



齐鲁工业大学
QILU UNIVERSITY OF TECHNOLOGY

本科毕业设计(论文)

**Preparation and electrocatalytic organic reaction performance study
of Pd-containing organic porous materials**

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2022 年 05 月 18 日

**Preparation and electrocatalytic organic
reaction performance study of Pd-containing
organic porous materials**

**含 Pd 有机多孔材料的制备及电
催化有机反应性能研究**

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齐鲁工业大学本科毕业设计（论文）

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Abstract

In recent years, organic electromechanical synthesis with the goal of green chemistry and sustainable development has attracted much attention. Compared with traditional organic synthesis methods performed under high temperature and pressure conditions, indirect electrochemical synthesis has the advantages of clean reaction, mild conditions and high atomic economy. However, the reported indirect electrolytic catalysts are mainly metal salts and organic small molecules, which usually suffer from poor recyclability and dimerization deactivation. Therefore, the design and development of novel recyclable and highly stable indirect electrolytic catalysts for efficient catalytic conversion of organic reactions is one of the current research hotspots.

In this paper, a covalent organic framework material with bipyridine structure was constructed by Schiff base reaction, and further introduced Pd catalyst on its backbone by coordination reaction to prepare covalent organic framework material with Pd catalytic center. The structure was characterized by X-ray crystal diffraction, absorption and desorption curve test at 77 K under nitrogen, and infrared spectroscopy test. Their catalytic performance as electrolytic cell cathodes for the hydrogenation of alkynes were initially investigated. The experimental results show that such materials have significant electrocatalytic performance for the selective reduction of alkynes to alkanes.

Keywords: Covalent organic frameworks (COF); Electrocatalysis; Organic Electrochemical Synthesis

摘 要

近年来，以绿色化学和可持续发展为目标的有机电合成备受关注。与传统高温高压条件下进行的有机合成方法相比，间接有机电合成具有反应洁净、条件温和、原子经济性高等优点。然而已报道的间接电解催化剂主要是金属盐和有机小分子，通常存在回收利用性差、二聚失活等问题。因此，设计开发新型可循环使用的高稳定性的间接电解催化剂，实现高效催化有机反应转化是当前研究热点之一。

本文通过席夫碱反应构筑了一种联吡啶结构的共价有机框架材料，并进一步通过配位反应，在其骨架上引入 Pd 催化剂，制备具有 Pd 催化中心的共价有机框架材料。通过 X-射线晶体衍射、氮气 77 K 下吸脱附曲线测试，红外光谱测试对其结构进行表征。初步探究了其作为电解池阴极对炔烃加氢反应的催化性能。实验结果表明此类材料对炔类有机物选择性还原为烷烃有显著的电催化性能。

关键词：共价有机框架 电催化 有机电合成

Chapter 1 Introduction

1.1 Primary Introduction

In the 21st century, the concept of green and sustainable chemistry is greatly emphasized, so the issue of scientific use of energy is also intensely discussed. It is well known that the development of modern industry cannot be separated from the consumption of energy. Traditional non-renewable resources such as coal, oil and natural gas are on the verge of depletion and have caused a series of environmental problems. As for new renewable energy sources, such as wind and tidal energy, they are regional and intermittent in character, resulting in unstable production capacity.^[1, 2] With the aim of green chemistry and sustainable development, electro-organic synthesis integrates organic synthesis and electrochemistry, which means that electricity can be used directly to produce valuable compounds.^[3] Therefore, it has been widely used in industry in recent years.

1.1.1 Organic Electrochemical Synthesis

In organic electrochemical synthesis, organic molecules or catalytic media are converted to each other by charge transfer at the "electrode/solution" interface to achieve the breakage of old bonds and the formation of new ones. Normally, electrochemistry is considered as an environmentally friendly tool for organic synthesis. It manifests itself in several ways: firstly, compared to traditional organic synthesis methods carried out under high temperature and pressure conditions, the reaction conditions of the organic-electrochemical synthesis method are milder, shorter and more efficient. Secondly, toxic or dangerous oxidizing and reducing agents in the reaction are replaced by clean electrons, reducing the consumption of substances and energy.^[4] For example, in 2018, the oxidative C-H amination of synthesized amides by using a cobalt catalyst in the absence of a metal oxidant was reported by the team of Sauermann, N. Instead, electricity was used as an oxidant.^[5] The third point is that the reaction avoids waste generation. The desired cross-coupling products are obtained by direct or indirect anodic oxidation, but also valuable hydrogen can be generated as an additional product by

simultaneous cathodic proton reduction.^[4] These advantages make electro-organic chemical synthesis a trend in green chemistry.

1.1.2 Indirect Electro-organic Synthesis

Typically, there are both direct and indirect methods of electromechanical synthesis. Direct electro-synthesis methods are based on the exchange of electrons between the reaction substrate and the electrode surface. However, this heterogeneous process of electron transfer between the substrate molecule and the electrode surface poses a high kinetic energy barrier. In addition, the reactions in the space close to the electrode surface also affect the electron synthesis and the consequent generation of reactive intermediates, which are the main cause of electrode deactivation. However, the electrode is the key to the organic electro-synthesis, and at this point, the direct electro-synthesis method loses its applicability.^[6] In order to circumvent these problems, the value of the indirect electro-synthesis method was then demonstrated.

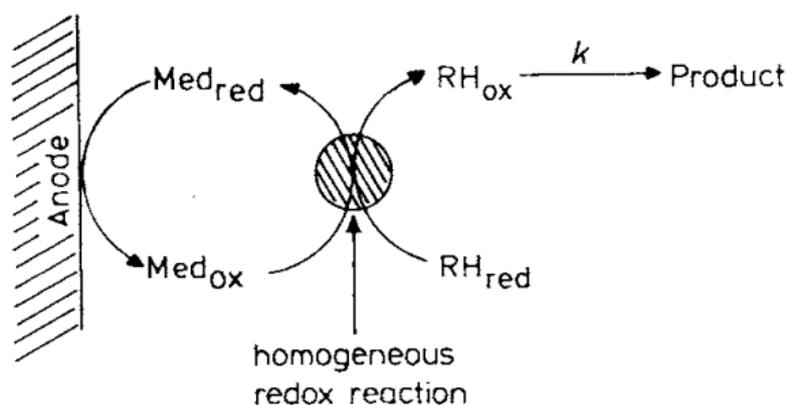


Figure 1. The principle of indirect electrolysis exemplified by an oxidation.^[7]

Indirect electro-synthesis is the use of a mediator that acts as an electron carrier. Firstly, the reduced or oxidized state is exchanged with the electrode in heterogeneous phase and then with the substrate in homogeneous or heterogeneous phase, so that the substrate can be easily transformed into the product, as illustrated in Figure 1.^[7] By choosing a suitable medium, many of the problems that exist in direct organic electromechanical synthesis can be solved by indirect organic electromechanical synthesis, such as slow reaction speed of the base paper, low current efficiency, and poor selectivity of the products.

