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# Application of Covalent Organic Frameworks (COFs) in Cyclic Carbonate Production using a Green Method: An Overview †

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**Abstract:** One of the strategies suggested for solving the greenhouse gas problem is the transformation of $CO_2$ into valuable chemicals, such as carbamates, cyclic carbonates, oxazolidones and tetramic acids. Among these chemicals, cyclic carbonates can be used in lithium-ion batteries as electrolytes. Cyclic carbonate production via $CO_2$ cycloaddition is feasible method in terms of thermodynamic and atom economy. However, $CO_2$ transformation processes require high energy. So, researchers have studied several catalysts. Covalent organic frameworks (COFs) can have success even under humid conditions in cyclic carbonate production via $CO_2$ cycloaddition. The features of COFs are low density, large surface area and adjustable pore size and structure.

**Keywords:** $CO_2$ cycloaddition; cyclic carbonate production; $CO_2$ utilization; electrolyte development for lithium-ion batteries

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## 1. Introduction

It is known that global warming occurs due to the release of greenhouse gases into the atmosphere. $CO_2$ is a major gas which causes global warming [1]. $CO_2$ capture is possible via its separation from the exhaust gas mixture that occurs due to the burning of fossil fuels. It is known that exhaust gas is composed of $CO_2$, nitrogen and some oxygenated compounds ($SO_2$, $NO_2$ and $O_2$). This process is called post-combustion capture. The process can take place in industrial plants and power stations [2]. The utilization of $CO_2$ capture 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 the direct utilization of $CO_2$ and the transformation of $CO_2$ into valuable chemicals.

$CO_2$ can be used directly in several industries, such as production of fire-extinguishers and soft drinks, among other things. In addition, 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 method is interesting because cultivated microalgae can be used as biofuel feedstock.

However, it is not possible to entirely consume the environmentally hazardous $CO_2$ industrial by-product via its direct use. Therefore, the researchers have found another way to evaluate $CO_2$. It is possible to convert $CO_2$ to chemicals via multiple reactions, such as $CO_2$ hydrogenation, $CO_2$ cycloaddition to epoxides and the $CO_2$ carbonylation of amines or alcohols. However, using $CO_2$ as a reactant is difficult because of its low Gibbs free energy features. So, the reactions involving $CO_2$ need high energy. To overcome this high energy barrier, one of the strategies is to react $CO_2$ with compounds that have high Gibbs free energy, such as methanol and hydrogen. Another strategy is to use heterogeneous catalysts in the reactions.

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

Cyclic carbonates are important types of 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 products for $CO_2$ conversion, because they have three oxygen atoms in their molecules. Cyclic carbonate production through the cycloaddition of $CO_2$ to epoxides is an industrial process. This process is regarded as a green reaction because it does not require hazardous chemicals, such as phosgene, and side products do not occur [1]. Several heterogenous catalysts that have been used in the cyclic carbonate production of epoxides and $CO_2$ are presented in Table 1, along with their performances.

**Table 1.** Current heterogeneous catalysts applications for the 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<br>- tetra butyl ammonium bromide as a co-catalyst, solvent-free | 99.9% conversion for all epoxides | Siddig et al. [3] |
| $ZnCl_2/Al_2O_3$ | - in a glass reactor at 60 °C, 4 atm during 6 h, styrene oxide as reactant<br>- Tetrabutylammonium iodide as a co-catalyst, solvent-free | 100% yield | Bondarenko et al. [4] |
| Zn-based MOF | - in a glass reactor at 80 °C, 2 atm during 20 h, styrene oxide as reactant<br>- tetra butyl ammonium bromide as a co-catalyst, solvent-free | 98% yield, 99% selectivity | Bondarenko et al. [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 for 6 h, propylene oxide as reactant<br>- co-catalyst and solvent-free | 99% yield, 99% selectivity | Ye at al. [6] |

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

## 2. Definition, Synthesis, Properties and Applications of COFs

COFs are composed of organic building units, which link with each other through strong covalent bonds. These organic building units can be C–C, C–N, C–O, B–O, C=N and C–Si. COFs have multiple chemical architectures, such as 1D, 2D and 3D. COFs form as the result of reversible condensation reactions. They have been accepted as crystalline porous solid materials. Their features can be classified as low density, with high surface areas and high stability under several chemical and thermal conditions, as well as having adjustable pore sizes and structures [7].

