Absorbent Biological Polymers and its submission in CO2 fascination responses

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ABSTRACT:

This review presents a comprehensive summary of the developments in designand synthesis of Porous Organic Polymers (POPs) with regard to fix carbon dioxide synthetically. It provides promising research activities and their prospects in the areas of carbon capture and storage and chemical fixation of carbon dioxide in constructing a future low-carbon global economy.

Key words: Porous organic polymers, CO2 fixation, natural pathways.

INTRODUCTION

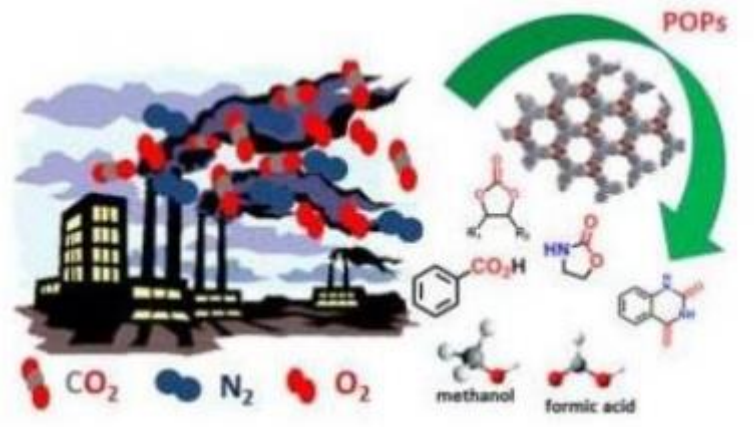
The natural sequestration of CO2 happens mainly by photosynthetic organisms present in the terrestrial as well as aquatic environments and this helps in maintaining the global carbon cycle. The major metabolic pathway through which CO2 is sequestered is the Calvin–Benson cycle which is the light independent reaction of photosynthesis. Today, six natural pathways for fixing CO2 is known to the mankind. But these have low efficiency and cannot meet with the demands imposed due to pollution and increasing CO2 in atmosphere. With a view of implementation of green chemistry concepts and to establish a sustainable society, a large scale research has been devoted to reduce carbon footprint. An attractive and promising pathway to effectively reduce anthropogenic CO2 emissions and produce fine chemicals is the Carbon Capture and Utilization Technique (CCU)1 . CO2 being inexpensive and abundantly available, acts a C1, non toxic source for synthetic chemistry. Since CO2 possesses inherent thermodynamic stability and kinetic inertness, the reaction pathways for CO2 fixation often requires harsh reaction conditions. The challenging part is to overcome the thermodynamic

constraints and to achieve the activation of inert CO2 under relatively less drastic conditions2 .

polymers (COFs), porous organic polymers (POPs)) have been exploited to achieve efficient, atom-economic and environment benign processes for catalytic CO2 fixation. With the significant development in covalent chemistry, Organic functional materials offer an unparalleled advantage of being able to design according to the requirements of functional groups on a molecular level. Any desired functionality can be introduced into porous materials through atomic level control over the structures and compositions. Organic functional materials have the capability of regulating the synergistic interactions among reactant molecules for achieving high efficiency catalysis. These organic macromolecule polymer possess very high molecular weight, nearly-perfect heterogeneity and fascinating architectural stability as well as exceptional designability which is undoubtedly considered as an ideal heterogeneous catalyst3 .

Out of these, POPs are the most appealing and promising purely organic forms which have low density, high surface areas, tunable pore sizes, designable catalytic active site and satisfactory physicochemical stability. POPs frameworks include subclasses like porous aromatic frameworks (PAFs), covalent triazine frameworks (CTFs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs), hypercrosslinked polymers (HCPs), and conjugated microporous polymers (CMPs)3 . These have many potential applications because of their high surface areas and uniform pore sizes, with large numbers of channels and active sites available for chemical reactions. POPs have thereby attracted a lot of attention for their use in the degradation of organic pollutants, energy storage, photocatalysis, H2 evolution, etc. POPs are insoluble in organic solvents due to their rigid chemical bonds and high degree of polymerizations and

therefore can easily be separated and recycled. Herein, the six natural pathways for CO2 fixation are explored followed by synthesis of POPs and it's application in CO2 fixation reactions



Autotrophic CO2 fixation

They inhale CO2 as C1 carbonsource and most of them exhale O2 as byproduct. The CO2 molecules are introduced in chlorophyll via CO2 acceptors. The assimilation of CO2 into cellular carbon needs reducing equivalents. Since CO2 (+4) state has to be reduced to carbohydrates (oxidation state of C is 0), 4reducing equivalents are needed. The reductive conversion of CO2 to cell carbon also needs energy which is provided by the hydrolysis of ATP 4 .

