本科毕业设计（论文）

Preparation and Catalytic Properties of Organic Porous Materials Containing Metal Centers

学院名称　化学与化工学院

专业班级　应化（国际班）18-1

学生姓名　许同舟

学　　号　201804300282

导师姓名　马丽

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Preparation and Catalytic Properties of Organic Porous Materials Containing Metal Centers

含金属中心的有机多孔材料的制备及催化性能研究

作者姓名　许同舟

专　业　应用化学（国际班）

指导教师姓名　马丽

专业技术职务　讲师

齐鲁工业大学本科毕业设计（论文）

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Contents

Abstract in English

Currently, the catalysts are playing a significant role in the chemical industry and laboratory research. Traditional metal homogenous catalysts have certain limitations such as environmental problems, low catalytic selectivity, stability and recyclability. Therefore, developing a high catalytic efficiency, high chemical stability, and recyclable catalysts materials is in top urgence. Organic porous materials containing metal center catalysts attracts a lot of interests due to its excellent properties. Covalent organic framework (COF) as one of the most potential POPs materials, has a certain prospect in the field of catalysis because of open pores, high porosity, and designable structure.

In this thesis, a TpBpy-COF was successfully synthesized by using monomers 1,3,5-triformylphloroglucinol and 2,2'-bipyridyl-5,5'-diamine through condensation reaction. Based on synthesized TpBpy-COF, $PdCl_2$ was used to introduce into the COF by using a post-modification method, and then Pd-TpBpy-COF was obtained. The surface area of synthesized COF was determined by using N_2 adsorption and desorption curve, which showed the specific surface area was 470 and 259 m^2/g respectively for before and after modification. Also, other characterizations such as SEM image, XPS test, and XRD test were done to prove the COF structure was constructed. And the catalytic performance of synthesized Pd-TpBpy-COF was researched by monitoring the catalytic results of two typical Suzuki coupling reactions. By comparing with several research literature, the experiment results showed that the synthesized Pd-TpBpy-COF gave a wonderful catalytic performance for aryl halide coupling with phenylboronic acid, presenting in more generous condition such as reacting in ambient atmosphere, lower reaction temperature, and less amount needs of catalyst.

Key words: Heterogenous catalysts; covalent organic framework; organic synthesis catalysts

Abstract in Chinese

摘 要

目前，催化剂在化学工业和实验研究中发挥着至关重要的作用。传统的金属均相催化剂存在环境污染、催化选择性低、稳定性低和回收率低等局限问题。因此，开发高催化效率、高化学稳定性和可回收的催化剂材料迫在眉睫。含有金属中心的有机多孔催化材料因其优异的催化性能而备受关注。其中，共价有机骨架（COF）作为最有潜力的有机多孔材料之一，由于其具有开放的孔道、较高的孔隙率以及结构可设计等优势，在催化领域表现出广阔的应用前景。

本论文以 1,3,5−三甲酰基间苯三酚和 2,2’−联吡啶−5,5’−二胺为原料，通过缩合反应成功地合成了 TpBpy-COF，再通过后修饰方式，将 $PdCl_2$ 配位到 COF 骨架上，即得 Pd-TpBpy-COF。经过 N_2 吸附和脱附曲线测定了合成 COF 的比表面积，结果表明，Pd 金属引入前后 COF 的比表面积分别为 470 和 259 m^2/g。此外，通过对合成 COF 的其他表征，如 SEM 图像、XPS 测试和 XRD 测试，证明了 COF 结构的成功构建。为研究合成的 Pd-TpBpy-COF 的催化性能，本文通过对两个典型的 Suzuki 偶联反应的催化结果进行监测。实验结果表明，合成的 Pd-TpBpy-COF 对卤代芳烃与苯硼酸的偶联反应具有良好的催化性能。与之前文献报道的以金属为中心的 COF 催化材料相比，反应进行的条件更为轻松，如可在空气中反应，反应所需温度更低，催化剂用量更少等。

关键词：非均相催化剂　共价有机框架　有机合成催化

Chapter 1 Introduction

1.1 Catalyst background

Nowadays, the modern industry is under great developing. As a significant element of industry, chemical industry has developed in an extremely fast speed since IUPAC proposed the definition of catalyst in 1981. Catalyst, as a determining factor in chemical reactions, can change the reaction speed or reduce the reaction difficulties in chemical industry, which will save a lot of resource including energy and raw materials in the production line. Both the big consumption of energy resources and the large amount production exacerbate environmental problem in the world, which is pressing a special need for a more sustainable and efficient chemical industry. This transformation can be done by developing a new highly selective, clean, and sustainable catalyst to reduce the process costs, and increase the yield and usages times of catalyst.

Traditionally, the most used catalysts are homogeneous catalyst. It is usually a soluble metal complex which typically works in the same phase with reactants. The advantages of this kind of catalysts are that the catalytic sites have the access to all reagents. And by introducing proper modification of homogenous catalysts, it can achieve high efficiency, selectivity and a high yield of production[1]. Due to this perfect catalytic performance, they are used in both laboratory and industry life. However, there are several big limitations in the industrial applications. Firstly, the catalysts contamination has a strict level, which is difficult to achieve in the industry plant, and the storage is costly. Secondly, homogeneous catalysts are in the same phase with reactants, thus the final purification and separation from final product are difficult. Moreover, the challenging recollection will make the catalysts disposable.

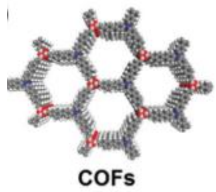
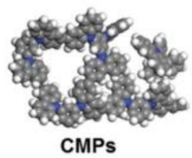
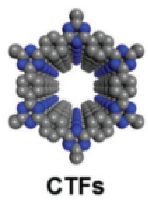
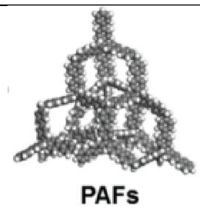
In order to solve the limitation of homogeneous catalysis, a new kind of catalyst called heterogenous catalysis attracts great interests by scientists. Different from homogeneous catalysts, heterogeneous catalysts do not exist in the same phase with reactants. They are usually under the support by certain materials, including using the solid catalysts in a liquid phase reaction[2]. According to some research, heterogenous catalysts display strong advantages among sustainability, and recyclability, especially in the separation process compared with homogeneous catalysts[3, 4]. Although heterogenous catalysts are sustainable and recyclable, there are still some issues such as less efficient than homogenous one. So, there is an urgent demand for developing a new kind of catalyst that could balance the benefits between homogenous and heterogenous substance.

Currently, porous organic polymers (POPs), as a typical representative of porous material, with an ideal porous structure to incorporate catalytically active species in the frameworks, has a high desired catalytic performance. Besides working as a support, POPs can also be used as a precursor for sacrificing themselves to synthesize another porous catalyst. The pore structure of POPs can be tunable, by pre-design or modification, it can get controllable functionalities, high surface area, low density, and good chemical stability[5]. Having these wonderful properties, POPs, with the support of some certain catalysts in their frameworks, will achieve high efficiency, good recyclability, and sustainability in catalytical reaction.

1.2 Representative POPs materials

There are six representative POPs materials (Table 1) divided by their different structural characteristics and preparation methods. Among these six, HCPs, PIMs, CMPs and COFs are the most common used structures, which will be discussed below.

