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Catalytic applications of porous organic polymers in CO_2 fixation

Compiled by Erfan Abdoli

Erfan Abdoli was born in Kermanshah, Iran in 1997, and has already accomplished impressive feats in his academic and research career. He completed his undergraduate studies in Medical Chemistry at Azad University in Kermanshah, Iran in 2021, and has since continued his education by pursuing a master's degree in Organic Chemistry starting in 2022, with the esteemed Professor Mohammad Ali Zolfigol as his supervisor.

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran
Email: erfanabdoli7697@gmail.com

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

In our modern industrialized era, environmental concerns and energy issues have become of utmost importance. The undeniable impact of climate change, partly attributed to CO_2 emissions, has created an urgent necessity for sustainable techniques to transform CO_2 [1-3]. A revolutionary advancement in many technologies and industries has been made through the development of porous organic polymers (POPs), a new category of porous materials. These materials possess exceptional characteristics such as high surface areas, robust physical and chemical stability, and adjustable organic functionalities. As a result, they hold significant promise for highly effective CO_2 adsorption and efficient conversion [4]. POPs are formed by covalently bonding lighter elements (C, H, B, O, N, S, P, etc.) through cross-linking [5]. Both homogeneous and heterogeneous catalysts play a crucial role in facilitating the adsorption of CO_2 through cycloaddition reactions. Heterogeneous catalysts include metal complexes, modified molecular sieves, metal-organic frameworks (MOFs), and polymers [6].

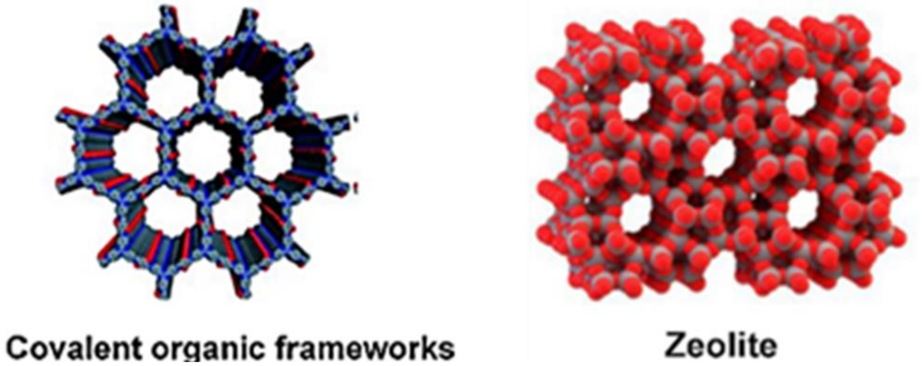
Currently, the most effective approach for utilizing CO_2 involves catalytic production of cyclic carbonates and polycarbonates by converting CO_2 and epoxides. These products possess desirable properties, such as high boiling points, low toxicity, and low vapor pressure. Traditionally, cyclic carbonates were synthesized using the highly toxic phosgene. However, a more environmentally friendly method involves incorporating CO_2 into the C-O bond of an epoxide substrate, presenting a greener pathway for cyclic carbonate synthesis [7].

POPs have demonstrated excellent performance in various fields, including gas adsorption/separation, sensing, catalysis, electrocatalysis, and batteries [8]. Notable examples of POPs include zeolitic imidazole frameworks (ZIFs), covalent microporous polymers (CMPs), metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and nanoporous ionic organic networks (NIONs) [9-10]. **Scheme 1** illustrates several types of POPs.

