Physical Properties of Cyclic Esters and its Application in Heterogeneous Electrocatalysis

Haonan Duan¹, Zanyao Niu², Xiaoqi Yang³

¹College of Textile and Materials Engineering, Dalian Polytechnic University, Dalian, Liaoning, 116034
²Leicester International Institute, Dalian University of Technology, Panjin, Liaoning, 124221
³School of Pharmacy, Guangdong Medical University, Dongguan, Guangdong, 523000

*Corresponding author: haonanduan@dlut.edu.cn

Abstract. Oxygen reduction is a key reaction in many energy conversion devices. Phosphorus-containing porous organic polymers not only have developed pores and surface structure, but also have strong adjustable modification and modification, so they have a wide application prospect in heterogeneous catalysis. At present, the preparation of phosphorus-containing porous organic polymers and their applications in heterogeneous catalysis have not been reviewed. In this paper, the research progress in this field in the past decade is summarized and reviewed. The synthetic methods of phosphorus-containing porous organic polymers are developing rapidly, including coupling Polycondensation, lithium salt-mediated Polycondensation, Friedel-Crafts Polycondensation, solvothermal olefin polymerization, Scholl Polycondensation, phenolic polymerization, aldehyde-amine condensation, phosphorization of polypyran salts and multistage polymerization. At the same time of briefly describing the mechanism of oxygen reduction reaction, combined with the research results of my own team, this paper focuses on the application of new porous materials (metal-organic framework MOF, conjugated microporous polymer CMP, etc.) in electrocatalysis. In view of the problems existing in the current electrocatalysts, the future research ideas are pointed out, including the use of advanced technical means to characterize the active sites of the catalysts in situ, based on the fact that there are a large number of phosphine ligands in the framework, phosphorus-containing porous organic polymers can be loaded with a series of metal compounds to make supported metal nanoparticles catalysts, or even monoatomic or unit point metal catalysts. The optimal structure of the catalyst was inversely calculated from the high active sites, and the preparation conditions of the materials were optimized. Under the guidance of theory and practice, a new type of electrocatalyst with high efficiency, stability, economy and environmental protection was developed on the premise of in-depth understanding of the mechanism of oxygen reduction reaction. Then an example is given to introduce the use of POPs to solve the basic scientific problems related to biomimetic catalysis, and show its great application potential. Finally, the challenges and opportunities in this emerging field are summarized and put forward.
Keywords: Porous organic polymer, Heterogeneous catalysis, catalyst, polycyclic, Oxygen reduction reaction

1. Introduction
With the development and utilization of mineral resources on a large scale, traditional fossil fuels such as coal, oil and natural gas and other non-renewable resources are facing the dilemma of resource shortage or even exhaustion. On the other hand, the unreasonable exploitation and use of traditional fuels pollute the natural environment such as water, atmosphere and soil. However, with the encouragement of national policies, the awareness of environmental protection has been deeply rooted in people's hearts. The relationship between scientific and technological development and environmental protection is also changing constantly. From contradiction to coordinated development is the requirement of the development of The Times. As a clean, efficient energy conversion device with a wide range of fuel sources, fuel cells can directly convert chemical energy into electric energy [1], which has attracted close attention from domestic and foreign new energy experts. However, the oxygen reduction reaction (ORR) on the cathode of fuel cells has a slow kinetics and requires a higher platinum load, so the activity and cost of the catalyst seriously limit the commercial application of fuel cells [2]. Nowadays, with the progress of science and technology, various advanced experimental means and characterization means, such as synchrotron radiation light source, have emerged one after another, which enables researchers to have a deeper understanding of the active sites and working states of catalysts, and has significant guiding significance for the design and synthesis of new catalysts [3].