Table 1. Examples of POPs materials[5]

Covalent organic frameworks		Conjugated microporous polymers	
Covalent triazine frameworks		Hyper-cross-linked polymers	
Polymer of intrinsic microporosity		Porous aromatic frameworks	

(1) Hyper-cross-linked polymers (HCPs)

HCPs are the polymers that are polymerized by hyper-cross-linked method. This hyper cross-linked method could prevent the tight stacking among the polymer chains to get an abundant micropores structure between the molecular chains. The material was first studied and investigated by Davankov and coworkers via Friedel-Crafts reaction using polymer as precursors, haloalkane as cross-linker[6]. At that time, the polymeric precursors can be linear polystyrene and polysulfone or copolymers of styrene with a certain amount of divinylbenzene. Recently, due to the development of cross-linker, simple and inexpensive materials such as benzene, pitch and polycyclic aromatics can be used for HCPs starting[7]. And nowadays, there are typical three ways to synthesize HCPs that are post-crosslinking method[8], self-condensation and polymerization of small molecule method[9], and external crosslinker knitting method[10]. Figure 1 shows the example of the hyper-cross-linking process of HCPs. Currently, HCPs have attracted many scientists' interests because of their various synthetic strategies, generous operation conditions, and ease of functionalization[6].

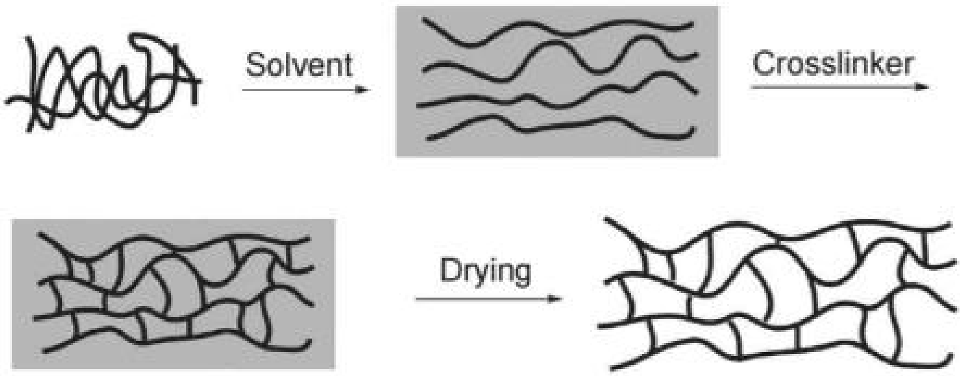


Figure 1. The hyper-cross-linking process[11]

(2) Polymers of intrinsic microporosity (PIMs)

PIMs are a special class of polymers with a very high specific surface area (S_{BET} >200 m^2g^{-1}), due to the presence of various rigid twisted structure in the molecules and the polymer cannot be effectively stacked when forming a dense accumulation, resulting in a large number of micropores, whose pore size is mostly less than 2 nm, providing a perfect channel for gas transmission. The earliest PIMs material could be tracked back in the early of 1980s, Masuda *et al.* developed a linear chain disubstituted glassy polyacetylenes which showed great gas permeabilities but failed because of the low selectivity[12]. In recent years, PIMs have been developed a lot and achieved great progress for example, Mckeown and Budd group researched a ladder PIMs which provided a big BET surface area (up to 1000 m^2g^{-1}), high gas permeability and big improvement of gas selectivity[13].

(3) Conjugated microporous polymers (CMPs)

Since the discovery of conductive polyethylene in 1977, a large number of conjugated polymers have been synthesized and widely used. One class of conjugated polymers has a special microporous structure and is called conjugated microporous polymers (CMPs). Commonly there are three different ways to synthesize CMPs, Sonogashira-Hagihara cross coupling reaction[14], Yamamoto cross coupling reaction[15], and electrochemical polymerization[16]. Compared with other conjugated polymers, CMPs' surface area ratio and porosity attract scientists' interests. Furthermore, CMPs have big surface area, good chemical stability, nice thermal stability and tunable structure. Due to these characteristics, CMPs have great potential applications in adsorption, separation, catalysts and gas storage[14].

(4) Covalent organic frameworks (COFs)

COFs are two-dimensional or three-dimensional crystalline porous polymer materials formed by organic structural units through covalent bond connections, which have the characteristics of high thermal stability, large specific surface area, rich pores, adjustable molecular structure and many active sites. Different from metal organic frameworks (MOFs), it can be composed entirely of light elements such as carbon, hydrogen, nitrogen and oxygen, it does not contain heavy elements such as metals. Scientists can create COFs of different pore sizes and change the substances that pass through them or are contained in these pores to achieve functional diversification. In three-dimensional COFs, organic units are connected by covalent bonds to form a three-dimensional network structure, which is more used in catalysis and gas adsorption, which is similar with MOFs. Moreover, in two dimensional COFs, organic units are connected to the two-dimensional atomic layer, and the atomic layers are further stacked to form a layer structure through π-π interactions, and the entire frame structure is determined by the covalent bonds in the layer and controlled by the non-covalent forces between the layers, so it has broad application prospects in the field of energy storage.

1.4 The applications of POPs supported transition metal catalysts

Transition metal-based catalysts play a significant role in the organic reaction, but it still has some problems in the recollection step after catalyzing. Due to the catalysts are in mixed with reactants, the purification and separation after the reaction can be difficult.

To achieve a good catalytic performance and sustainability of catalysts, numerous supports have been developed, such as organic and inorganic hybrids, carbon materials and biomaterials[17]. Although they have shown good chem-selective property in the catalytic process, their structure and functional tunability are limited, which narrows down their wide application[18].

POPs materials with high porosity surface area, tunable pore size, and recollection possibility, represent an excellent class of candidate supports. Recently, POPs applied as transition metals supports have gotten great attention. In the following section, some common POPs supported transition metal catalytic reaction examples are reviewed and discussed.

The synthesis from CO_2 and epoxides to cyclic carbonates is one of the commonest reactions with the help of an active metal center supported by porous organic polymers. Usually, the containing metal in the active site is the main group metal zinc. This property is not only confined to the main group metal, but some transition metal can also be encountered to POPs. For example, Dai *et al.* synthesized a bipyridine-constructed and hierarchical Cu and Co supported POPs (Cu/POP-Bpy and Co/POP-Bpy) by using 5,5'-divinyl-2,2'-bipyridine (v-Bpy) to make a solvothermal polymerization in DMF with the help of AIBN (azobisisobutyronitrile), which showed great catalytic activity to the cycloaddition of CO_2 and epichlorohydrin[19]. Especially, for Cu/POP-Bpy, loading 0.5 mol% ratio could lead to a 99.0% conversion rate for epichlorohydrin after 48 hours. Besides the yield, this catalyst performed good stability and recyclability. The Cu or Co/POP-Bpy structure and its catalytic mechanism is drawn in Figure 2.

POPs supported transition metal catalysts have a great effect on the organic oxidation reaction, especially for oxidation of alkenes. The most interesting finding is that this catalyst material shows great recyclability compared with other related polymer structure. Gu *et al.* reported a manganese-porphyrin-POP material catalyzing the epoxidation of styrene reaction can be recycled 5 times with only a small decreasing of yield[20]. In contrast, compared with the traditional homogeneous catalyst (TPP) MnCl analogue (the structure is shown in Figure 3) which can be decomposed easily, Mn/PPOP affords a higher styrene oxide yield (around 80% while previous catalyst has only 60% conversion rate) due to its high concentration of active sites inside the pore structure[21].

