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Heterogeneous Catalysts for CO_2 Chemical Transformations in Sustainable Pathways

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ABSTRACT

The increasing demand for green and sustainable fuel and industrial practices has emerged as a crucial issue in the past year, particularly within the chemical industry. Most of them, the capture and utilisation of carbon dioxide (CO_2) by porous heterogeneous material, particularly COF, into value-added products is a promising approach to address the sustainable energy crisis and control the reduction of the atmospheric CO_2 content for environmental remediation. Nowadays, catalytic cycloaddition of carbon dioxide into various cyclic carbonates like α-alkylidene and 2-oxazolidinones cyclic carbonates via CO_2 fixation reaction has focused on the creation of low-cost, environmentally friendly, and efficient catalysts. Looking ahead, this chapter offers a visionary viewpoint on harnessing heterogeneous materials for the sustainable capture and conversion of CO_2, which is a promising sustainable reaction.

Keywords: *CO_2 Fixation; Cycloaddition; Green Pathway; Heterogeneous Catalysis*

Introduction

Due to increased human activities, the manufacturing revolution, and such widespread activities as deforestation, fossil fuel consumption and industrialisation, carbon dioxide emissions have histrionically increased, which is a significant impact on climate change. The use of chemicals from industry has increasingly demonstrated significant scientific and economic value, garnering widespread attention. Through the development of efficient catalytic technology, researchers are going through a new phase in the twenty-first century regarding an ever-growing demand for new, proficient and green methods to carry out chemical reactions (Du, Ouyang & Tan, 2021). Although the synthetic strategies were related with some disadvantages, such as low selectivity, low functional group tolerance, hazardous reaction conditions, and finally recyclable deficiency, etc. To overcome these problems, production of new synthetic pathways is highly demanding. For this reason, During the past two decades, various categories of porous materials, specifically porous carbons and newly developed metal–organic frameworks (MOF) and porous organic polymers (POP) more one covalent organic framework (COF), owning their periodic framework and having a tuneable porosity, highly crystalline materials and high surface area, have been widely applied for capture and utilisation of CO_2. Due to these merits, nowadays some COF materials show numerous applications in nanotechnology, including electrocatalysis, organic catalytic transformations, and photocatalysis. On the other hand, due to the huge amount of CO_2 emissions, the normal temperature of the earth has been altered in recent times, and as a result, global warming is gaining attention. In this respect, numerous studies to suppress CO_2 emissions or adsorption (carbon capture and storage, CCS) have been conducted (Park *et al.*, 2022). In the past researchers focused on limiting fossil fuels but mainly used sources of CO_2 emissions and emerging alternative energy systems. From a sustainability perspective, in a recent study, different protocols for the carbon dioxide fixation into different organic substrates have been used (Karishma *et al.*, 2024; Chen *et al.*, 2024). The production of cyclic carbonates is fully atom-efficient, economically viable, and has a wide range of industrial applications, including use as electrolytes in lithium-ion batteries, fuel additives, intermediates in pharmaceutical manufacturing, and in the production of lubricants and polymers. Numerous heterogeneous catalytic systems – particularly those based on transition metals – have been developed and extensively investigated for carbon dioxide cycloaddition into fine chemicals. Because of CO_2 itself being both thermodynamically stable and kinetically inert, converting it efficiently and selectively typically demands extreme reaction conditions. Covalent organic frameworks (COFs), with their distinctive structural features, stand out as highly adaptable materials suitable for applications such as heterogeneous catalysis, gas capture and storage, sensing technologies, and optoelectronic devices. The role and function of the supported materials over the mediated sustainable liquid phase reactions, like cyclic carbonate synthesis reactions, 2-oxazolidinones, *α*-alkylidene cyclic carbonates, etc., under CO_2 absorption.

Literature Review

Application of Heterogeneous Catalysts Over Some Organic Transformations in Presence of CO_2