Moreover, the combination of electrochemical synthesis with transition metal catalysis has allowed the discovery of various new reaction mechanisms, thus making possible the functionalization of new resource-economic bonds. The concept of indirect electrolysis with

redox agents, unique to electrochemistry, can improve the efficiency and chemoselectivity of electrosynthesis compared to the commonly used chemical redox reagents.^[8]

1.2 Electrocatalyst

The cleavage of stable bonds in redox reactions is the step where high activation energy barriers determine the rate, and catalysts are essentially always needed to increase the rate of these reactions.^[9] A variety of homogeneous electron transfer mediators (ETMs) have been developed, including N-oxygen radicals, hypervalent iodine species, halides, amines, and transition metals. Transition metals are attractive compared to other catalysts because the reactions catalyzed by transition metals are versatile and their redox potentials can be tuned by ligand modification.^[10]

Usually, platinum and palladium are considered to be the most widely used efficient electrocatalysts, however they are extremely rare metals, resulting in high prices. In the past decades, despite the extensive research on non-precious metal catalysts. For example, doped carbon materials, iron and cobalt-based electrocatalysts, which are considered as possible alternatives to platinum-based catalysts. However, due to the low stability and poor durability of these materials, these non-precious metal catalysts still need to be improved.^[11] For pure metal nanoparticle catalysts, their poor stability, poor electrical conductivity, and complex synthesis also make it impossible to meet the activity and durability requirements of electrochemistry. Therefore, platinum combined with other metals in the form of alloys or heterogeneous nanostructures has been developed to significantly improve activity and/or durability while reducing the amount of rare metals.^[9, 12] For example, by using H₂O (D₂O) as a source of H(D) as reported by Wu, Y team in 2022, the Pd-P alloy nanoparticle network proved to be an efficient cathode than was used for the electrocatalytic semi-hydrogenation of various functionalized alkynes to hydrogenated and deuterated alkenes. The main reason is the enhancement of the specific adsorption of alkynes due to the addition of phosphorus, which allows higher activity and selectivity than pure Pd.^[13] The importance of developing electrocatalysts for efficient electromechanical synthesis is thus evident.

1.3 Covalent organic frameworks (COFs)

Porous materials are rich in porous channels, cavity structures and particle interstices on their inner or outer surfaces. They have been widely studied by scientists due to their diverse options of building units and functions. By now, porous materials have made significant

contributions to society, such as catalysis and molecular separation, as well as being applied to develop new technologies in energy and health. Among them, porous organic frameworks constructed from organic building blocks with strong covalent bonds have attracted great attention for their great potential in various applications. It is a general term for covalent organic frameworks (COFs), covalent triazine frameworks (CTFs), porous aromatic frameworks (CTFs), etc.^[14, 15] And this article is mainly focused on the covalent organic frameworks.

Covalent organic framework materials (COFs) are porous organic solids with two or three dimensions composed entirely of building blocks of light elements (hydrogen, boron, carbon, nitrogen, and oxygen) bonded by strong covalent bonds. Examples include diamond, graphite and boron nitride, all of which are excellent lightweight materials.^[16, 17] Among many crystalline porous materials, COF materials have the advantages of low density, large surface area, and adjustable pores, which make COF materials have high potential for further applications in gas storage, adsorption, and optoelectronics.^[18]

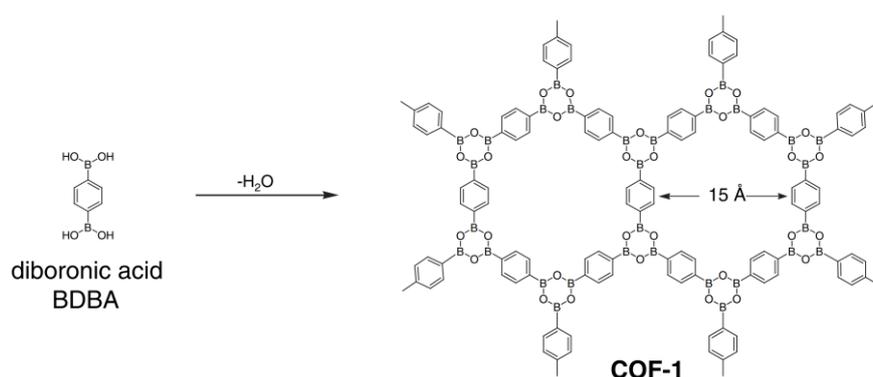
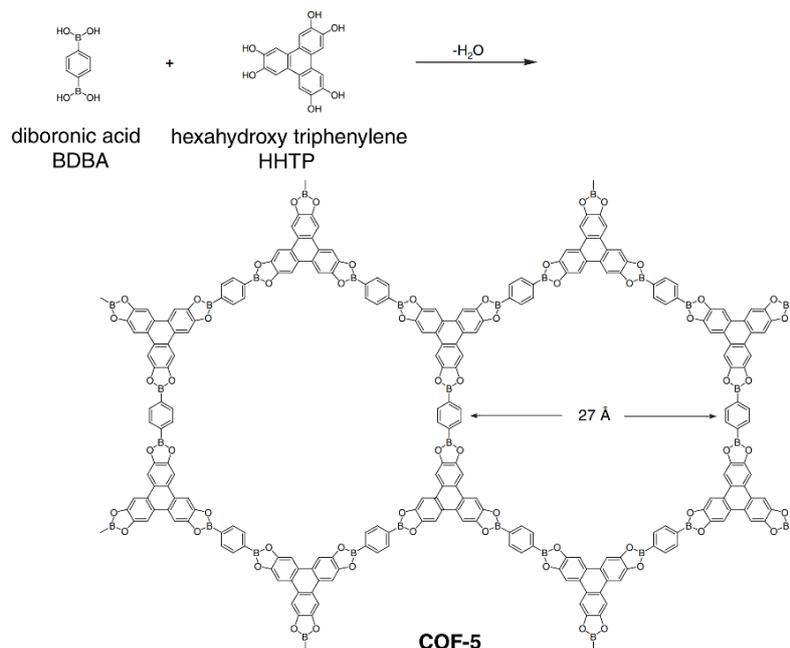
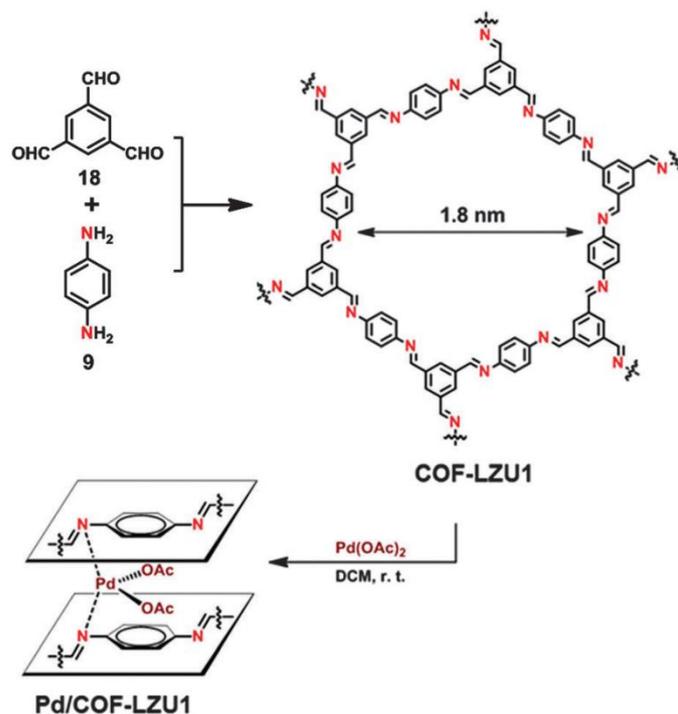


