_2 and transforming CO_2 to valuable chemicals.

CO_2 can be used directly in several industries such as production of fire-extinguishers, soft drinks, etc. Besides that, Supercritical CO_2 is a popular solvent for reactions and it has been used in nanoparticle synthesis. Another way to utilize CO_2 directly is to cultivate microalgae. This way seems interesting because cultivated microalgae can be used as biofuel feedstock.

However, it is not possible to consume whole industrial by-product and environmentally hazardous CO_2 via directly using. So, the researchers have found another way to evaluate CO_2. It can be possible to convert CO_2 to chemicals via several reactions such as CO_2 hydrogenation, CO_2 cycloaddition to epoxides, CO_2 carbonylation of amines or alcohols, etc. However, CO_2 using as a reactant is hard because of its low Gibbs free energy feature. So, the reactions include CO_2 need to high energy. To exceed this high energy barrier, one of the strategies is to react CO_2 with the compounds which have high Gibbs free energy such as methanol and hydrogen. The another strategy is to use heterogeneous catalyst in the reactions.

Heterogeneous catalysts possess several unique properties such as excellence stability, providing simplicity in separation. However, catalytic CO_2 conversion to the chemicals has also drawbacks. Since, the process requires high temperatures and pressures, high catalyst loading and long duration times. And, the conversion of the reactions is low because of stability tendency of CO_2 [1]. Researchers have developed new catalysts and methods to solve this problem.

Cyclic carbonates are important types of the carbonates which can be used as precursors to synthesize polycarbonates, polar solvents and electrolyte material for lithium-ion batteries. Cyclic carbonates are also suitable target product to CO_2 conversion, because they have three oxygen atom in their molecules. Cyclic carbonate production through cycloaddition of CO_2 to epoxides is an industrial process. This process is regarded as a green reaction because it does not need hazardous chemicals like phosgene and side products do not occur [1]. Several heterogenous catalysts which have been used in cyclic carbonate production from epoxides and CO_2 and their performance are presented in Table 1.

The aim of this review was to enlight the future of COFs in the cyclic carbonate production through cycloaddition of CO_2 to epoxides.

Table 1. Current heterogeneous catalysts applications for cycloaddition of CO_2 to epoxides.

Catalyst	**Reaction Conditions**	**Catalytic Activity**	**Reference**
bismuth-functionalized Metal Organic Framework (MOF)	* Photocatalytic reaction at 80 °C under atmospheric pressure during 24 h, propylene oxide, styrene oxide, epichlorohydrin, 2-(4-chlorophenyl) oxirane , tert-butyl glycidyl ether and 1,2-epoxy-3-phenoxypropane as reactants * tetra butyl ammonium bromide as a co-catalyst, solvent-free	99.9 % conversion for all epoxides	Siddig et al. (2022) [3]
$ZnCl_2/Al_2O_3$	* in a glass reactor at 60 °C, 4 atm during 6 h, styrene oxide as reactant * Tetrabutylammonium iodide as a co-catalyst, solvent-free	100 % yield	Bondarenko et al. (2019) [4]
Zn based MOF	* in a glass reactor at 80 °C, 2 atm during 20 h, styrene oxide as reactant * tetra butyl ammonium bromide as a co-catalyst, solvent-free	98 % yield, 99 % selectivity	Bondarenko et al. (2021) [5]
NH_2-functionalized imidazolium ionic liquid and B-doped mesoporous SiO_2	* in a high-pressure stainless steel autoclave at 110 °C, 20 atm during 6 h, propylene oxide as reactant * co-catalyst and solvent-free	99 % yield, 99 % selectivity	Ye at al. (2022) [6]

2. Definition, Synthesis, Properties and Applications of COFs

COFs compose of organic building units which link each other with strong covalent bonds. These organic building units can be C-C, C-N, C-O, B-O, C=N and C-Si. COFs have several chemical architectures such as 1D, 2D and 3D. COFs form the result of reversible condensation reactions. They have been accepted as crystalline porous solid materials.

Their features can be ordered as low density, high surface area, high stability under several chemical and thermal conditions, adjustable pore size and structure [7].

The researchers have been tested COFs in several applications such as drug delivery, chemical sensing, gas adsorption, catalysis, gas separation, proton conductivity, energy storage and chromatographic separation [7].

The synthesis methods of COFs show change with respect to desired linkage type. For example, COF-1 and COF-5 types materials possess B-O linkage. To synthesize COF-1, the researchers carried out self-condensation of 1,4-phenylenediboronic acid (BDBA). They obtained the material included layers which had hexagonal pores. On the other hand, COF-300, COF-43 are the several types of COFs which have C-N linkage. Among them, COF-300 was synthesized via imine condensation of aldehyde and amine linkers. COF-300 has 1360 m^2/g surface area. Compared to imine based COF-300, COF-43 has more stability because of its hydrazone linkage. COF-43 was synthesized condensation of aldehydes and hydrazide linkers. Another type of COFs is LZU-22. It can be possible to produce LZU-22 via condensation of dimethyl acetals and amines. It is accepted as azine-linked COF. Besides that, LZU-22 has –C=N- bond in its structure. It has been known that LZU-22 has high thermal stability [8]. Other types of COFs which have several linkages have been produced such as carbamate, borosilicate, phenazine and squaraine linkage. These various linkage types of COFs are effective on stability. Since properties and structures of the COFs originate from differences in linkages [9].