Researchers have 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 the desired linkage type. For example, the COF-1 and COF-5 types of materials possess B–O linkage. To synthesize COF-1, researchers have carried out the self-condensation of 1,4-phenylenediboronic acid (BDBA). They obtained a material with layers that had hexagonal pores. On the other hand, COF-300 and COF-43 are types of COFs that display C–N linkage. Of the two, COF-300 was synthesized via the imine condensation of aldehyde and amine linkers. COF-300 has a 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 through the condensation of aldehydes and hydrazide linkers. Another type of COFs is LZU-22. It is possible to produce LZU-22 via the condensation of dimethyl acetals and amines. It is accepted as an azine-linked COF. Moreover, LZU-22 has an –C=N- bond in its structure. It is known that LZU-22 has high thermal stability [8]. Other types of COFs, which have several linkages, such as carbamate, borosilicate, phenazine and squaraine linkages, have been produced. These various COFs linkage types are effective in terms of stability, since the properties and structures of COFs originate from differences in linkages [9].

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

COFs have been used as catalysts in several reactions, such as Michael addition, Diels–Alder, oxygen evolution and the Heck-epoxidation tandem. This reveals that it cis possible to use COFs as an heterogeneous catalyst or a catalyst carrier in other types of reactions [10]. The presence of COFs in $CO_2$-related applications is a relatively novel topic. Therefore, research in this area is scarce. Additionally, it is desirable for the material to have specific properties for $CO_2$ capture, such as large $CO_2$ adsorption capability and high thermal and chemical stability in order to achieve high selectivity so that it can be used more than once. COFs meet some of these desired specifications. However, researchers are still studying the improvement of stability by increasing the number of condensation reactions during 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 discussed below.

Yan et al. [11] 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.

Roeser et al. [12] synthesized triazine-based covalent organic frameworks, which were named 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 the trimerization of the above-mentioned dicyanocompounds. The surface area of the catalysts were found to be 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 for 4 h. Starting epoxide was selected as epichlorohydrin. The researchers reached a 100% conversion rate and a nearly 95% chloropropene carbonate selectivity for both catalysts under solvent-free conditions.

Tong et al. [13] 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 for 4 h in the presence of TBAB. They obtained an over 90% conversion rate, product selectivity and yield for propylene oxide, butylene oxide, epichlorohydrin, butyl glycidyl ether, glycidyl ether, allyl glycidyl ether and styrene oxide.

Singh and Nagaraja et al. [14] developed polar functionalized COF as a metal-free heterogeneous catalyst. The 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 over 24 h in a stainless steel reactor with a magnetic stirrer in the presence of TBAB. Before the reactions were synthesized, the catalyst was activated at 100 °C in vacuum for 12 h. Catalyst reusability tests were carried out by washing the 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 being nearly 100%. The catalysts were recycled and reused for five cycle, and no significant loss occurred in catalytic conversion [14].

Das et al. [15] synthesized TpPa-1 photocatalyst for photocatalytic $CO_2$ cycloaddition to epoxides under visible light. TpPa-1 was formed via the reaction between TFP (2,4,6-triformyl phloroglucinol) and p-phenylenediamine in dimethyl formamide solvent under an inert atmosphere and at 140 °C. The reaction setup was composed of a balloon, $CO_2$, LED light source, magnetic stirrer and flask. For the styrene oxide epoxide source, researchers obtained a 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 and Remarks

Global warming is a serious problem that threatens our planet. To overcome this problem, the utilization of $CO_2$, which originates from industrial processes, is a hot topic in multiple scientific fields. The direct utilization $CO_2$ is not enough to deal with all the released gas. So, the researchers have developed a strategy to generate chemicals from $CO_2$-based reactions. However, these reactions require high energy because of the stable form and low Gibbs free energy of $CO_2$. Thus, catalysts and co-reactants with high Gibbs free energy can be used to overcome this issue. COFs are solid and crystalline materials which comprise covalent bonded organic building units, such as C–C, C–N, C–O and B–O. In $CO_2$-related applications, COFs are successful because of their unique properties, such as high surface areas, huge $CO_2$ adsorption capabilities and high stabilities under several chemical and thermal conditions. The only drawback of these materials is their low stability under high-pressure conditions. Cyclic carbonates are important materials due to their varied application possibilities. They can be used as polar aprotic solvents, electrolytes in lithium-ion batteries and in polycarbonate production. As an industrial process, cyclic carbonate synthesis via the cycloaddition of $CO_2$ to epoxides is an important process, as it occurs without hazardous chemicals. In addition, no side reactions occur as a result of this reaction. The COFs used in this reaction are relatively novel in the literature. Additionally, it can be seen that researchers obtained good results (fairly high conversion rates, yields and selectivity) in the cyclic carbonate synthesis via the carbonylation of epoxides at low temperatures, especially for propylene oxide, styrene oxide and epichlorohydrin reactants.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/IOCN2023-14479/s1, Presentation Video: Application of Covalent Organic Frameworks (COFs) in Cyclic Carbonate Production by a Green Way: An Overview.

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