Figure 2. The synthesis of COF-1.^[16]

The creative synthesis of COF-1 and COF-5, reported by Yaghi's team in 2005, marked the beginning of a family of two-dimensional COFs and the first synthesis of covalent organic framework materials, as shown in Figures 2,3. COF-1 is a planar six-membered B₃O₃ (boroxine) ring formed by dehydration condensation between molecules of benzenediboronic acid (BDDBA), while COF-5 is a five-membered BO₂C₂ ring synthesized by dehydration between BDDBA and hexahydroxytriphenylene (HHTP). Similarly, in 2007, Yaghi's team was the first to successfully synthesize crystalline 3D COFs (called COF-102, COF-103, COF-105, and COF-108).^[19] These provided a solid foundation for the modification of covalent organic framework materials and their applications.


 Figure 3. The synthesis of COF-5.^[16]

 Figure 4. Chemical structure of COF-LZU1 and Pd/COF-LZU1.^[18]

In 2013, simple structural units 18 and 9 were used by Ding, S. and Wang, W. to synthesize a new imine-linked COF material, Pd/COF-LZU1, by coordination with Pd(II) at room temperature, as shown in Figure 4. This material was used to catalyze the Suzuki-Miyaura coupling reaction. Its excellent catalytic performance is not only reflected by its wide range of reactants, but also by its excellent yield (96-98%). At the same time the catalyst exhibited an

extremely high stability and easy recyclability.^[18] The great potential of this covalent organic framework material with imine structure can be seen in the field of chemical catalysis. Later in 2015, 2,3-dihydroxyterephthalaldehyde (2,3-Dha) and 5,10,15,20-tetrakis(4-aminophenyl)-21*H*,23*H*-porphine units (Tph) were used by Shinde's team^[20] to synthesize a catalytically active COF 2,3-DhaTph was successfully, which showed excellent catalytic activity for cascade reactions without compromising its recoverability in high yields.

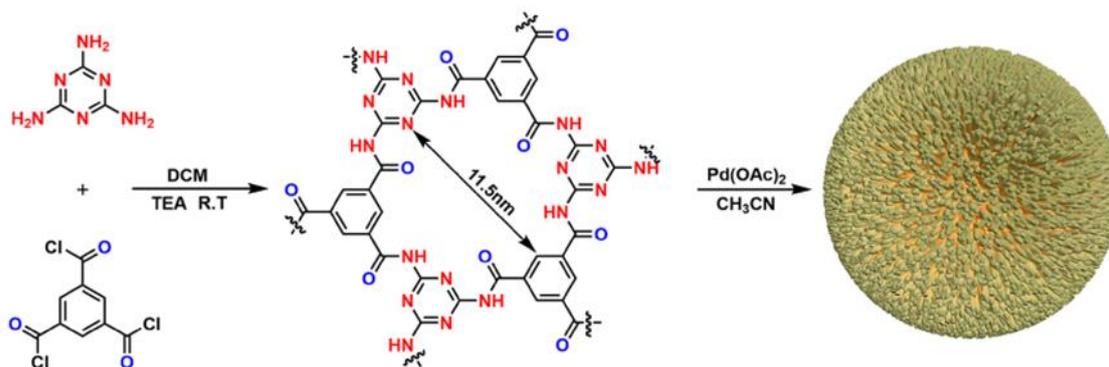


Figure 5. Preparation of the Pd@COF-TM catalyst.^[21]

In 2020, Wu's team^[21] synthesized crystalline COF-TM from tricarbochloride (TM) and melamine (MA) at room temperature. Then a new Pd@COF-TM catalyst was successfully prepared by supramolecular assembly of COF-TM and Pd(OAc)₂, as shown in Figure 5. This catalyst can be used for Suzuki-Miyaura coupling reaction with water as the solvent at room temperature, and the yield is up to 99%. More importantly, this highly efficient catalyst was found to be highly active and persistent, and could be easily recovered from the reaction mixture with the catalytic activity retained for at least nine consecutive cycles. This opens up a new world of applications for COF materials.

In the same year, in 2020, Wang's group^[22] reported a novel synthesis of Cu@porphyrin-COFs nanorods as an efficient photocatalyst for CO₂ reduction. Under photocatalytic (PEC) conditions, C1~C3 chemicals such as methanol, ethanol, ethane-1,1-diol and acetone can be obtained with an extremely high formation rate of 5352 μM g⁻¹ h⁻¹ due to the effective adsorption of protons on the surface of Cu crystals. In addition, Cu crystals grown on the surface of COFs can trap protons and accelerate the electron transfer at the photocathode, which leads to higher chemical yields. This provides a new perspective on the structure-property relationship of efficient photocatalytic materials.