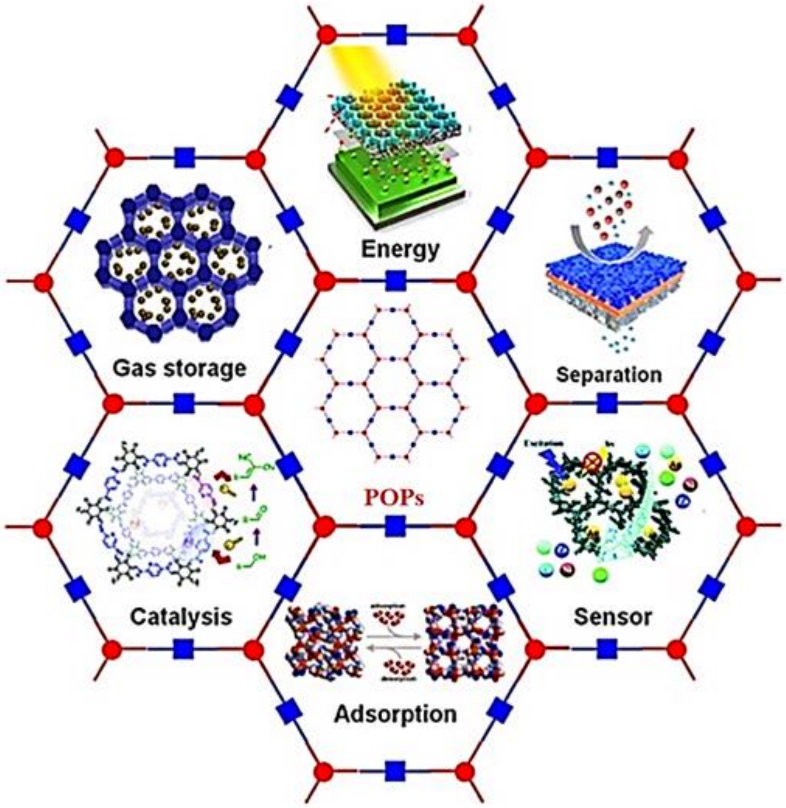
These materials offer distinct advantages, such as affordability, durable nanopores with exceptional porosity, high activity and stability, and adjustable photoelectric properties, which have made them highly sought-after in various fields of research, including photocatalysis [11-12].

In the early 2000s, Yaghi et al. introduced a series of novel porous two-dimensional crystalline polymers known as covalent organic frameworks (COFs). These COFs were created through a condensation reaction between boronic acid (BDBA) and hexahydroxy triphenylene (HTTP) [13-14]. COFs can be classified into two categories: two-dimensional (2D) and three-dimensional (3D) COFs. In 2D COFs, the building blocks exhibit geometric symmetry, and the organic units are covalently bonded, forming restricted 2D sheets that stack together through p-p interactions to create a layered structure [15].

COF materials are synthesized by covalently linking organic molecules in a repetitive manner, resulting in a porous crystal structure that is ideal for gas adsorption and storage. Extensive efforts have been dedicated to designing and synthesizing COF-based materials for various electrochemical applications, including fuel cell electrodes, membranes, supercapacitors, and batteries [16-17]. **Scheme 2** showcases some of the applications of POPs.



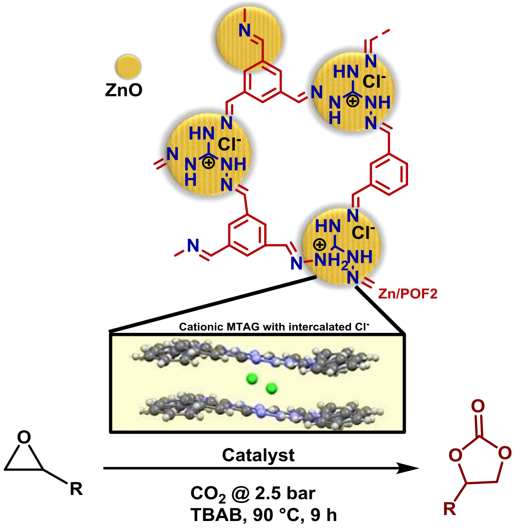
Scheme 1. Several types of porous organic polymers [9-10].