Cyclic Carbonate Synthesis from Epoxide

Because of the ecological and economical concerns and CO_2 being nontoxic, cheap, and abundant, the researchers give more attention to chemical CO_2 fixation into valuable chemicals (Pal, De & Bharadwaj, 2022). One of the most powerful synthetic methods utilising CO_2 for the production of five-membered cyclic carbonates from epoxide is demonstrated in Figure 1. Various other value-added chemicals like carbamates, glycols, dialkyl carbonates and pyrimidines can be prepared from cyclic carbonate. For the production of cyclic carbonates, the conventional technique uses poisonous and hazardous materials. Therefore, synthetic chemists discover greener pathways where epoxide and CO_2 combine to offer cyclic carbonate. Yano *et al.* (1997) firstly reported metal oxide-catalysed cyclic carbonate synthesis. MgO, which is easily available in the market, catalysed the cycloaddition of carbon dioxide with epoxides to provide cyclic carbonates. But in that case at 2 MPa of carbon dioxide pressure and 135 °C temperature for 12 h in a DMF solvent medium, only 60 % yields of styrene carbonate were obtained. Further on for the reaction, Yamaguchi *et al*. (1999) reported a bimetallic oxide-based catalyst at 0.5 MPa CO_2 pressure and 100-120 °C temperature in DMF for 15-24 h (Then some researchers have developed more superior and effective catalytic systems for the cyclic carbonate synthesis under solvent-free conditions, which is a much greener and cost-effective route). Various Co-catalysts like TBAB, TBAI, KI etc. were utilised for the ring-opening reaction of epoxides via nucleophilic attack in most of the cases. Several metals, such as Al, Cr, Co and Sn, supported porphyrin-based catalysts that were well known for this reaction. However, in maximum cases the catalyst either required high CO_2 pressure or they are homogeneous in nature. Both the reaction conditions were not suitable. As a result, Al complex was anchored on Merrifield resin for five-membered cyclic carbonate synthesis under atmospheric pressure, and it was first reported as a heterogeneous catalyst that could catalyse the reactions at 1 atmospheric pressure (He *et al*., 2023; Wang *et al*., 2023). A variety of metal-free catalytic systems were reported just to avoid the contamination of metal with product (Sarkar, Ghosh & Islam, 2022). Since then, many researchers developed much more perfect and greener catalytic systems under the green pathway (Singh, Prakash & Nagaraja, 2023; Sarkar, Ghosh & Islam, 2022).

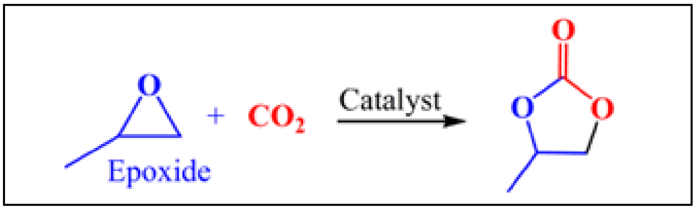

Figure 1: Scheme for Cycloaddition Involving CO_2 and a Terminal Epoxide

The following steps are involved in the process of synthesising a cyclic carbonate's reaction from CO_2 and epoxides catalysed by a bifunctional catalytic system. Metal centre acts as lewis acid centre, and the halide ion acts as a nucleophile in this bifunctional catalytic system. In the initial step, halide ions disconnected from the cocatalyst, and at the same time, the oxygen centre of the epoxide produced a coordination to raise the electrophilic character of the carbon atom where nucleophole halide ion attacks to give an alkoxide intermediate. Alkoxide intermediate with a negative charge will react with the carbon atom of carbon dioxide to produce a linear carbonate structure (Figure 2). Then the cyclic carbonate is formed via an intramolecular ring-closing nucleophilic reaction.

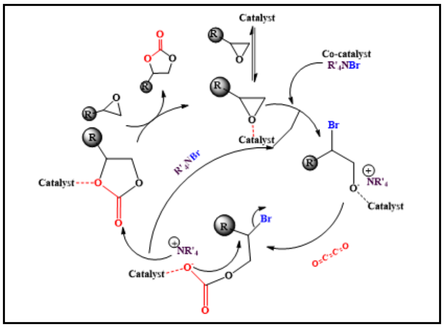

Figure 2: Plausible Reaction Mechanism for Cyclic Carbonate Synthesis Based on Literature

α-Alkylidene cyclic carbonates from propargylic alcohol

The CO_2 fixation reaction is greatly attractive and essential in the vision of environmental as well as economic issues, as it is the most important greenhouse gas but also a cheap, abundant, easily available C1 resource and renewable. Various methods have been promoted to CO_2 into several high value chemical but one of them most promotive synthetic path of α-Alkylidene cyclic carbonates is the carboxylative cyclization of easily obtainable propargyl alcohols and CO_2 (1atom). The cyclisation reaction of propargyl alcohols and CO_2 was developed by a transition metal, phosphine and carbene as the efficient catalyst.