In order to facilitate the recovery and reuse of the metal-phosphine complex catalyst, researchers attempted to prepare the anchored metal-phosphine ligand catalyst by anchoring the phosphine ligand on an organic polymer carrier or an inorganic carrier. Anchoring phosphine ligands with soluble polymers is one of the most representative methods. Soluble polymers can be dissolved in reaction systems close to homogeneous catalysts, and functionalized phosphine ligands are easily introduced by grafting or copolymerization. Therefore, a large number of soluble polymer-based phosphine ligand catalysts have been reported at the end of last century. However, soluble polymer-based catalysts need to be recycled by adding precipitants, microfiltration or ultrafiltration and other means, and small molecular polymer chains may remain in the products and cause pollution, so they are gradually discarded by researchers [4]. With the rise of inorganic-organic hybrid materials, researchers combine functional phosphine ligands with inorganic materials by adsorption or chemical bonding to prepare phosphorus-containing heterogeneous catalysts. Representative inorganic materials include ordered mesoporous silicon materials with high specific surface and Fe3O4 nanoparticles with magnetic properties [5]. However, the surface active site of inorganic materials is single and the chemical modification potential is very limited, which greatly limits the development of phosphine ligand-based inorganic carrier catalysts.

2. Mechanism of catalyst

2.1. Catalytic activity and molecular binding energy

ORR refers to the process in which oxygen is reduced to hydroxide ion in alkaline solution and to hydrogen peroxide in acidic solution. It is generally divided into two paths: direct four-electron and two-electron. The four-electron pathway has high catalytic efficiency, and can effectively reduce the corrosion of hydrogen peroxide on electrode supporting materials and enhance the stability of the catalyst, so it has become an ideal path for cathodic reaction in fuel cells. ORR involves multiple reaction intermediates (OOH*, OH* and O*). On the one hand, the adsorption of these oxygen-containing species on the catalyst surface is a necessary condition for electron transport, on the other hand, it obscures the active sites on the catalyst surface, resulting in low catalytic efficiency. Figure 1 shows the volcanic relationship between the catalytic ORR activity and the binding energy of different metals [16]. The best catalyst and reaction intermediate should have moderate binding energy [16mur19]. The weak adsorption of intermediates is not conducive to the transfer of protons and electrons, on the contrary, it
will lead to the difficulty of desorption of oxygen-containing species, resulting in the occupation of active sites, thus hindering the progress of ORR. On the other hand, the larger the relative position of the electronic structure d-state of the metal and the Fermi level (the highest occupied state), the stronger the interaction between the catalyst surface and the intermediate [20]. Therefore, the best oxygen reduction activity can be obtained by developing the best electronic structure and proper binding energy catalyst.

![Fig 1. Orr catalytic activity and binding energy of different metal molecules](image)

**2.2. Use of porous organic polymers**

Porous organic polymers are organic polymers with large specific surface area and adjustable pore structure. In recent years, metal-organic framework (MOF) and conjugated microporous polymer (CMP) have been widely used in gas storage and separation, catalysis, energy storage and other fields, and have also received widespread attention in ORR.

Both phosphorus-containing monomers and comonomers have effects on the physical properties of polymers (specific surface area, pore volume, pore size distribution, etc.), and are closely related to the catalytic performance of polymer-based catalysts. The amount of polycondensation catalyst can also affect the physical properties of the polymer. The higher the catalytic dose is, the better the polycondensation. In a certain range, the pore size of the synthesized polymer decreases and the specific surface area increases with the increase of the polycondensation catalytic dose [27]. According to Table 1, the pore size distribution of phosphorous porous organic polymers synthesized by coupling polycondensation is generally narrow.