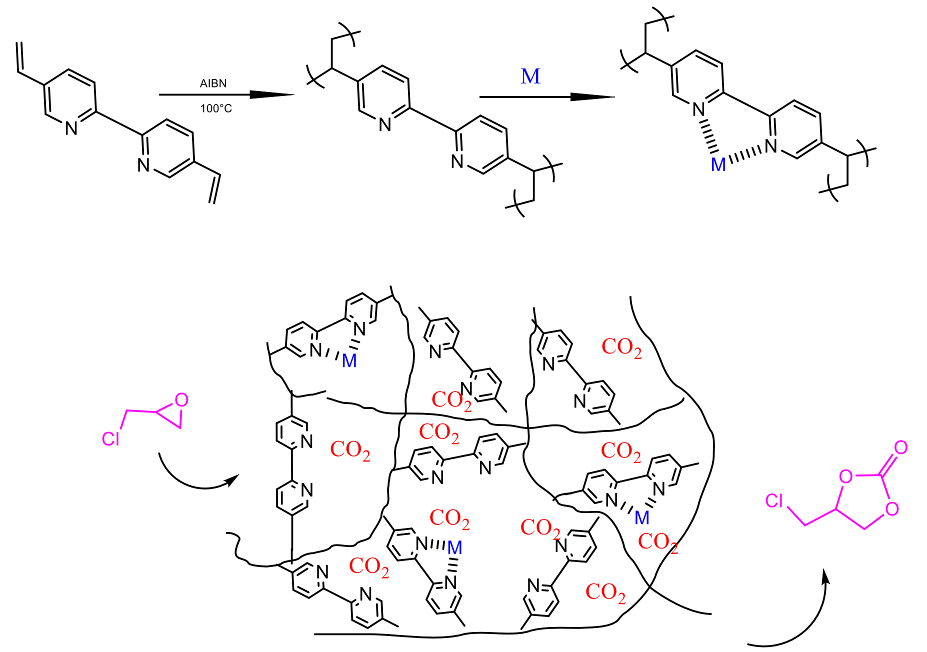


Figure 2. Cu or Co/POP-Bpy structure and its catalytic mechanism

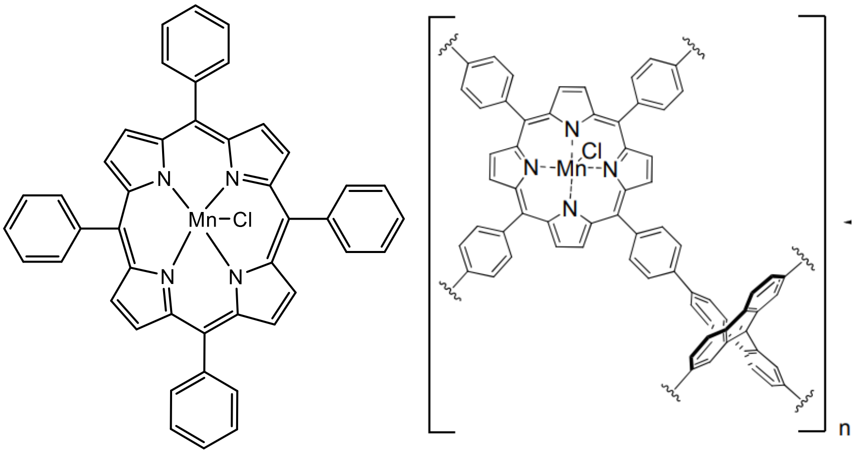


Figure 3. Traditional homogeneous catalyst (TPP) (Left), Mn/PPOP catalyst (Right)[21]

Transition metal POPs can also be seen working as catalysts in the overall reduction reaction. The Simplest and easiest reduction reaction is the hydrogenation of alkene and alkyne. Traditionally, for the hydrogenation reaction, precious metals like platinum, and palladium based microporous systems play an important role but the material of catalysts costs a lot. And for earth-abundant metals, they are mainly utilized on homogenous catalysts such as phosphine and nitrogen based ancillary ligands structured. A research group explored a series transition metalated POPs including vanadium, chromium, manganese, cobalt and nickel. The results showed that V, Cr, Mn/POPs presented great activity and selectivity for alkyne semi-hydrogenation[22].

Coupling reaction involving carbon and carbon bond, and carbon heteroatom bond forming, which shows great potential on organic synthesis, pharmaceutical intermediate production, and material sciences technology[23]. More importantly, due to the harsh reaction condition, such as temperature and large number of catalysts, finding the proper and efficient catalysts has become the top attraction. In traditional, copper-based materials especially heterogenous catalysts are typically used for this coupling reaction. However, research showed that although this kind of catalysts can be easily recollected after the reaction, the catalytic activity during the reaction is not high due to the low surface area[24]. In 2013, Sun *et al.* obtained a POP supported copper with a high surface area, good porosity, large pore volume and great chemical and thermal stabilities. The research results proved that this Cu/POP could be much more active than previous catalysts for a more generous Glaser homocoupling condition of alkynes and Huisgen 1,3-diolar cycloaddition of alkynes with benzyl acid. Moreover, this Cu/POP could perform well with a low catalyst loading for saving catalyst materials, and it could be easily recovered or recycled without catalytical activity loss until running times up to 10[25].

COF materials as an essential branch of POPs materials, compared with other POPs materials, it has a lot of advantages such as lower highly ordered periodic structures, more controllable pore distribution, wonderful thermal and chemical stabilities, and ease of modification, which are studied a lot during these years. Also, as an important catalysis branch of organic synthesis, metal catalysis has been researched for decades. In order to combine the advantages of these two materials, anchoring metals into COFs to achieve the cooperation of these two materials catalyzing organic reaction is naturally and widely developed[26].

However, it is not a simple process for combination of metal complexes with COFs material. Because there are various building blocks in COFs which may have different incorporation units. That means even the same substrate might have different incorporation products when the metal complexes are introduced into COFs. Hence, this situation could bring many possibilities for the catalytic activity and efficiency. For instance, Chen *et al.* reported that the synthesizing environment might have effects on the catalytic performance of COFs. They found that Cu-COF_{HX}, which is synthesized under dichlorobenzene and n-butanol, showed higher surface area, higher crystallinity, stability as well as better selectivity in oxidation reaction, compared with Cu-COF_{DMF} which is synthesized in DMF[27].

In 2017, Cui *et al.* reported a modified COF which had a chiral structure with controlled crystallinity and good stability serving as a heterogenous catalysts for diverse asymmetric reactions[28]. In this research, various metal ions are introduced into this CCOF material such as Zn^{2+}, Fe^{2+}, Co^{2+}, and V^{4+}. All these catalysts can bring a relative high yield of the reactions and they can be recycled at least 5 times. This approach showed that the chemical stability, crystallinity, catalysis efficiency, and recyclability of COF material could be improved after several modification and redesign, which also presented the flexibility of COF working as a supporting catalysis material.

1.5 The purpose and significance of this thesis

In recent years, the research on organic porous materials containing metal center catalysts is being more and more in-depth due to its excellent properties. Covalent organic framework as one of the most potential POPs materials, has a certain prospect in the field of catalysis because of its special properties and continuous enrichment of post modification methods.

This thesis by using monomers 1,3,5-triformylphloroglucinol and 2,2'-bipyridy-5,5'-diamine through condensation reaction successfully synthesizes a TpBpy-COF. Based on synthesized TpBpy-COF, $PdCl_2$ is used to introduce Pd metal into the COF, which is named Pd-TpBpy-COF. And the catalytic performance of synthesized Pd-TpBpy-COF is researched by monitoring the catalytic results of two typical Suzuki coupling reactions.