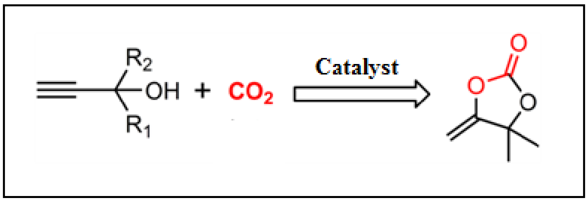

Figure 3: Scheme for the Synthesis of α-Alkylidene-Substituted Cyclic Carbonates

α-alkylidene cyclic carbonates have been extensively utilised as the intermediates of pesticide, pharmaceutical, and fine chemical production. These cyclic carbonates are also very useful for a variety of organic transformations. Numerous materials have been efficiently used for the production of cycloaddition of carbon dioxide via this carboxylative cyclisation process. Few of them – phosphines, alkoxide-functionalised imidazolium betaines/CO_2 adducts, bicyclic guanidines, N-heterocyclic olefin/CO_2 adducts, azole-anion-based aprotic ionic liquids, and N-heterocyclic carbene/CO_2 adducts, etc. – have been employed as metal-free catalysts for the cyclisation. Moreover, these reaction conditions are highly problematic, like high temperature and CO_2 pressure. Hence, the improvement of well-organized catalyst for the CO_2 fixation reaction under sustainable conditions are still highly valued and actively pursued. Researchers promoted more and more ideal and greener catalytic systems for the synthesis of α-alkylidene cyclic carbonates with time. Recently, Giri and his group (2024) developed Cu NP-embedded MOF (Cu-NPs/MOF) which has high catalytic performance for *α*-alkylidene cyclic carbonates by CO_2 coupling with propargylic amines and alcohols. Moreover, Yang *et al*. (2024) demonstrated carboxylative cyclisation of propargyl alcohols with CO_2 at room temperature using by Silver Nanoparticles on Porphyrinic Triazine-Based Frameworks.

In Figure 4, a probable mechanism is demonstrated for the synthesis of α-alkylidene cyclic carbonates in the presence of a catalyst (Hu *et al*., 2016). It is believed that the CO_2 incorporation into propargyl alcohols proceeds through the following reaction pathway:

Firstly, the catalyst (1) activates the propargyl alcohol, followed by the base facilitating CO_2 activation, leading to the formation of a carbonate intermediate salt. The catalyst interacts with the triple bond, promoting the formation of intermediate 2 by facilitating

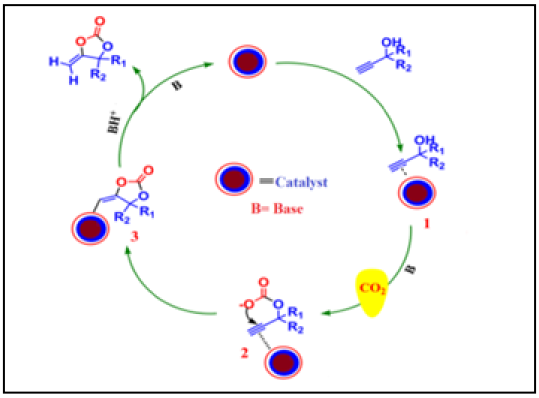

Figure 4: Probable Reaction Mechanism for α-Alkylidene Cyclic Carbonates Synthesis

the bonding between the adjacent oxygen atom and the internal carbon of the C≡C group. Subsequently, a five-membered exo-trig cyclisation (3) takes place, followed by proton abstraction from BH^+, leading to the formation of the target product and regeneration of the catalyst under optimised conditions. For activation of the *alkyne, the catalyst played* important parts to provide a driving force for the annulation reaction.