**3. Functional center domain**

**3.1. The flexible control**

Studies have shown that the active site of the enzyme is flexible, and the conformation of the active site of the enzyme molecule will change when it binds to the substrate, and it is a dynamic process in the catalytic process. However, traditional porous materials, such as activated carbon and silicon-based materials, are rigid, and loading often leads to limited movement of catalytic centers and spatial isolation of active sites, which makes it difficult to achieve intramolecular collaboration and greatly limits their performance. Therefore, improving the flexibility and degree of freedom of the functional center domain is the key to improve the performance of the immobilized system. Here, we use the rigid and flexible design of porous organic polymer framework, aiming at metal-organic catalysis, design and synthesis through flexible porous polyphosphine ligand, and successfully construct a series of highly efficient catalytic systems.
Fig 2. Schematic illustration of flexible frameworks construction to promote the cooperation between ligands.

It is well known that the type and amount of ligands play a decisive role in regulating the activity and selectivity of the reaction, such as hydroformylation reaction (the largest homogeneous catalytic reaction with annual output of about 20 million tons) [10]. In this kind of reaction, the formation of active species requires the co-existence of multiple ligands, so the reaction process requires a large excess of ligands (ligand-metal ratio is about 50 : 1, the molar ratio).

3.2. Conjugated microporous polymers
Using toluene as reaction monomer, porous organic polymers rich in benzene ring functional groups were synthesized based on Friedel-Crafts alkylation reaction. The results show that the material has a high specific surface area, in which the mesoporous specific surface area is 293.9m2 max g and the microporous specific surface area is 336.2m2/g. In this experiment, Fourier red was used to characterize the surface groups of phenyl porous organic polymers, the absorption peak near 750cm-1 was the out-of-plane bending vibration absorption peak of monosubstituted benzene, and the absorption peak near 1450cm-1 was the C-C double bond stretching vibration absorption peak of benzene ring.

Fig 3. Synthesis roadmap of porous organic polymer materials.

At the same time, in order to improve the catalytic selectivity, we extended this synthesis strategy to bisphosphine ligands and successfully prepared a series of flexible porous polybispshospine ligands to improve the regional selectivity of hydroformylation reaction [13]. Moreover, in order to further optimize the reaction performance, we combined the flexible polymer ligand design concept with the catalytic center microenvironment regulation to construct the bionic reactor.

4. Conclusions
A series of highly efficient catalytic systems were successfully constructed from the aspects of secondary environmental regulation of active center, flexible regulation of functional center domain and construction of hydrophobic channel environment. Most of the methods for the synthesis of phosphorous
porous polymers use specific functionalized phosphine ligands. The development and synthesis of functionalized phosphorous monomers is a major challenge for the application of phosphorous polymer-based catalysts. Strengthening the research and development of phosphorous polymer-based non-noble metal catalysts is of great significance to reduce the cost of catalyst preparation and promote the industrial application process. Porous organic polymers with high specific surface area and multi-layer pore distribution are ideal choices for controllable carbon-based materials.

References
[1] Ning Xingshuang, Chen Xi, Wen Ruijiang, Wu ci, Cui Yan, Shen Baozhen, Huang Daliang. Preparation of hydrophobic hypercrosslinked porous organic polymer and its application in the detection of polycyclic aromatic hydrocarbons in aquatic products [J]. Journal of Dalian University of Technology, 2020, 39 (06): 412-418.
[2] Wang Pingli, Chen Yanlong, Hu Yuling, Li Zongke. Progress in preparation and application of covalent organic polymers for sample pretreatment in food safety analysis [J]. Chromatography, 2021 and 39 (02): 162-172.
[3] Chen Yaju, Ren Qinggang, Zhou Xiantai, Ji Hongbing. Progress in synthesis of cyclic carbonate from carbon dioxide catalyzed by porous organic polymers [J/OL]. Chemical progress: 1-20 [2021-01-21]. Https://doi.org/10.16085/j.issn.1000-6613.2020-1502.
[4] Chen Silu. Study on the preparation of composite metal oxides and porous carbon materials from metal-organic skeleton compounds [D]. Jilin University, 2015.
[5] Zheng Fangcai. Synthesis of porous carbon-based nanomaterials based on metal-organic framework compounds and their application in lithium battery anode materials [D]. University of Science and Technology of China, 2015.