3. Cyclic Carbonate Production via CO_2 Cycloaddition to Epoxides on COFs

COFs have been used as catalyst in several reactions such as Michael addition, Diels-Alder, oxygen evolution and Heck-epoxidation tandem. This situation shows us it can be possible to use COFs as heterogeneous catalyst or catalyst carrier in other types of reactions [10]. COFs in CO_2 related applications is a relatively novel topic. And so, the researches in this area is scarce. And, it is desired to the material have specific properties for CO_2 capturing such as large CO_2 adsorption capability, high thermal and chemical stability, to reach high selectivity, to use more than once. So, COFs meet some of this desired specifications. However, researchers have still studied about developing stability through increasing the number of condensation reactions during the synthesis, increasing CO_2 uptake performance under high pressure conditions, and so on [7]. Several studies about cyclic carbonate production via CO_2 cycloaddition to epoxides on COFs are given below.

Yan et al. (2022) developed an ionic liquid-immobilized COF to produce cyclic carbonates without using solvent and co-catalyst at 40 atm pressure and 110 °C temperature during 12 h. They used different epoxides such as propylene oxide, epichlorohydrin, 1,2-epoxyhexane, 1,2-epoxyoctane, butyl glycidyl ether, 3,4-epoxy-1-butene and styrene oxide. The researchers obtained maximum yield (100%) for propylene oxide [11].

Roeser er al. (2012) synthesized triazine-based covalent organic frameworks which were named as CTF-1 (1,4-dicyanobenzene based) and CTF-P (2,6-dicyanopyridine based). The COFs were obtained in zinc chloride solvent medium at 600 °C via trimerization of the before mentioned dicyanocompounds. Surface area of the catalysts were found as 2087 m^2/g for CTF-1 and 1745 m^2/g for CTF-P. Reactions were carried out in a high pressure stainless steel reactor at 130 °C and 7 atm during 4 h. Starting epoxide was selected as epichlorohydrin. The researchers reached 100 % conversion and nearly 95 % chloropropene carbonate selectivity for both catalysts under solvent-free conditions [12].

Tong et al. (2022) produced a cobalt loaded salen-based covalent organic framework. They used this catalyst in the synthesis of cyclic carbonates from propylene oxide, butylene oxide, epichlorohydrin, butyl glycidyl ether, glycidyl ether, allyl glycidyl ether, styrene oxide, cyclohexane oxide, diglycidyl ether, 1,3,5-tris(glycidyloxy)benzene, trimethylene oxide and 3-ethyl-3-methyloloxetane. They carried out the catalytic tests in a stainless steel autoclave at 20 atm CO_2 pressure and 120 °C temperature during 4 hours in the presence of TBAB. They obtained over 90% conversion, product selectivity and yield for propylene oxide, butylene oxide, epichlorohydrin, butyl glycidyl ether, glycidyl ether, allyl glycidyl ether, styrene oxide [13].

Singh and Nagaraja et al. (2021) developed polar functionalized COF as a metal-free heterogeneous catalyst. Polar functionality of the catalyst originated from –NH (basic site of the catalyst), and –SO_3H (acid sites of the catalyst) groups. The reactions occurred at 1 atm pressure and 80 °C temperature during 24 h in a stainless steel reactor with magnetic stirrer in the presence of TBAB. Before the reactions synthesized catalyst was activated at 100 °C in vacuum during 12 h. Catalyst reusability tests were made via washing catalyst with acetone and drying it. Among the used epoxide starters, the best results were obtained for propylene oxide and epichlorohydrin. At this time, conversion and product selectivity were determined as nearly 100%. Recycling and reusing catalyst during five cycle were conducted and no significant loss occurred in catalytic conversion [14].

Das et al. (2021) synthesized TpPa-1 photocatalyst for photocatalytic CO_2 cycloaddition to epoxides under visible light. TpPa-1 was formed via reaction between TFP (2,4,6-triformyl phloroglucinol) and p-phenylenediamine in dimethyl formamide solvent under inert atmosphere and at 140 °C. The reaction setup composed of a balloon included CO_2, LED light source, magnetic stirrer and flask. For styrene oxide epoxide source, researchers obtained 83% cyclic carbonate yield with TBAB as co-catalyst and acetonitrile as solvent, at 80 °C and under 1 atm CO_2 pressure [15].

4. Conclusions

Global warming is a serious problem that threat our planet. To overcome this problem, utilization of CO_2 which originates from industrial processes is a hot topic in the scientific area. Via direct utilization CO_2 is not enough to evaluate all releasing gas. So, the researchers have developed a strategy to generate chemicals from CO_2 based reactions. However, these reactions require high energy because of stable form and low Gibbs Free Energy of CO_2. So, it can be used co-reactants which have high Gibbs Free Energy and catalyst to overcome this case. COFs are solid and crystalline materials which comprise covalent bonded organic building units such as C-C, C-N, C-O, B-O. In CO_2 related applications COFs have success because of its unique properties such as high surface area, huge CO_2 adsorption capability and high stability under several chemical and thermal conditions. Only drawback of this material is regarded as its low stability under high pressure conditions. Cyclic carbonates are important materials due to their application areas. They can be used as polar aprotic solvent, electrolyte in lithium ion batteries and in polycarbonate production. As an industrial process, cyclic carbonate synthesis via cycloaddition of CO_2 to epoxides is an important process. Since, it occurs without hazardous chemicals. Besides that, no side reaction happens as a result of this reaction. COFs using in this reaction is a relatively novel in the literature. And, it was seen that the researchers obtained good results (quite high conversion, yield and selectivity) in the cyclic carbonate synthesis via carbonylation of epoxides at low temperatures for especially propylene oxide, styrene oxide and epichlorohydrin reactants.

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