COFs materials have many applications in addition to their photovoltaic and catalytic effects. With their diverse structures and good properties, various functional groups can be used to

modify COFs, which makes it possible to use them as alternative materials for biosensors. COF materials have been widely used in biosensing applications, such as explosive sensing, humidity sensing, gas sensing, etc.^[23]

1.4 The Purpose and Meaning of the Research

As one of the organic porous materials, covalent organic frameworks have promising applications in the field of catalysis due to some special properties and the continuous enrichment of post-modification means. In this paper, we investigate the application of covalent organic frameworks containing transition metal Pd in the field of electroorganic catalysis through the synthesis of covalent organic frameworks. This study enriches the application of post-modified covalent organic frameworks and promotes the research of covalent organic frameworks. The main research of this thesis consists of two parts:

- (1) COF materials with imine structures were synthesized from 1,3,5-triformylphloroglucinol and 2,2'-bipyridyl-5,5'-diamine using a condensation reaction strategy. Then Pd metal was embedded into this material to prepare Pd-COF covalent organic framework catalysts.
- (2) The electrocatalytic properties of Pd-COF were explored to further investigate its ability to act as a non-homogeneous catalyst for the selective reduction of alkynes and to explore its application in catalysis.

Chapter 2 Experiment Section

2.1 Reagents

Table 1. Experimental reagents

Reagents	Purity	Manufacturer
1,3,5-triformylphloroglucinol	AR	Jinlin Chinese Academy of Sciences Yanshen Technology Co., Ltd
2,2'-bipyridyl-5,5'-diamine	AR	Jinlin Chinese Academy of Sciences Yanshen Technology Co., Ltd
Dimethylacetamide (DMAc)	AR	Shanghai Aladdin Biochemical Technology Co., Ltd
1,2-dichlorobenzene (o-DCB)	AR	Shanghai Saen Chemical Technology Co., Ltd
Acetic acid	AR	Tianjin Dasen Chemical products Co., Ltd
Methanol	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Tetrahydrofuran (THF)	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Palladium (II) chloride	AR	Shanghai Aneji Chemical Co., Ltd
Ethanol	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Polyvinylidene difluoride (PVDF)	99%	Shanghai Saen Chemical Technology Co., Ltd
PdCl ₂	AR	Shanghai Saen Chemical Technology Co., Ltd
Acetonitrile	AR	Tianjin Fuyu Fine Chemical Co., Ltd

Information about the reagents used in the experiments, such as the purity of the reagents and the manufacturer, is presented in Table 1.

2.2 Apparatus

The information about the instruments used in the experiments and the manufacturers are shown in Table 2.

Table 2. Experimental apparatus

Instrument	Manufacturer
Circulating water vacuum pump	Gongyi Yuhua Instrument Co., Ltd.
Ultrasonic cleaner	Kunshan Ultrasonic Instrument Co., Ltd.
Electric blast drying oven	Shanghai Yiheng Scientific Instrument Co., Ltd.
Vacuum drying	Shanghai Yiheng Scientific Instrument Co., Ltd.
Intelligent magnetic stirrer	Hualu electric heating Instrument Co., Ltd.
Rotary evaporator	Gongyi Yuhua Instrument Co., Ltd.
Deionized water machine	Shanghai gaosen Instrument Co., Ltd.
Portable ultraviolet analyzer	Hangzhou Qiwei Instrument Co., Ltd.

2.3 Experimental synthesis

2.3.1 The synthesis of the COF material

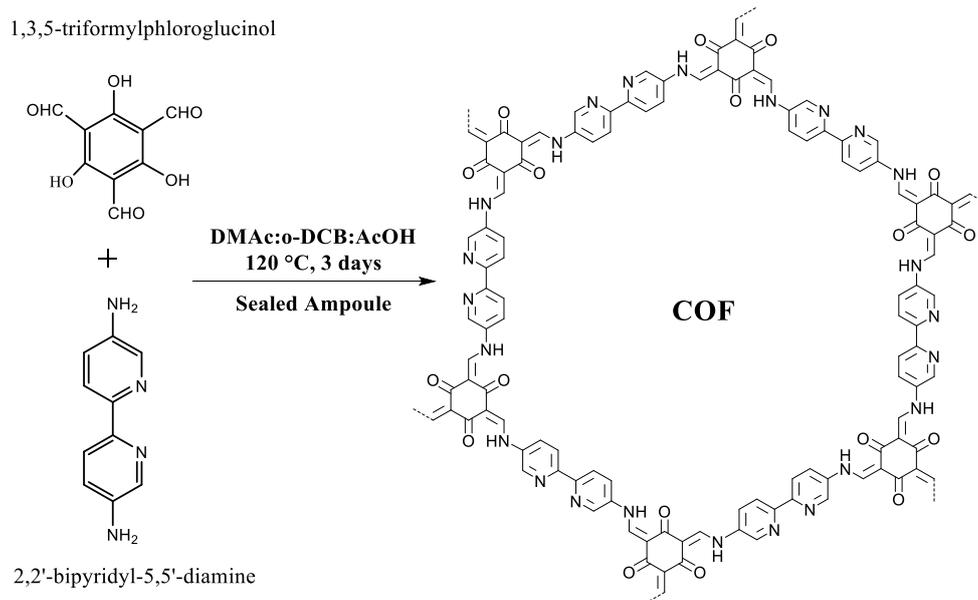


Figure 6. The synthesis of the COF.

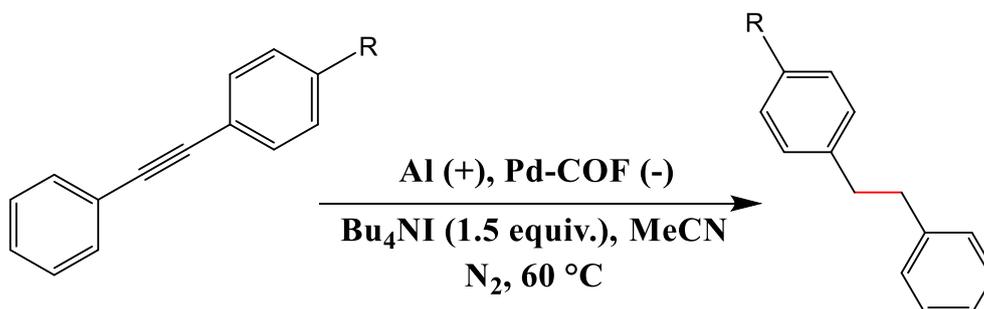
The synthetic route of the COF is shown in Figure 6. During this synthesis, an ampoule tube was used to perform the mixing of substrates. First, 1,3,5-triformylphloroglucinol (21 mg) and 2,2'-bipyridyl-5,5'-diamine (27.9 mg) were added to the ampoule tube, then 1.5 mL of DMAc and 0.5 mL of o-DCB were added sequentially. The ampoule tube was sealed with a sealing film and placed in an ultrasonic cleaner, and ultrasonication was performed for 20 min to mix the raw material with the solvent. After ultrasonication, 6 M acetic acid was added to the well-mixed ampoule for the purpose to provide an acidic environment. Next, liquid nitrogen was used to freeze the liquid in the ampoule. Then the ampoule tube was degassed through freeze-pump-thaw cycles. This operation needs to be repeated three times. Finally, a flame spray gun was used to seal the ampoule and it was placed in a constant temperature oven at 120 °C for 72 h.