Chapter 2 Experiment Section

2.1 Reagents and apparatus

2.1.1 Reagents

Table 2. Experiment reagents

Reagents	Purity	Manufacturer
1,3,5-triformylphloroglucinol (Tp)	AR	Jinlin Chinese Academy of Sciences Yanshen Technology Co., Ltd.
2,2'-bipyridyl-5,5'-diamine (Bpy)	AR	Jinlin Chinese Academy of Sciences Yanshen Technology Co., Ltd.
Dimethylacetamide (DMAc)	AR	Shanghai Saen Chemical Technology Co., Ltd.
1,2-dichlorobenzene (o-DCB)	AR	Shanghai Saen Chemical Technology Co., Ltd.
Acetic acid	AR	Tianjin Dasen Chemical products Co., Ltd.
Acetone	AR	Yantai Yuandong Fine Chemicals Co., Ltd.
N, N-dimethylformamide (DMF)	AR	Tianjin Fuyu Fine Chemical Co., Ltd.
Tetrahydrofuran (THF)	AR	Tianjin Fuyu Fine Chemical Co., Ltd.
$PdCl_2$	AR	Shanghai Aneji Chemical Co., Ltd.
Methanol	AR	Tianjin Fuyu Fine Chemical Co., Ltd.
Ethanol	AR	Tianjin Fuyu Fine Chemical Co., Ltd.

2.1.2 Apparatus

Table 3. Experiment apparatus

Instrument	Manufacturer
Electronic balance	Beijing Doris Science 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.
Circulating water vacuum pump	Gongyi Yuhua Instrument Co., Ltd.
Deionized water machine	Shanghai gaosen Instrument Co., Ltd.
Rotary evaporator	Gongyi Yuhua Instrument Co., Ltd.
Portable ultraviolet analyzer	Hangzhou Qiwei Instrument Co., Ltd.

2.2 The synthesis of TpBpy-COFs

Tp (21 mg), Bpy (27.9 mg), DMAc (1.5 mL) and *o*-DCB (0.5 mL) were added into a 10 mL Ampoule tube. The mixture was ultrasonicated for 10 min to disperse homogeneously. Then, 6 M aqueous acetic acid was added. Next, the new mixture was degassed via three successive freeze-pump-thaw cycles. After that, the Ampoule tube was sealed in vacuum condition by using a flame spray gun, and then it was put into a 120 °C constant temperature oven. A huge number of insoluble substances could be produced in the system after 3 days reaction time. In the end, a yield of around 70% of TpBpy-COF can be gained after several processes of purification. The overall reaction formular is shown in Figure 4.

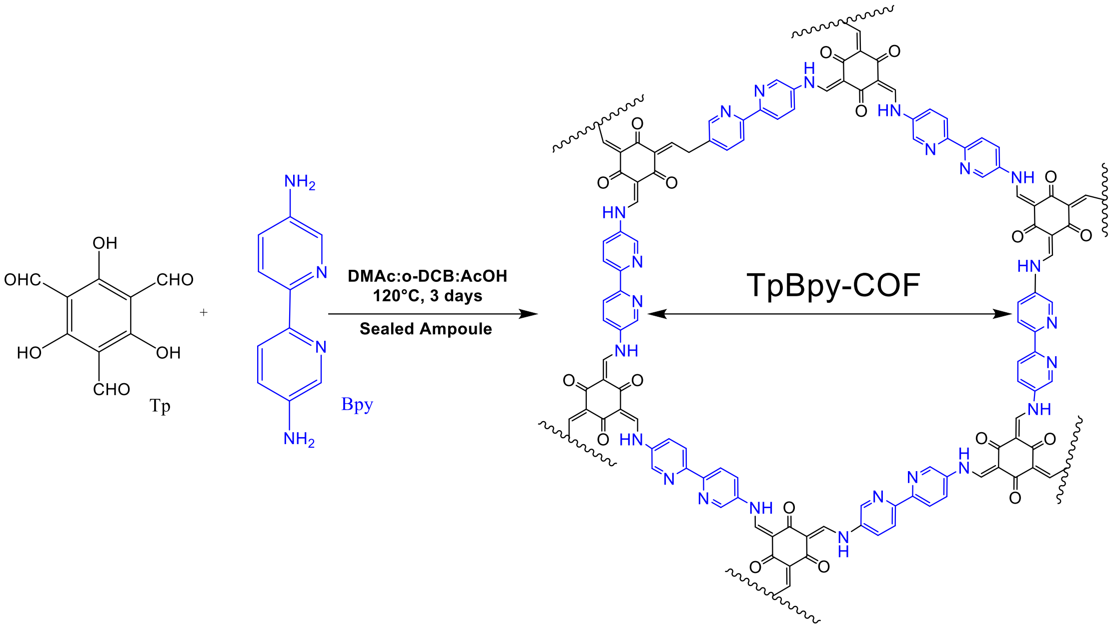


Figure 4. Synthesis of TpBpy-COF

2.3 Purification of produced COFs materials and preparation of Pd-TpBpy-COF

In this paper, the purification of produced COFs materials could be serval steps below. Firstly, the red solid which is at the bottom of the bottle is removed by filtration after the reaction. Then, acetone and DMF are used to wash out the un-reacted monomers. After that, the Soxhlet extraction method is applied, which is a purification method of purifying the COF by using Soxhlet extractor. The purification efficiency of Soxhlet extractor can be relatively high in the final products with using only a small amount of solvent due to the reusing of solvent, and its target is to remove the insoluble raw materials and oligomers in the final system. Specifically, the solid product is extracted by using THF as the solvent for 2 days (48 hours), then the product is dried and activated under vacuum at 60 °C for 24 hours. After these operations, TpBpy-COF is purified and obtained.

The Pd-TpBpy-COF was prepared by reacting TpBpy-COF with $PdCl_2$ in the presence of dry methanol at room temperature with an overnight-stirring. The solid precipitate was filtered out, then washed with excess THF and ethanol for three times. The obtaining material was dried under vacuum for overnight. The process of preparing the COFs is shown in the Figure 5.