Anaerobes generally use a low potential electron donor like reduced ferredoxin whereas aerobes use NAD(P)H as a reductant. A carboxylating enzyme attaches to CO2 or HCO3- with an organic receptor molecule.

The inorganic carbon speciesare pH-dependent.

The enzymes catalyzing the difficult steps of the pathways evolved during the evolution and are conserved till date, making them key enzymes.

Ribulose-1,5-bisphosphate carboxylase, CO dehydrogenase/ acetyl CoA synthase are such enzymes. Today, 6 autotrophic CO2 fixation mechanisms are known. Let us have a brief overview of them.

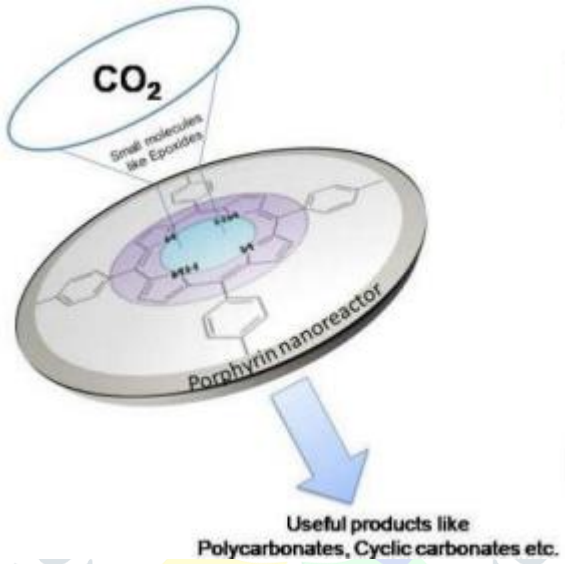
CALVIN CYCLE

The Calvin-Benson Cycle

6 molecules of 3-PGA are converted to 6 molecules of Glyceraldehyde-3-P (G3P) by consumingthe energy of ATP and reducing power of NADPH in the reduction phase. In regeneration phase,ribulose-1,5-bisphosphate is regenerated so that the cycle continues. This step involves many complex series of reactions yielding carbon sugar phosphates.

CO2 Fixation Reactions

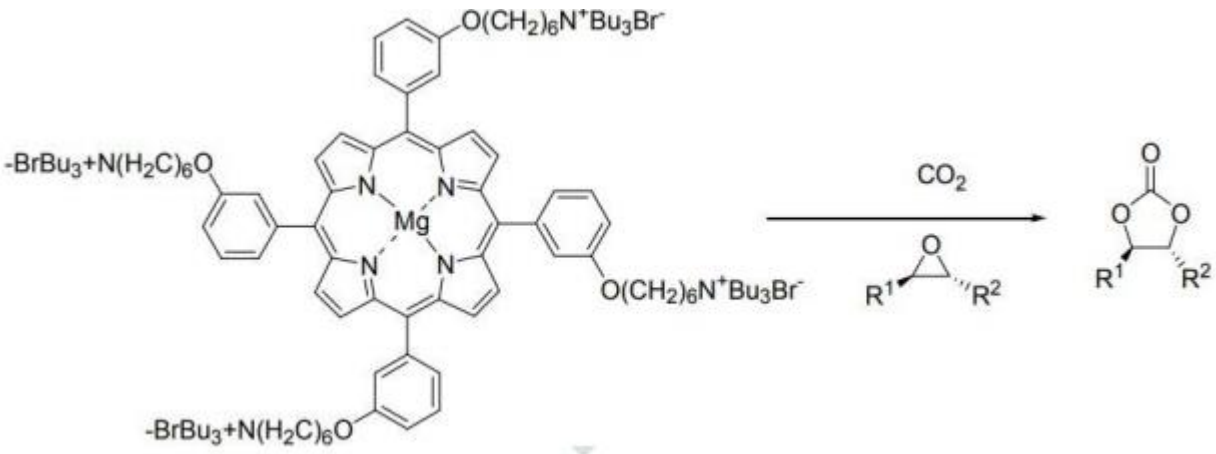
The Co2-philic nature of POPs bearing inbuilt metal centres like Fe, Mn, Co, Zn can be very useful as heterogeneous catalyst for CO2 conversion reactions. They form rigid cross-linked polymers of large molecular dimensions which are responsible for generation of large microspores and mesopores in organic frameworks1 . Porphyrin moieties also add up as buildingblock bearing unique macrocyclic structure by introducing porosity in the organic framework.



Metalloporphyrin based POPs used for cycloaddition of CO2 into epoxides

Low amounts of metal ions are loaded in porphyrin based POPs and the turn over frequencies are very high. The robustness of the framework also offer recyclability. The CO2 molecules interact with multiple pore surfaces simultaneously in a porphyrin nanoreactor14.