At the end of the reaction, a covalent organic framework material product with a yield of about 70% can be obtained by purifying the insoluble material in the system. In this experiment, the purification of the COF consisted of the following two steps. At first, the red solid at the bottom of the ampoule at the end of the reaction was separated by filtration. Secondly, Soxhlet extraction method was employed to effectively remove impurities such as insoluble materials and oligomers from the product. In the Soxhlet extraction method, tetrahydrofuran (THF) was used as a solvent to extract the solid product for 48 h, and the resulting solid was then dried under vacuum at 60 °C and activated for 24 h. By Soxhlet extraction method, the covalent organic framework material is purified and obtained. In this method only a small amount of solvent is used, while the purification efficiency is relatively high, which is the main reason for using this method.

2.3.2 The preparation of Pd-COF

Figure 7 illustrates the preparation process of Pd-COF. Purified COF and PdCl₂ were placed in a methanol environment at room temperature. After overnight stirring, the solid was obtained by vacuum filtration using methanol, and then tetrahydrofuran and ethanol were used to wash and centrifuge the solid three times, respectively. Finally, the solid powder of Pd-COF was obtained by drying.

2.5 Electrocatalytic reduction of aromatic acetylene



The experiment was performed in an electrolytic cell in which aluminum was used as the anode and 1 mol% Pd-COF was used as the cathode. The electrolyte was tetrabutylammonium iodide and acetonitrile was used as the solvent. The entire experiment was controlled in a nitrogen atmosphere and kept at a constant temperature of 60 °C .

Chapter 3 Results and Discussion

3.1 TEM test of synthesized COF materials

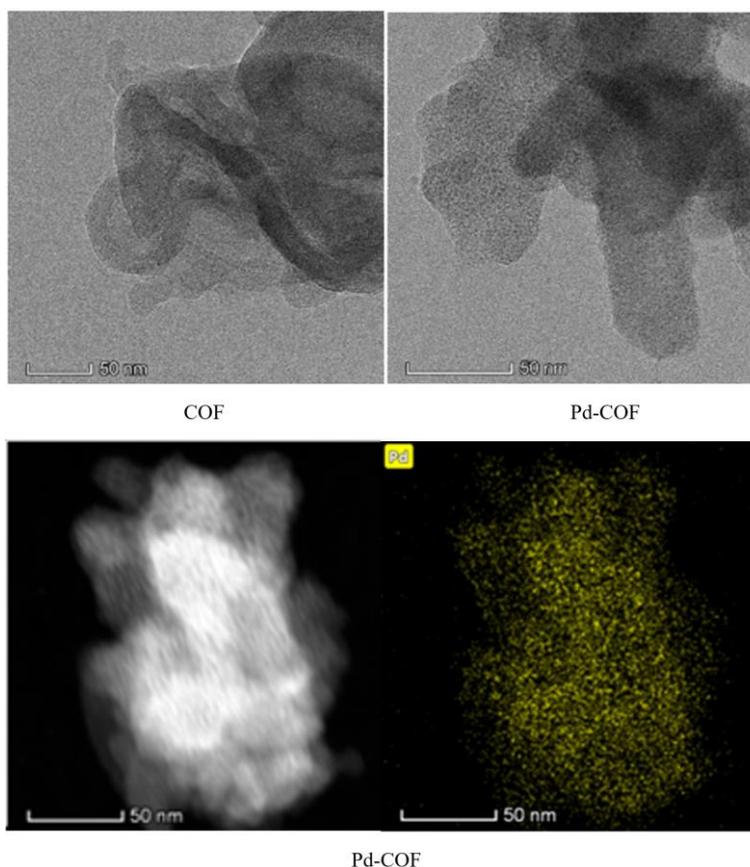


Figure 8. TEM and TEM-mapping of the COF and Pd-COF.

It can be seen in Figures 8, the sample materials are stacked layer by layer and have a sheet-like structure. Comparing the COF and Pd-COF samples, it can be found that the Pd metal is more uniformly dispersed in the structure.

3.2 Crystallinity study of Pd-COF

Covalent organic frameworks connected by covalent bonding can form periodically arranged porous crystalline COFs in this experiment, X-ray diffraction (XRD) tests were employed to determine the crystallinity of the COF as well as the crystallinity of the Pd-COF obtained after modification. From Figure 9, it can be concluded that the COF and Pd-COF show peaks at 3.81°

and 3.82° , respectively, indicating the crystallinity of the COF is quiet well, but the crystallinity of Pd-COF is not satisfactory because the peak of Pd-COF is not obvious. Meanwhile, the peak of Pd-COF at 26.8° indicates its π - π stacking between the COF layers.