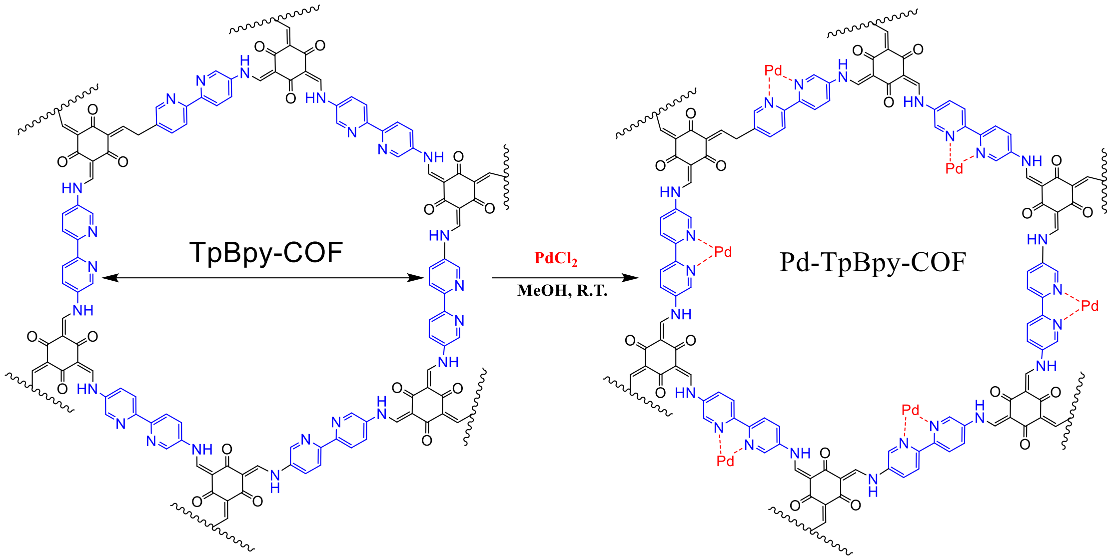


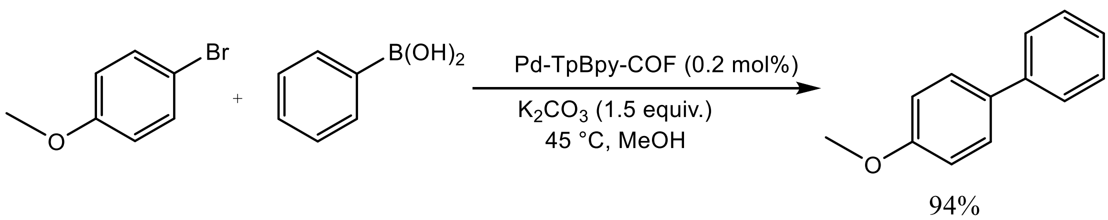
Figure 5. Synthesis of Pd-TpBpy-COF

2.4 Pd-TpBpy-COF catalyzed Suzuki Coupling reaction

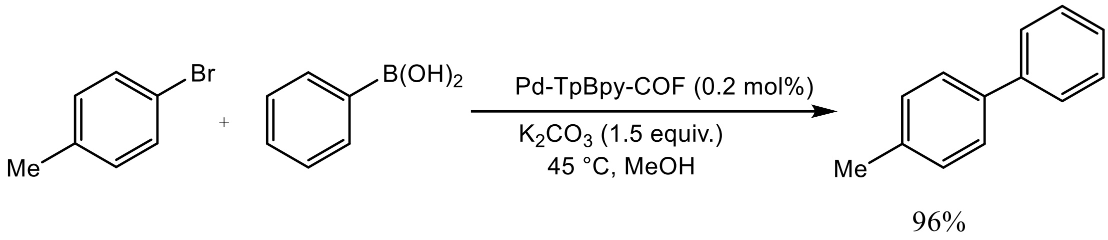
To test the catalytic performance of Pd-TpBpy-COF, two typical Suzuki reactions are made during the process.

In this experiment, aryl halide (0.2 mol), phenylboronic acid (0.25 mol), inorganic base K_2CO_3 (1.5 equiv.), Pd-TpBpy-COF (0.02 mol%) are added in a two-necked round-bottom flask, while MeOH is used as solvent. To stir the mixture during the reaction time, a magnetic stirring is needed. The reaction temperature is under controlled at 45 °C by using the oil bath and the reaction is monitored by TLC. After the completion of reaction, the mixture is brought to post treatment. The mixture was first centrifugated, as well as the solid was washed by using 5 mL dichloromethane three times in total. Prue water was used to wash the organic phase in order to remove the K_2CO_3. Then a reduce pressure evaporation was done for the organic phase to separate the crude products and then further purification was done by using column chromatography (Petroleum Ether: Ethyl Acetate=20:1). Then it is dried in a rotary evaporator. Finally, the conversion ratio is obtained by using ^{1}H NMR spectroscopy.

2.4.1 Reaction of 1-bromo-4-methoyxbenzene with Phenylboronic Acid



2.4.2 Reaction of 1-bromo-4-methlbenzene with Phenylboronic Acid



Chapter 3 Results and Discussion

3.1 Characterization of synthetized COF material

3.1.1 Bruunauer-Emmett-Teller (BET) surface area

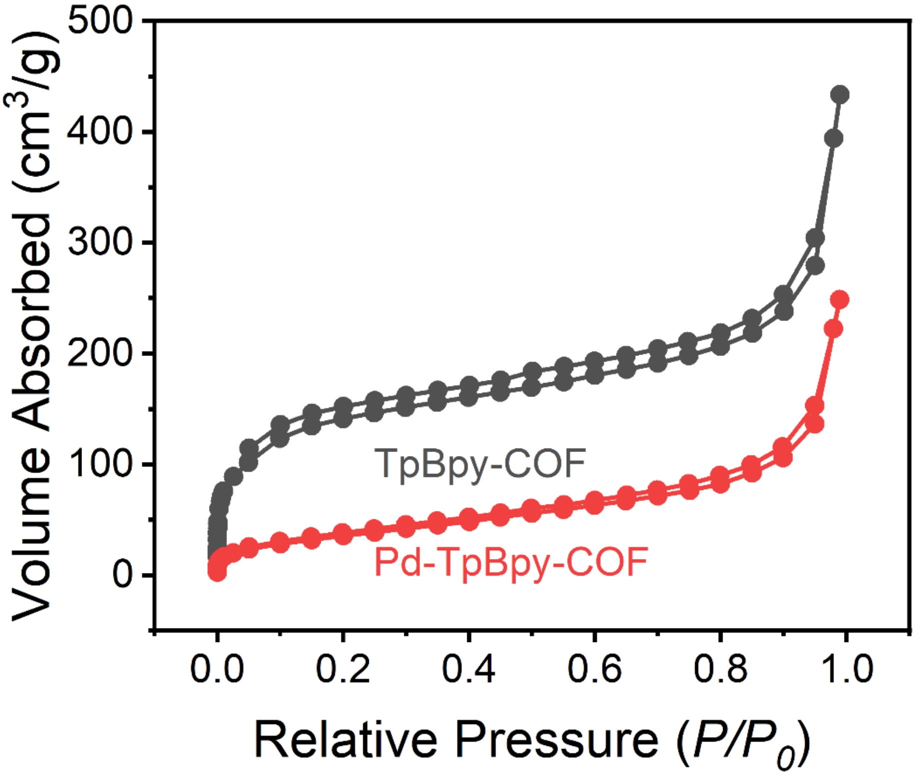


Figure 6. N_2 adsorption-desorption isotherms of prepared materials (TpBpy-COF, black; Pd-TpBpy-COF, red).

Covalent organic framework has plenty good physical and chemical properties, such as good specific surface area, pore size distribution, rigid topology and so on. To test the microporous characteristics in the synthesized materials and obtain the BET surface areas of synthesized TpBpy-COF and Pd-TpBpy-COF, the nitrogen isotherm adsorption test is carried. All the collected data are drawn in a nitrogen adsorption isotherm shown in Figure 6. From the test result, it shows that most of the pores on the synthesized TpBpy-COF and Pd-TpBpy-COF are mesopores. And there is an upward convex inflection point in the adsorption curve of isotherm in the lower P/P_0 range (0-0.1) and in the higher range of relative pressure (0.3-0.8), the adsorption capacity increases slowly probably due to multilayer adsorption of synthesized materials, which indicates the adsorption curve should be IV type according to the classification of adsorption isotherm by IUPAC. After the model calculation, the BET surface areas of TpBpy-COF and Pd-TpBpy-COF are obtained, which are 470 and 259 m^2/g respectively. The larger specific surface area of TpBpy-COF gives a better active area for post treatment of its pore surface wall. In addition, the decline of surface area of Pd-TpBpy-COF indicates that the catalyst Pd metal is fixed by the mesoporous structure of the COF material before modification.