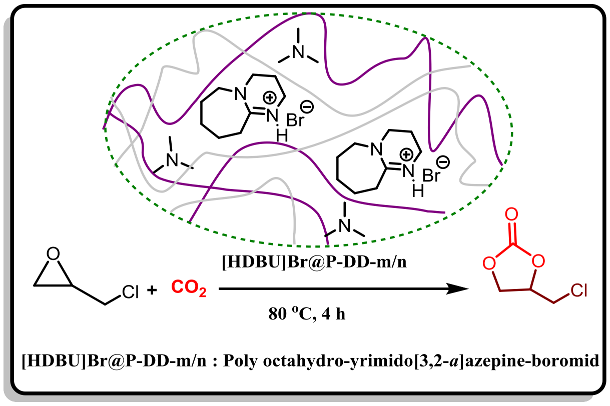
Scheme 2. Several different applications of POPs [16-17].

Abstracts

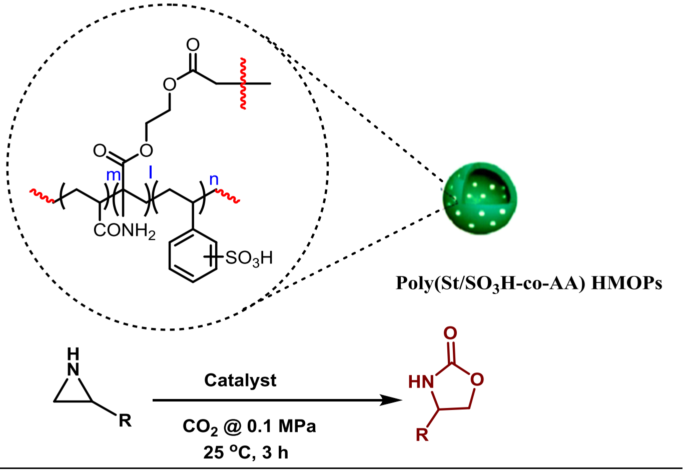
(A) In 2022, Ji and colleagues made significant advancements by developing a series of bifunctional catalysts based on metal localizations and imidazolium salt-containing ionic porous organic polymers (POPs). These catalysts demonstrated the ability to perform dual functions in CO_2 conversion. The metal ions, such as Zn and Al, played a crucial role as epoxide activating sites, while the counter anions associated with the ionic building units in the POPs acted as nucleophiles for CO_2 conversion. The presence of N-rich functionalities, Lewis acidic Zn (II) centers, and the CO_2-philic porous architecture motivated them to explore the catalytic performance of Zn/POFs in the conversion of CO_2 and epoxides into cyclic carbonates [18].



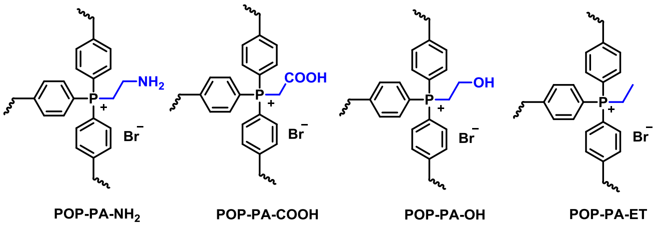
(B) The conversion of CO_2 into valuable cyclic carbonates holds immense potential and sustainability in addressing energy and ecological challenges. In this study, a series of porous organic polymer-supported ionic liquids (PSILs) called [HDBU]Br@P-DD-m/n were synthesized through a one-pot four-component reaction involving DMAEMA (dimethylamino ethyl methacrylate), DVB (divinylbenzene), 4-bromobutyric acid, and DBU (diazabicyclo[5.4.0]undec-7-ene). The [HDBU]Br@P-DD-m/n materials obtained were thoroughly characterized and subjected to an initial assessment. Subsequently, their catalytic performance in facilitating the cycloaddition of CO_2 and epichlorohydrin (ECH) was evaluated under the conditions of 80 °C temperature and 1 atmosphere CO_2 pressure for a duration of 4 hours [19].