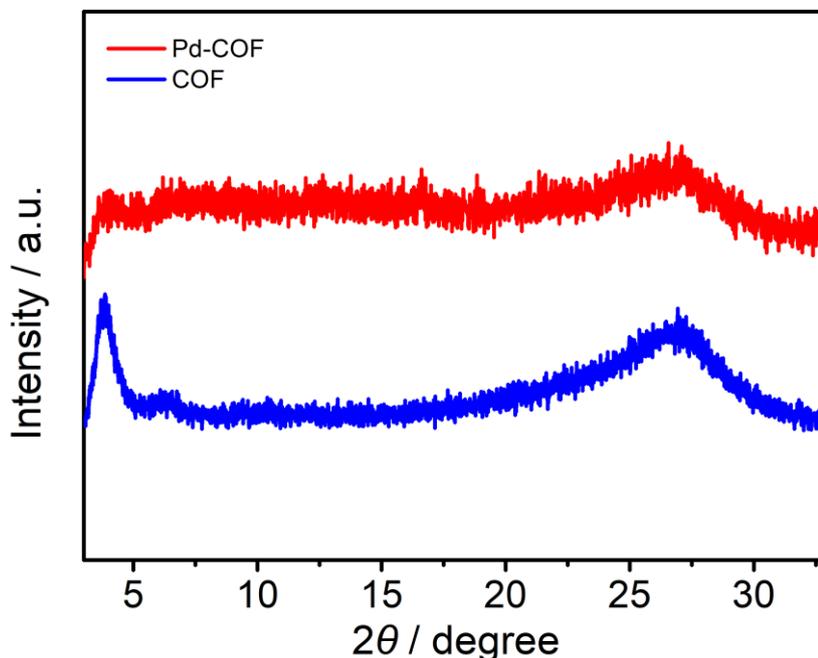
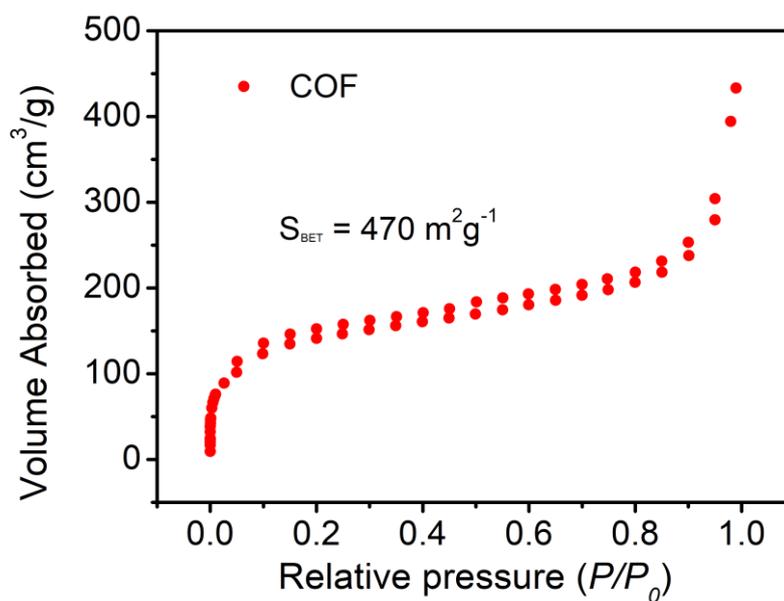


Figure 9. XRD of the COF and Pd-COF.

3.3 Porosity test of Pd-COF



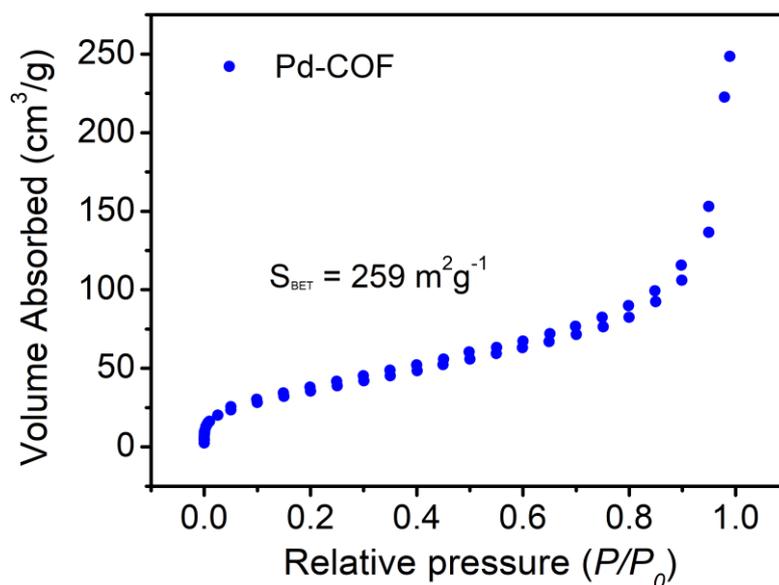


Figure 10. N₂ adsorption-desorption isotherms of prepared materials (COF, red; Pd-COF, blue).

The covalent organic framework has the advantages of highly ordered pore structure, adjustable pore size, and large specific surface area. To characterize the microporous properties of the synthesized covalent organic frameworks, the nitrogen isothermal adsorption and desorption curves of the COF and Pd-COF were determined, and the collective results are shown in Figure 10.

According to the International Union of Pure and Applied Chemistry (IUPAC) classification for adsorption isotherms, the nitrogen adsorption isotherms of this COF material belong to class IV, implying that the material of the COF has a predominantly mesoporous structure inside, thus proving the existence of a microporous structure inside. Furthermore, the specific surface areas of the COF and Pd-COF synthetics were determined by the Brunauer-Emmett-Teller (BET) model and were 470 and 259 m²/g, respectively. The presence of a better specific surface area of the COF provided a better active area for post-modification of its pore walls. And the post-modified Pd-COF material showed a significant decrease in specific surface area, indicating that Pd was effectively immobilized by the mesoporous structure of the COF material.

3.4 Fourier Transform Infrared Spectrometer (FT-IR) test

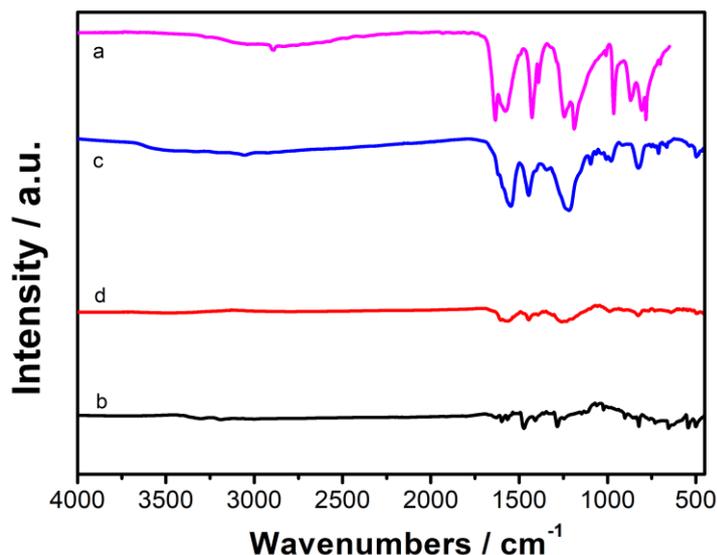


Figure 11. IR spectra of monomers synthesized COF materials (a. 1,3,5-triformylphloroglucinol, b. 2,2'-bipyridyl-5,5'-diamine, c. Pd-COF, d. COF).