3.1.2 TEM test of synthesized COF materials

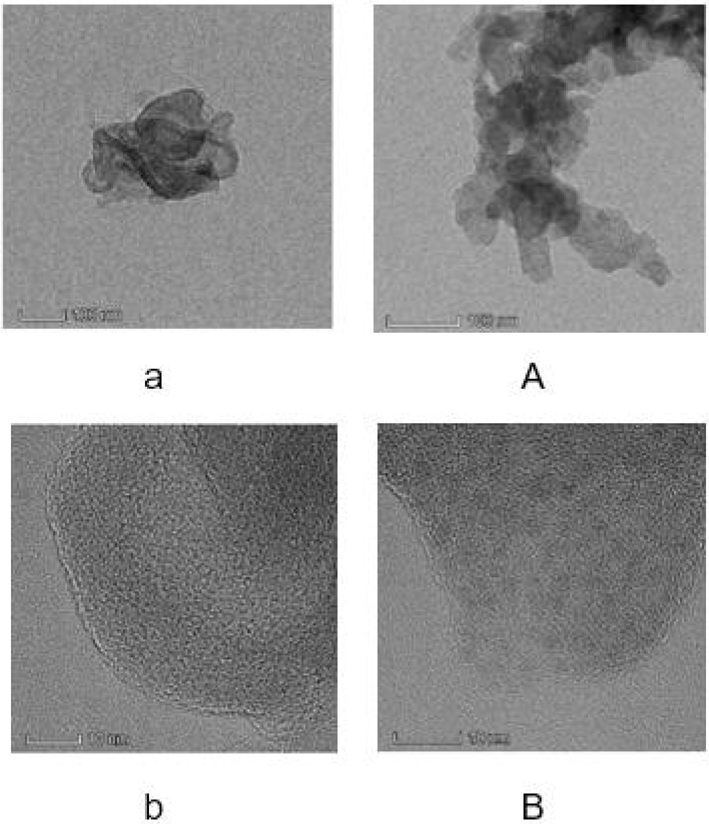


Figure 7. TEM image of synthesized COF materials (TpBpy-COF: a, b; Pd-TpBpy-COF: A, B)

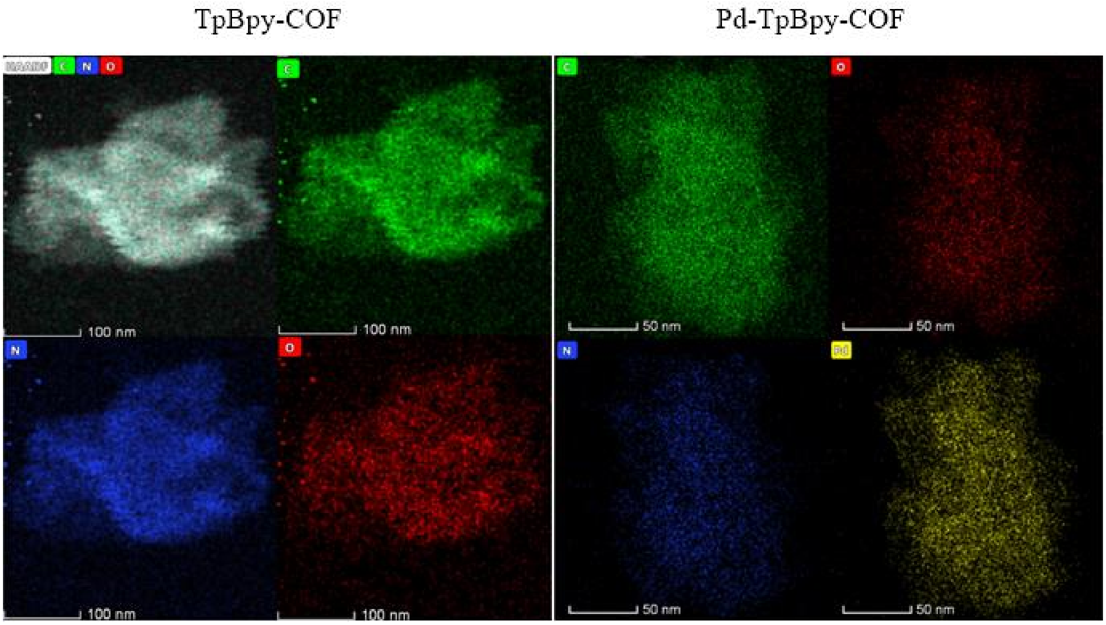


Figure 8. TEM-mapping of synthesized COF materials

The TEM test shows that the synthesized COF materials are in a sheet-layer stacked structure. From TEM analysis of the test material, it is obvious that catalyst metal Pd is dispersed uniformly in Pd-TpBpy-COF.

3.1.3 XPS test

By using the XPS test to analyze the synthesized Pd-TpBpy-COF, the oxidation state of Pd in the framework can be confirmed. The main elements of the Pd-TpBpy-COF are tested and analyzed. The result of XPS analysis is presented in Figure 9. Zooming the binding energy from 328 eV to 348 eV, the energy peaks of Pd element can be further analyzed. From Figure 10, it can be easily observed that the characteristic binding energy peaks of Pd-TpBpy-COF, which are the binding energy peaks of Pd 3d5/2 and Pd 3d/2, are at 337.8 eV and 343.1 eV, respectively. And the results indicate the element Pd in the substance is presenting as Pd (II). Finally, according to the XPS analysis, the atomic ratio of Pd is 5.49%.