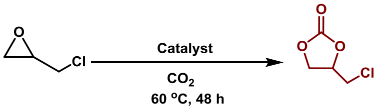
(C) Green and sustainable chemistry poses a significant challenge when it comes to metal-free catalysis. However, functional hosts offer distinct advantages in CO_2 conversion reactions by utilizing their nitrogen- and oxygen-rich functional sites to stabilize CO_2 additives and intermediates. This results in a high yield (>90%) of carbonate production. In a remarkable study by Coskun and colleagues, they introduced sterically constrained NHC ligands for CO_2 fixation. Even at room temperature, and under low CO_2 pressure (0.1 MPa), an impressive conversion efficiency of 97% was achieved [20].



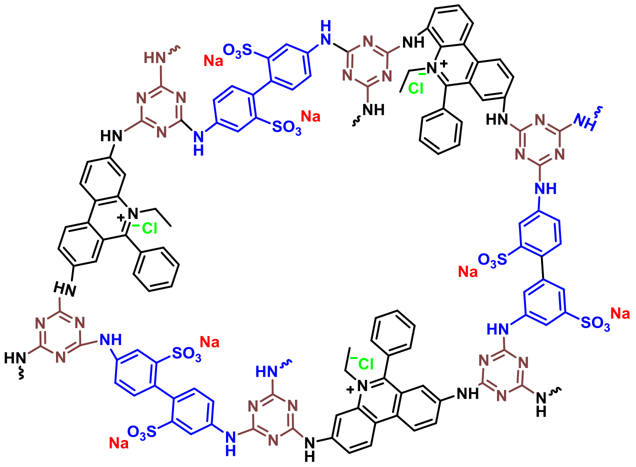
(D) A simple post-synthetic approach was employed to obtain various polar functionalized porous organic polymers (POP-PA-COOH, POP-PA-OH, and POP-PA-NH_2). These compounds exhibit remarkable potential as effective heterogeneous catalysts in the cycloaddition reaction of CO_2 with epoxides, all without the need for additional co-catalysts, under the mild reaction conditions. Interestingly, it has been demonstrated that POP-PA-NH_2 displays significantly higher catalytic activity compared to POP-PA-OH and POP-PA-COOH [21].



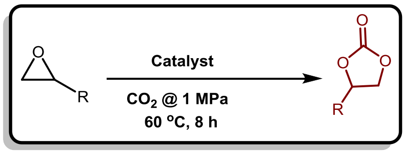
Structure illustration of the various polar group-functionalized porous organic polymers



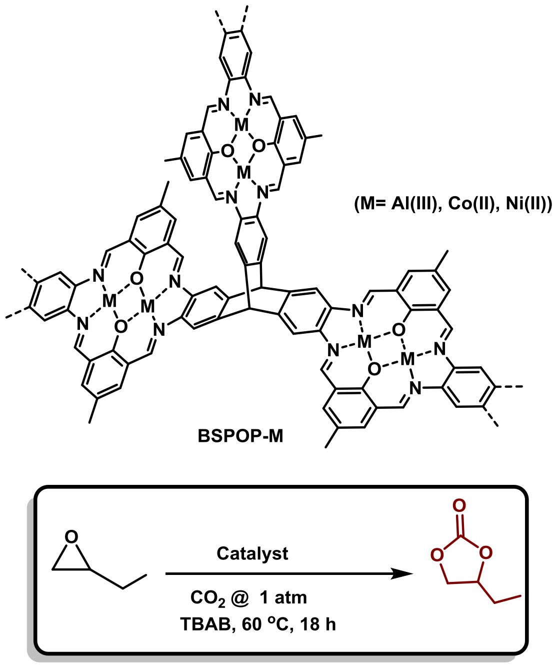
(E) In a separate investigation, a novel approach involved the utilization of multiple building blocks with distinct ion exchange functional sites to construct di-ionic multifunctional porous organic frameworks (POF-DI). These POF-DI materials possessed di-ionic sites and served as substrates for preparing a series of di-ionic multifunctional POF heterogeneous catalysts, namely POF-Zn^{2+}-Cl$^-$, POF-Zn^{2+}-Br$^-$, and POF-Zn^{2+}-I$^-$. The synthesis was accomplished through a feasible ion exchange method. The unique combination of two functionalized sites within these catalysts, comprising the Zn^{2+} cation as the Lewis acid and halogen anions (Cl$^-$, Br$^-$, or I$^-$) as nucleophiles, resulted in a synergistic effect. As a result, the three bifunctional POF catalysts, POF-Zn^{2+}-Cl$^-$, POF-Zn^{2+}-Br$^-$, and POF-Zn^{2+}-I$^-$, exhibited exceptional catalytic activity for the efficient conversion of CO_2 to cyclic carbonate. Notably, these conversions occurred under mild reaction conditions without the need for additional co-catalysts. This study not only introduced a novel pathway for developing innovative POF catalysts for CO_2 conversion but also highlighted the versatility of di-ionic POFs as a versatile type of ion exchange platform material with broad applications [22].