In order to determine the molecular structure of the substances, the way the groups are connected between the products and the extent of the reaction, we obtained infrared absorption spectra of the reacting monomers 1,3,5-triformylphloroglucinol, 2,2'-bipyridyl-5,5'-diamine, the COF and Pd-COF. By comparing the IR absorption spectra of the small molecule and COF materials, we can clearly observe each characteristic absorption peak in the spectra. In the infrared spectrum of 1,3,5-triformylphloroglucinol (Figure 11(a)) at 2894 cm^{-1} is the stretching vibration peak of C-H of the aldehyde group and 1632 cm^{-1} is the stretching vibration absorption peak of C=O of the aldehyde group. In the IR spectrum of 2,2'-bipyridyl-5,5'-diamine (Figure 11(b)) the 3309 cm^{-1} absorption peak is the characteristic absorption peak of -NH_2 . By comparing Figure. 11(a)(b)(d), we can find that the stretching vibration peak of -NH_2 located at 3309 cm^{-1} disappears and the stretching vibration peak of C=O located at 1632 cm^{-1} diminishes. It indicates that the COF is synthesized. And by comparing (c) and (d) in Fig. 11, the peaks of Pd-COF and the COF are significantly different at 1216 cm^{-1} , indicating that the Pd metal might be combined with C-N bond.

3.5 Pd-COF selective reduction alkyne reaction

Loading the catalyst material directly onto the electrode surface can increase the electron transfer rate between the catalyst and the electrode and promote the catalytic reaction. Diphenylacetylene is selected as the reaction substrate for the electrochemical reaction.

3.5.1 Electrocatalytic reduction of 1-methyl-4-(phenylethynyl)benzene

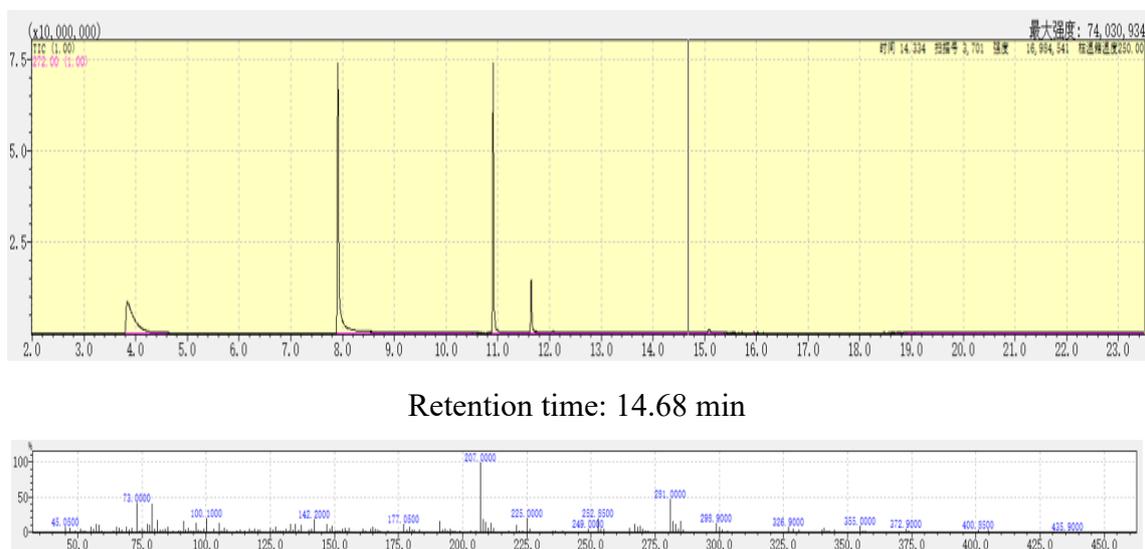
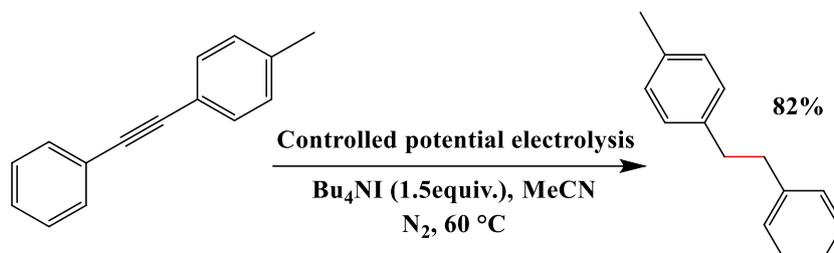


Figure 12. GC-MS plot of the experiment using 1-methyl-4-phenethylbenzene as the reaction substrate.

The reaction system with 1-methyl-4-phenethylbenzene as the substrate was analyzed using GC-MS, as shown in Figure 12, and the peak of 1-methyl-4-phenethylbenzene could be observed at a retention time of 14.68 min, indicating that 1-methyl-4-(phenylethynyl)benzene in which the unsaturated alkyne bond was successfully reduced to alkyl bond. Moreover, the yield of the reaction measured by the experiment was 82%.