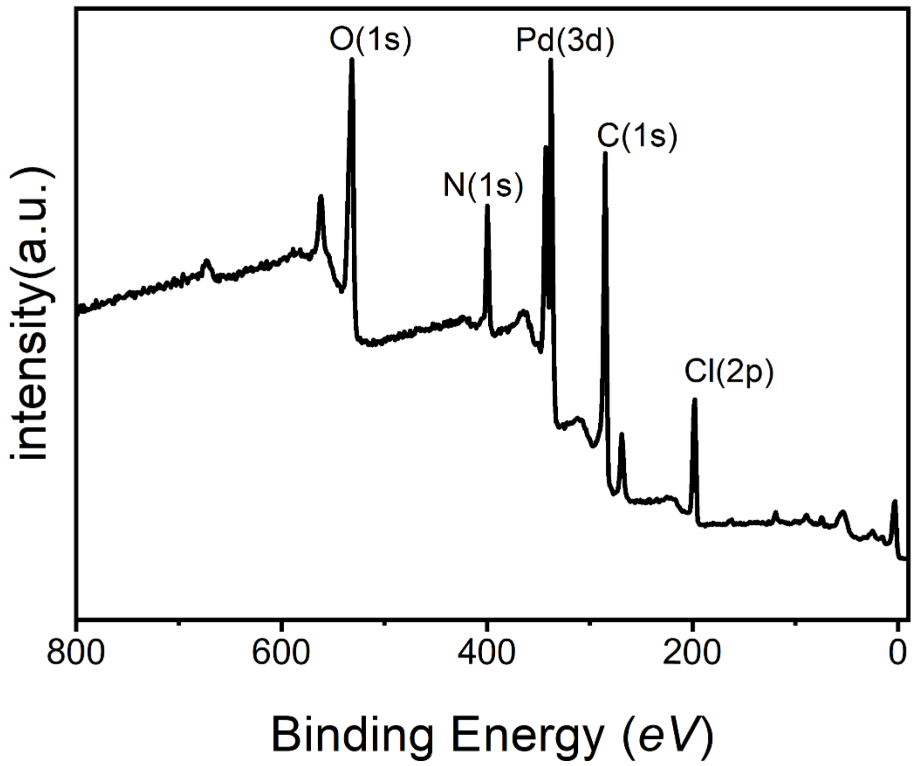


Figure 9. XPS analysis of Pd-TpBpy-COF

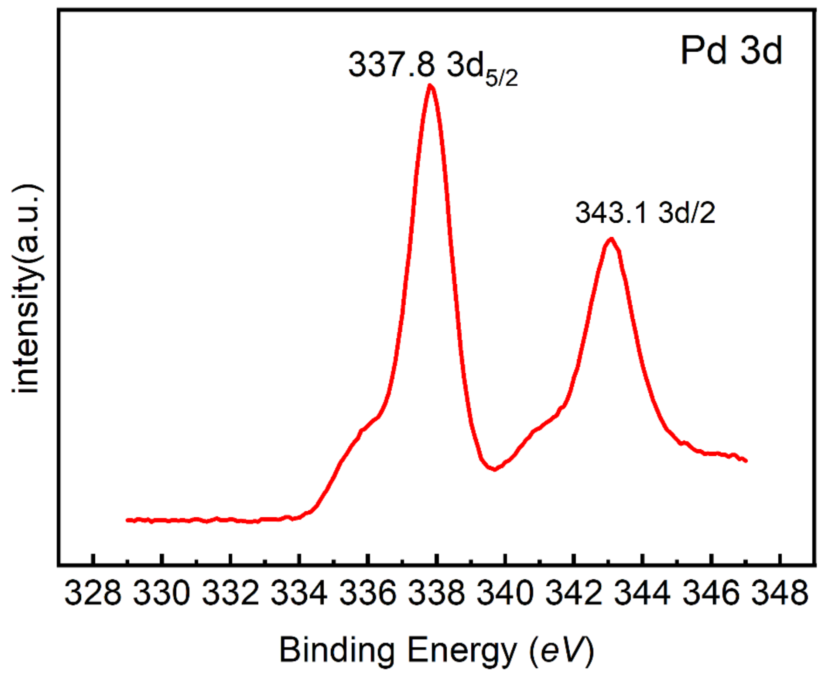


Figure 10. The analysis of Pd element in Pd-TpBpy-COF

3.1.4 XRD test

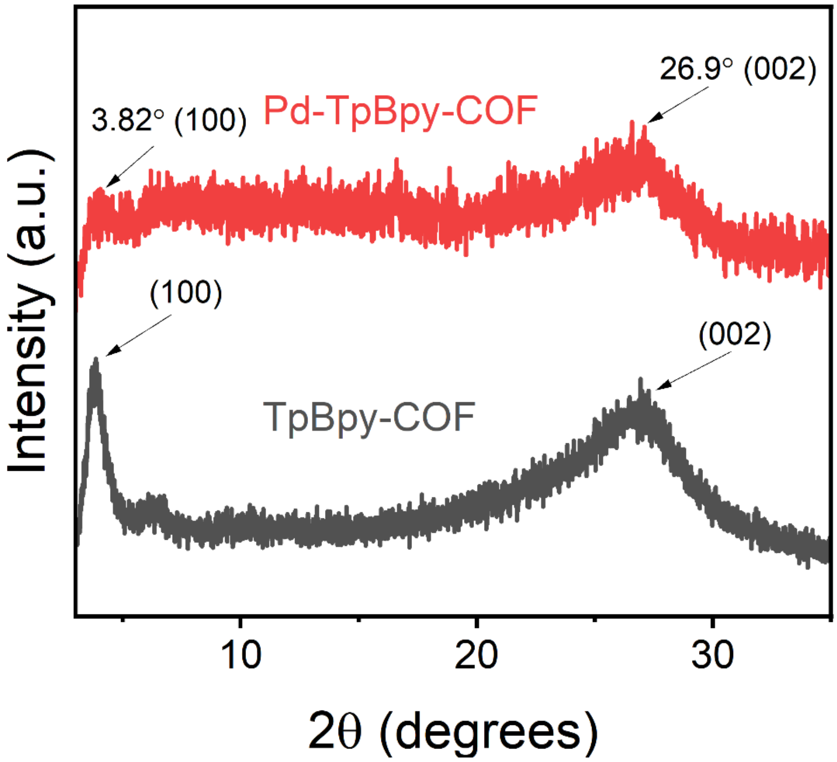


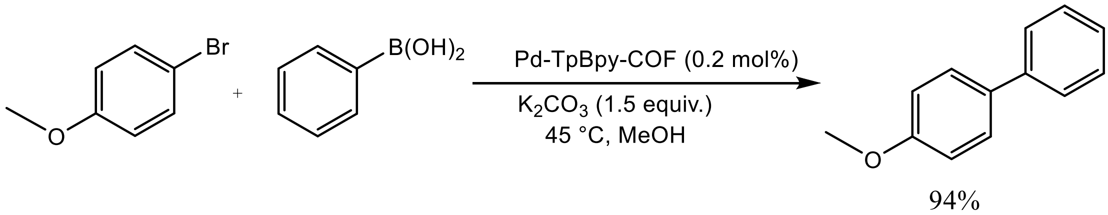
Figure 11. XRD of synthesized COF materials

Aiming for checking the crystallinity of synthesized COF materials, XRD test has been done. Figure 11 shows the results of XRD test. From the image of XRD, it shows that there is a reflection from (100) plane peak at 3.82° (2θ) for both TpBpy-COF and Pd-TpBpy-COF. However, the crystallinity of Pd-TpBpy-COF is not as high as TpBpy-COF's. In addition, there is a presence of π-π stacking between the COF layers which is indicated by the (002) reflection peak at 26.9°.

3.2 The catalytic performance of Pd-TpBpy-COF in Suzuki coupling reaction

The catalytic performance and activity of Pd-TpBpy-COF is tested in one of the most representative Pd-catalyzed reaction, Suzuki coupling reaction. Although Suzuki coupling reaction has been widely developed by using homogenous catalyst condition to form C-C bonds, its industrial application is still limited because of the challenging problem of separating and recycling the expensive Pd catalysts from the mixture system. However, COF material, as one of the most popular POPs materials, supported Pd catalysts could solve or relieve the difficulties of separating and recycling phase as well as improve the catalytic activity and efficiency at the same time.

3.2.1 Reaction of 1-bromo-4-methoyxbenzene with Phenylboronic Acid



After several processes of purification for the resultant of first reaction, the product is tested by nuclear magnetic resonance (NMR). The test result proves that the product of reaction is the desired product 4-methoxy-1,1'-biphenyl. The NMR result is shown in Figure 12. And the reaction yield is calculated, which is around 94%. Compared with previous research made by Ding *et al.*[29], this experiment uses more than half amount less catalysts and more generous react temperature (in Ding's group, the reaction temperature is 150 °C), resulting in a similar product yield, which indicates the catalytic performance of synthesized Pd-TpBpy-COF is good for reaction of 1-bromo-4-methoyxbenzene with phenylboronic acid.