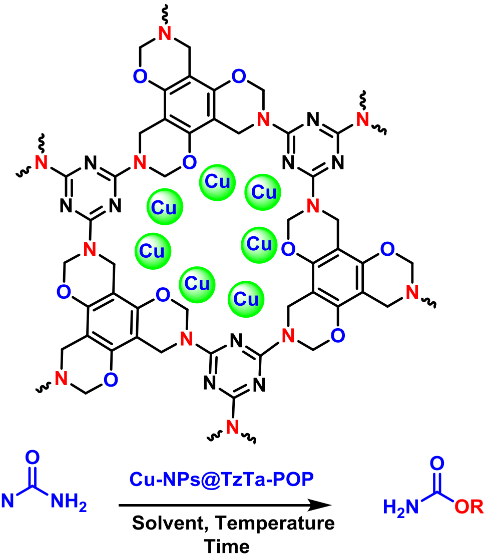
POF-DI



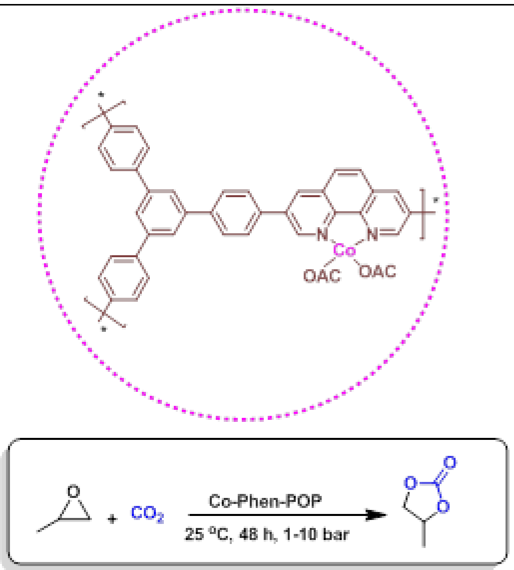
(F) Researchers have successfully designed and synthesized a diverse range of triptycene-supported bimetallic salen porous organic polymers. In this innovative approach, triptycene units were strategically incorporated to support the alignment of bimetallic salen macrocycles along the lateral walls of the polymer channels, resulting in enhanced exposure of catalytic metal sites. The experimental findings showcased the remarkable presence of permanent porosity and demonstrated high adsorption capabilities, as indicated by the measured isothermal heat values at different temperatures (196 K, 273 K, and 298 K) for BSPOP-Co. Notably, a cobalt-containing porous organic polymer exhibited exceptional catalytic efficiency in the coupling of epoxides and CO_2, even under mild reaction conditions. This breakthrough methodology not only introduces a novel type of porous organic polymer but also unlocks a new avenue for maximizing the exposure of active catalytic sites, thereby enhancing the effectiveness of heterogeneous catalysis. The reported study holds great promise, providing valuable insights into the development of advanced porous organic polymers and opening up new possibilities for the utilization of highly active catalytic sites in efficient heterogeneous catalytic processes [23].