3.5.2 Electrocatalytic reduction of 1-(tert-butyl)-4-(phenylethynyl)benzene

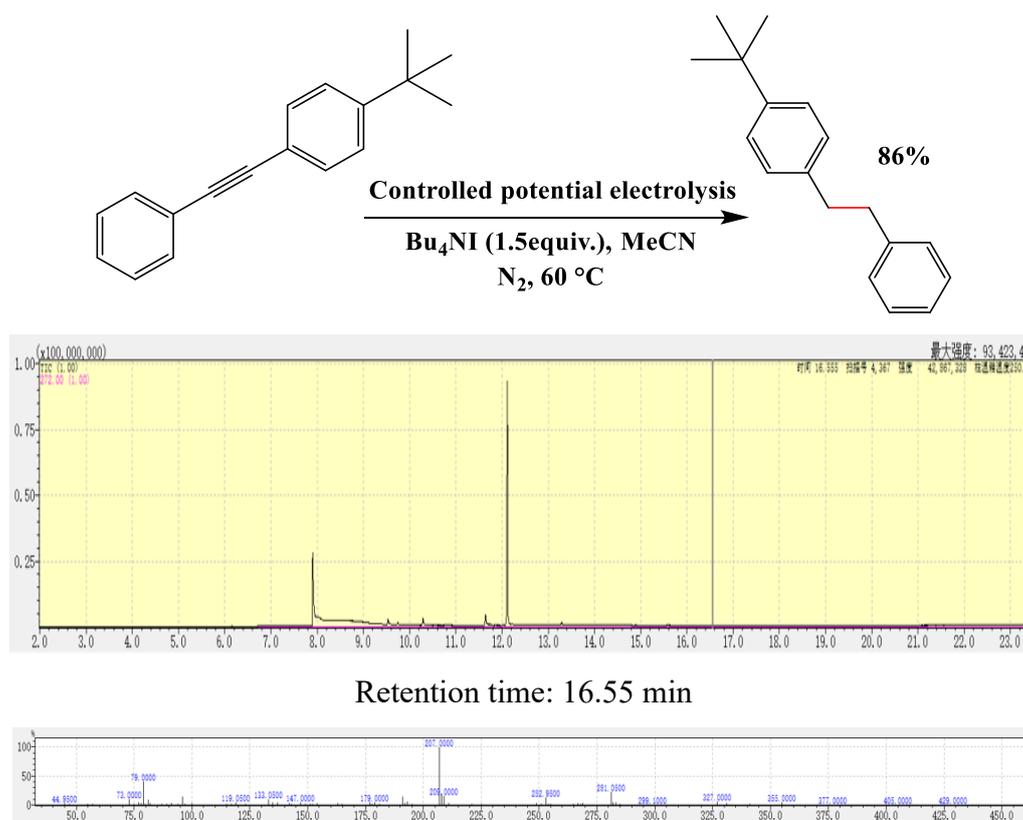
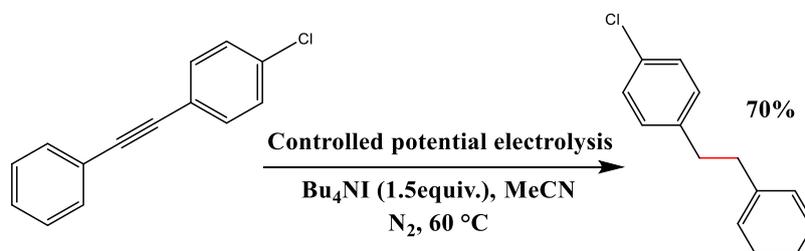


Figure 13. GC-MS plot of the experiment using 1-(tert-butyl)-4-phenethylbenzene as the reaction substrate.

The reaction system with 1-(tert-butyl)-4-(phenylethynyl)benzene as the substrate was analyzed by gas chromatography-mass spectrometry, and as shown in Figure 13, the peak of the reduced product 1-(tert-butyl)-4-phenethylbenzene at the retention time of 16.55 min could be clearly observed, indicating that 1-(tert-butyl)-4-(phenylethynyl)benzene was successfully reduced and the yield of the reaction was 86%.

3.5.3 Electrocatalytic reduction of 1-chloro-4-(phenylethynyl)benzene



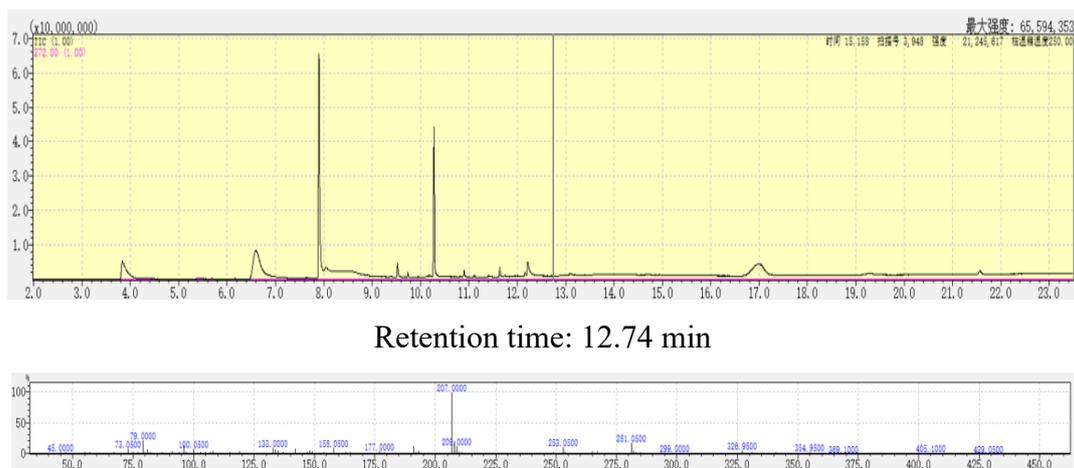


Figure 14. GC-MS plot of the experiment using 1-chloro-4-phenethylbenzene as the reaction substrate.

In the third experiment, GC-MS was also utilized to analyze the reaction system with 1-chloro-4-(phenylethynyl)benzene as the substrate, and as shown in Figure 14, the peak of the product 1-chloro-4-phenethylbenzene could be clearly shown at a retention time of 12.74 min. This indicates that 1-(tert-butyl)-4-(phenylethynyl)benzene was successfully reduced. However, the yield of the reaction measured in the experiment was only 70%, which was presumed to be due to the addition of halogen to the reactants that caused a certain spatial barrier to the reaction.

Chapter 4 Conclusion

Using 1,3,5-triformylphloroglucinol and 2,2'-bipyridyl-5,5'-diamine as organic building units, the COF with bipyridinic structures was successfully constructed by a condensation reaction strategy. Then, the Pd-COF covalent organic framework catalyst with efficient electrocatalytic performance was prepared by successfully embedding Pd metal into this COF material in an alcohol environment. The catalyst exhibited high selectivity for the reduction of alkynes to alkanes as well as high yields. It fully demonstrates that Pd-containing organic porous frameworks have good prospects for application in electrocatalysis.

It is undeniable that covalent organic frameworks are emerging promising crystalline materials among porous materials. It has already shown promising applications in the fields of catalysis, gas storage and separation, sensors, and biomedicine, etc. Wu's team^[13] used Pd-P nanomaterials as cathodes, which allowed the enhancement of the specific adsorption of alkynes, and the semi-hydrogenation of alkynes could be accomplished at a lower potential. For the covalent organic materials containing Pd metal synthesized in this experiment perhaps in the introduction of P-doping can improve the yield of this reduction reaction. Due to the time limitation, only alkynes containing aryl groups were selected for the determination of the electrocatalytic ability of Pd-containing COF materials in this experiment, and more different types of alkynes need to be employed to determine their catalytic ability. In addition, the recovery rate of the synthesized COF materials needs to be measured in future experiments to reflect the excellent performance of this catalyst.

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