2-Oxazolidinones Synthesis

2-Oxazolidinones are saturated five-membered cyclic carbamates (Figure 5) that have extensive uses as chiral auxiliaries, chemical intermediates and antibacterial pharmaceuticals in medicinal and synthetic chemistry (Giri *et al*., 2024). Near the beginning, the synthesis of oxazolidinones was performed via the reactions of 1,2-amino alcohols and phosgene or its derivatives or amino alcohols with CO_2 under high pressure (Arshadi *et al*., 2019). Later on, various techniques have been promoted to manufacture oxazolidinones, including the reaction of CO_2 with propargylamines or ethyleneimines, the cycloaddition reaction of epoxides with isocyanates, and the carbonylation reaction of *β*-amino alcohols with CO_2 or dialkyl carbonates. But, in recent times, propargylic amine cyclisation with CO_2 has concerned much attention to get 2-oxazolidinones. In this route CO_2 is utilised as a highly suitable C1 resource to obtain various organic compounds. Various catalytic systems for the carboxylative cyclisation of propargylic amines with CO_2 have been promoted, which covers transition metal-based catalysts such as Pd, Ru, Ag, Cu, Au, and organocatalysts like N-heterocyclic carbene, superbases, and protic ionic liquids. Particularly, Yamada *et al*. have confirmed that AgOAc is an effective catalyst for the reaction of various propargylic amines and carbon dioxide into 2-oxazolidinones under mild conditions (Yoshida *et al*., 2009). Recently Mondal and his team (2025) are going on the synthesis of oxazolidinones in the presence of a highly active 2D imine-linked covalent organic framework (Ag@TPT-TP COF) under mild conditions. Moreover, Srinivasappa and his team (2023) explored the selective one-pot strategy for CO_2 fixation into "oxazolidinone" by using stable porous trimetallic oxide foam (PTOF) as a new catalyst. Thanks to its distinctive synthesis method and the unique combination and proportion of metal oxides, the PTOF catalyst displayed highly interconnected porous channels along with uniformly distributed active sites on its surface. Well ahead, the PTOF catalyst was screened for the fixation of CO_2 into oxazolidinone

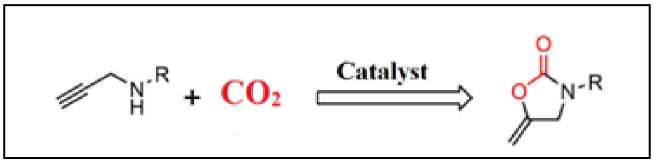

Figure 5: Scheme for the Synthesis of 2-Oxazolidinones

Most of the protocols for the synthesis of oxazolidinone have certain limitations, such as long reaction times, utilisation of high-pressure CO_2, limited substrate scope, harsh reaction conditions and requiring toxic reagents. But nowadays, therefore, a convenient, green, low-cost, large-range substrate-scope protocol which works under moderate reaction conditions will be particularly favoured. Therefore, designing highly efficient heterogeneous catalysts with densely packed basic and catalytic sites holds great potential for the effective capture and conversion of CO_2 into 2-oxazolidinones under ambient conditions. Thus, developing highly efficient heterogeneous catalysts with concentrated basic and catalytic sites is crucial for the effective capture and conversion of CO_2 into 2-oxazolidinones under ambient conditions (Rani, Das & Nagaraja, 2025).

Conclusion

In this view it is concluded the current status and major challenges and opportunities in the conversion of CO_2 into more valuable chemicals using chemical catalysis are more highlighted. This process can be effectively endorsed by various kinds of newly synthesised porous heterogeneous catalysts with Lewis acidic and nucleophilic sites. Moreover, Covalent Organic Frameworks (COFs) are indeed a promising class of materials due to their organic composition and flexibility in structure. The key advantages mentioned, such as their low cost and readily available monomer units, make them highly attractive compared to metal-containing inorganic catalysts or Metal-Organic Frameworks (MOFs), which can be more expensive and sometimes harder to synthesise or scale. The ability to tailor the electronic and steric properties of COFs by selecting different monomer units is one of their most notable features. This fine-tuning capability allows researchers to design COFs with specific functionalities, such as optimised surface areas, porosity, and chemical reactivity, which are essential for applications like CO_2 capture and reduction. The structural tunability of COFs can also enhance their selectivity and efficiency in these reactions, enabling better performance in energy conversion and storage technologies, like carbon capture or catalysis for the production of valuable chemicals. These materials combine the structural advantages of COFs with the enhanced catalytic properties provided by metal centres to create a hybrid material that can be tailored for a range of important reactions, including coupling reactions, carbonylation reactions, and CO_2 fixation reactions. Their catalytic activity was observed in coupling reaction for the synthesis of cyclic acetals and dicoumarol, carbonylation reaction for the preparation of α-ketoamides and finally carbon dioxide fixation reaction for the production of cyclic carbonate from epoxide, α-alkylidene cyclic carbonates from propargylic alcohol and 2-oxazolidinones. The reaction conditions were optimised by varying several solvents, catalyst amount, temperature etc. to obtain the highest yield of the desired products. These catalytic systems are highly stable and recyclable. This chapter judges a significant development in the field of porous polymeric network-based heterogeneous catalysis and gives high inspiration for the synthesis of reusable and recyclable heterogeneous material for diverse CO_2 conversions into value-added fine chemicals.

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