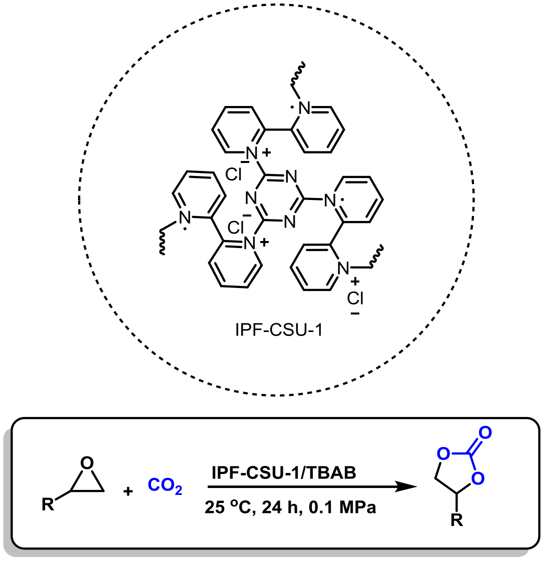
(G) In a study by Hague et al., they introduced triazine diamine-derived porous organic polymers (TzTa-POP) supported by copper nanoparticles (Cu-NPs@TzTa-POP). This novel catalyst demonstrated remarkable efficiency in synthesizing N-methylated products through CO_2 fixation and primary carbamates from alcohols and urea [24].



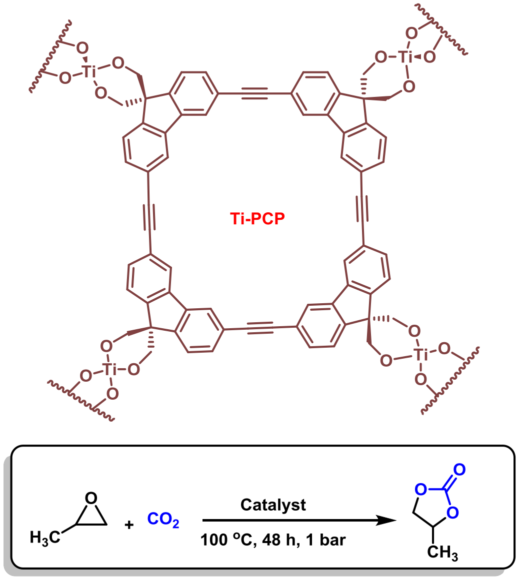
(H) In 2021, Tao and colleagues made a significant breakthrough by developing an ultralow cobalt (Co) loading phenanthroline-based porous organic polymer (POP) as a highly efficient heterogeneous catalyst for CO_2 fixation to cyclic carbonates. The catalytic performance of the Co-Phen-POP catalyst was assessed in the cycloaddition reaction of CO_2 and epoxides at room temperature (25°C) and low CO_2 pressure (1-10bar) in the presence of Tetrabutylammonium bromide (TBAB) as a co-catalyst. Remarkably, this reaction was carried out without the need for solvents and with an ultralow loading of the catalyst metal [25].



(I) In 2018, Yu conducted a groundbreaking study on the one-pot synthesis of an ionic porous organic framework designed for metal-free catalytic CO_2 fixation under ambient conditions. The developed framework, known as IPF-CSU-1, exhibited exceptional characteristics such as a remarkably high nitrogen content (20.3 wt. %), a high-density and uniform charge distribution. IPF-CSU-1 was employed as a metal-free catalyst for the conversion of CO_2 into cyclic carbonates, achieving impressively high yields of over 95%. These conversions took place under ambient conditions, specifically at a temperature of 298 K and a pressure of 0.1 MPa [26].



(J) Through a transesterification process, involving the reaction between a 1,3-diol-substituted shape-persistent arylene-ethynylene macrocycle and $Ti(OiPr)_4$, researchers have successfully synthesized a novel type of porous coordination polymer known as Ti-PCP. This polymer is characterized by the presence of titanium alkoxide linkages. The synthesized Ti-PCP has demonstrated its utility in applications such as gas adsorption and separation, as well as in catalyzing the conversion of CO_2 into cyclic carbonates [27].



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