In 1986, Inoue et al. developed first porphyrin bases homogeneous single site catalyst with an aluminium center (fig). CO2 and epoxides can be converted to cyclic carbonates under solvent free conditions using a bifunctional Mg porphyrin catalyst15(fig) and fig gives it's plausible mechanism.



Synthesis of cyclic carbonates from epoxides and CO2

Source: Tadashi Ema YM, Shohei Koyama, Yuya Yano, Takashi Saka. Chemical Communications. 2012;48(37)

A zinc coordinated conjugated microporous polymer, referred to as Zn-CMP (fig) is synthesized by attaching salen zinc with 1,3,5-triethynylbenzene. It exhibits extraordinarycatalytic activity towards formation of cyclic carbonates and hence is a highly efficient heterogeneous catalyst16 .

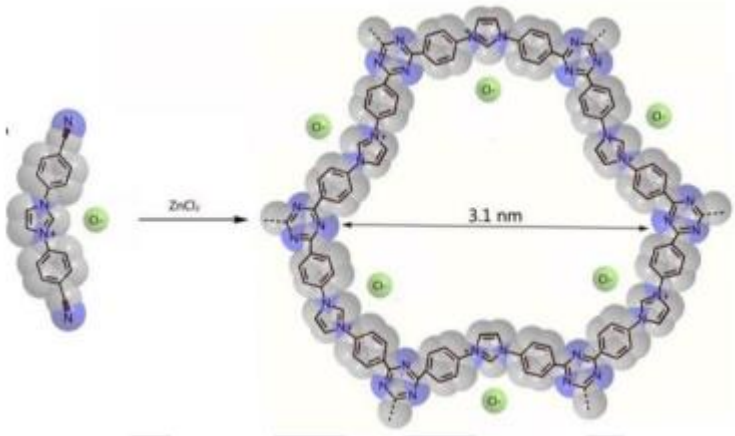
CO2 Fixation over metal-free POPs

CO2 is thermodynamically stable and exists in gas phase. It is a non-reactive species. It requiresharsh conditions like high temperatures, pressure and catalysts to activate and react to give

organic molecules. To activate the CO2, catalysts need to have basic sites where as to activate thesubstrates, the catalyst needs to have acidic, basic or reactive metal site. Cao et al. reported the synthesis of porous cationic covalent triazine frameworks (CCTFs) (fig) by employing cyano funtionalized imidazolium moiety in the porous organic framework17 . The positive charge of the imidazolium ion helps in adsorption of CO2 at the pore surface via dipole-quadruple interactions.

Guanidine, ionic liquids and N-heterocyclic carbenes are highly CO2-Philic in nature and can easily be incorporated in POP network using respective monomers. In presence of CO2, guanidine based organocatalyst can efficiently catalyse the synthesis of imidazolidin-2-ones and oxazolidinones from primary and secondary propargylamines.

Ionic liquids, as homogeneous organocatalyst can effectively catalyse the synthesis of quinazoline-2,4-dione via fixation of CO2 in 2- aminobenzonitrile.



Synthesis of CCTFs

NPs supported POPs are also seen to enhance the electrochemical reduction of CO2 to methane,methanol and ethylene. These improve the catalytic activity of the material enormously as they induce rigidity (fig). These are quite useful in electrochemical reduction of CO2.

Source: Rana R. Haikal ABS, Muhamed Amin, Stavros G. Karakalos, Youssef S. Hassan, Ahmed M. Elmansi, Inas H Hafez, Mohammed R. Berber, Abdou Hassanien, Mohammed Alkordi. Applied catalysis b-Environmental. 2017;207:347-357.

Conclusion

All the synthetic routes discussed above for designing POPs have multiple possibilities to tune the surface properties depending on the nature of functional group, shape, size and symmetry of the building molecular units. POP framework can be synthesized with introduction of highly reactive metal centres, fluorescent building blocks, pi-conjugated networks and post surface functionalization; these make them ideal candidate as catalyst to.

The aromatic moieties in the organic framework can be functionalized such that the reactive functional groups help in yielding materials with enhanced CO2 capture property and its subsequent conversion reactions. POPs result in new materials with interesting properties which can be employed to explore frontline applications of energy, environment.

The heteroelements in POP not only enhance the CO2 uptake but also help to promote the CO2 fixation reactions for the synthesis of value added organic fine chemicals and fuels in atom economic, green and facile way.

These POPs can therefore act as adsorbent and C1 source in CO2 fixation reactions and contribute significantly in constructing a future low-carbon global economy. As for future perspectives, the study of decomposition of these polymers would help to reflect on it's sustainability. More efforts should be made to design metal free organic polymers which would be cost efficient and green.

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