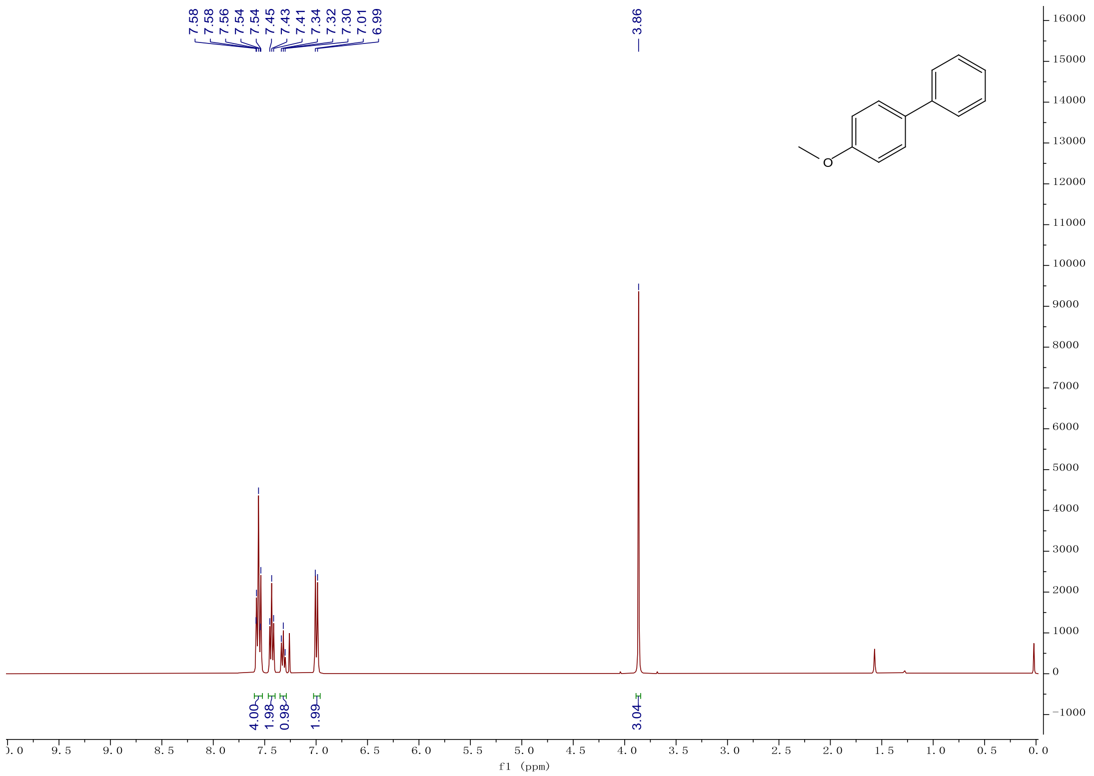
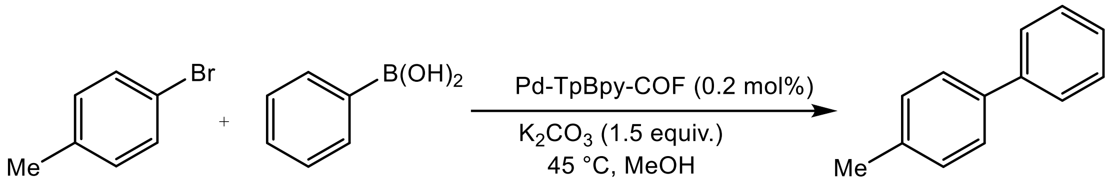


Figure 12. NMR of first reaction resultant

3.2.2 Reaction of 1-bromo-4-methlbenzene with Phenylboronic Acid



96%

After the reaction is finished, the similar procedure is done for the second reaction. Also, the product is tested by NMR and result is shown in Figure 13. After analyzing the NMR test, the product is identified as the desired substance, 4-methyl-1-1'-biphenyl, which has 96% conversion rate. The catalytic performance of Pd-TpBpy-COF is shown by a comparison made with a Pd@SP-POP2 catalyst[30]. Instead of using 1% mol Pd@SP-POP2 and 80 °C reaction condition, this experiment uses only 0.2 mol% catalysts and 45 °C react temperature, which not only saves the amount of catalysts but also energy consumption for a higher conversion rate.

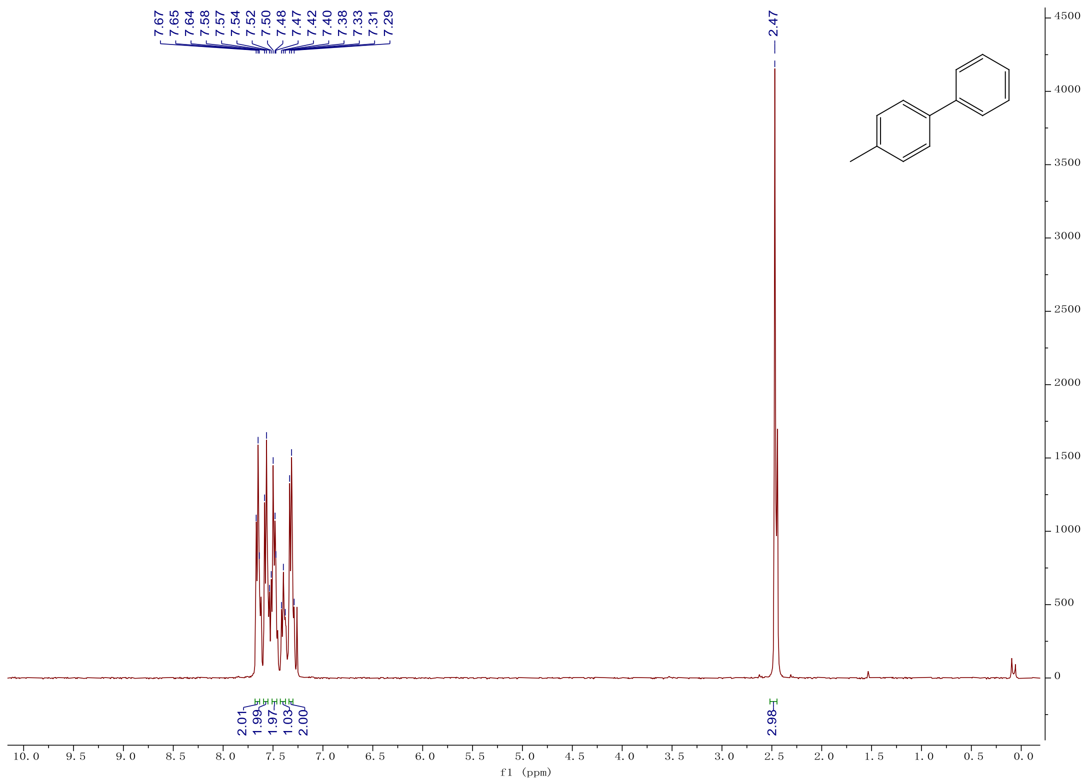


Figure 13. NMR of second reaction resultant

Chapter 4 Conclusion

In summary, a TpBpy-COF material is successfully synthesized by using monomers 1,3,5-triformylphloroglucinol and 2,2'-bipyridyl-5,5'-diamine through condensation reaction. After utilizing $PdCl_2$ to make the post modification, a Pd-TpBpy-COF is obtained. And the catalytic performance of synthesized Pd-TpBpy-COF is monitored by using two typical Suzuki coupling reactions. Several comparisons are made with previous literature synthesized POPs supported metal catalysts. The results show that the new Pd-TpBpy-COF gives wonderful performance for catalyzing aryl halide coupling with phenylboronic acid, presenting in more generous condition such as reacting in ambient atmosphere, lower reaction temperature, and less amount needs of catalyst.

However, this experiment still has several points could be improved. For example, the XRD test results shows the crystallinity of TpBpy-COF is general good but for the crystallinity of Pd-TpBpy-COF does not reach a desired level. There are mainly two possible reasons for this result. One is the enol tautomerism in the material structure, which could make a worse reversibility of the reaction. And if the reaction rate is fast, it might lead to a poor crystallinity. The other explanation is that Pd metal is added between the layers which will destroys the order of the material. This could also make the crystallinity lower. So, it could be better if there is possible condition to monitor the formation process of COF material, which might help the final properties of COF itself.

Also, the experiment could be more complete by adding the recycling process of the synthesized Pd-TpBpy-COF and after each recycle, the catalyst can be dried and then directly put into next generation of catalysis without any further treatment to exam the recycling properties of this material.

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