

学校编码: 10384

分类号\_\_\_\_\_密级\_\_\_\_\_

学号: 20520141151589

UDC\_\_\_\_\_

厦 门 大 学

硕 士 学 位 论 文

# Pd-UiO MOFs 催化剂的设计、制备及其串联催化 CO<sub>2</sub> 加氢、酯化制甲酸乙酯的性能

Design and Preparation of Pd-UiO MOFs Catalyst and Performance for Catalytic Tandem Hydrogenation and Esterification of Carbon Dioxide to Ethyl Formate

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专业名称: 物 理 化 学

论文提交日期: 2017 年 05 月

论文答辩时间: 2017 年 05 月

学位授予日期: 2017 年 月

答辩委员会主席: \_\_\_\_\_

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2017 年 05 月

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## 摘要

随着现代工业的蓬勃发展，全球二氧化碳（CO<sub>2</sub>）排放量已经达到每年数百亿吨。CO<sub>2</sub>作为主要的温室气体，其大量排放导致的全球气候变暖正得到全世界的普遍关注。同时，CO<sub>2</sub>也是一种无毒、不可燃、地球上蕴藏量最为丰富且廉价易得的C<sub>1</sub>资源。将CO<sub>2</sub>转化为有价值的燃料或化学品不仅可以减少CO<sub>2</sub>的排放减缓温室效应，而且还可以变废为宝，因此得到许多科学家的重视，是现代科学研究的热点之一。

在众多的CO<sub>2</sub>转化产物中，甲酸乙酯（HCOOEt）作为一种重要化工品，在食品、医药、香料、有机合成中有着广泛应用。根据已经报道的文献研究，由CO<sub>2</sub>加氢合成HCOOEt需要经过两步反应。第一步：CO<sub>2</sub>加氢生成甲酸中间体，其中金属纳米颗粒，如Pd纳米颗粒（Pd NPs）具有良好的加氢活性。第二步：生成的甲酸中间体与溶剂乙醇（EtOH）的酯化反应，反应需要酸或酸性位点。因此所需要的催化剂至少需要加氢和酯化两种催化活性位点。此外，碱或碱性位点的引入有助于CO<sub>2</sub>吸附，促进第一步加氢反应。

金属有机框架化合物（MOFs）是一类具有明确结构的杂化材料，可以在同一个结构内安排多个功能不同的催化中心。具体表现为：（1）金属节点可以作为催化活性位点催化反应。（2）通过对有机配体功能化修饰可以引入催化活性位点；（3）限域在MOFs的孔道内的金属纳米颗粒可以催化化学反应。

本文的主要工作是以MOFs为平台设计并合成多功能催化剂用于串联催化CO<sub>2</sub>加氢、酯化制HCOOEt。主要研究工作如下：

1、利用H<sub>2</sub>bpydc（H<sub>2</sub>bpydc=2,2'-联吡啶-5,5'-二羧酸）配体螯合Pd<sup>2+</sup>生成功能配体H<sub>2</sub>L（H<sub>2</sub>L = PdCl<sub>2</sub>(H<sub>2</sub>bpydc)），通过溶剂热法制备含有H<sub>2</sub>L和H<sub>2</sub>bpdc（H<sub>2</sub>bpdc = 联苯二甲酸）配体的UiO-L<sub>x</sub>/bpdc<sub>6-x</sub> MOF并对其进行还原处理制得Pd(z)-UiO-bpydc<sub>x</sub>/bpdc<sub>6-x</sub> MOF。XRD、IR、SEM、TEM、<sup>1</sup>H NMR表征结果表明该MOF具有与UiO-67 MOF（只有H<sub>2</sub>bpdc配体）相同的形貌和结构，同时含有Pd NPs、碱性配体bpydc和酸性金属节点。Pd NPs可以催化CO<sub>2</sub>加氢还原生成甲酸中间体；在乙醇（EtOH）作为溶剂的条件下，酸性金属节点Zr<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub>可以催化甲酸中间体与溶剂EtOH发生酯化反应生成HCOOEt；碱性配体bpydc在反应中，有助于CO<sub>2</sub>的吸附，促进第一步加氢反应。其中，Pd(1)-UiO-bpydc<sub>1</sub>/bpdc<sub>5</sub>

在5 mL EtOH为溶剂，4 MPa的反应气 ( $\text{CO}_2/\text{H}_2 = 1/3$ )，135 °C条件下反应10 h，HCOOEt的最高生成速率达到1333  $\mu\text{mol}/\text{g}_{\text{cat}}/\text{h}$ ，TON值为475。

2、利用溶剂热法合成含有 $\text{H}_2\text{bdc}$  ( $\text{H}_2\text{bdc} =$  对苯二甲酸) 与 $\text{H}_2\text{bdc-NH}_2$  ( $\text{H}_2\text{bdc-NH}_2 =$  2-氨基对苯二甲酸) 的UiO-66、UiO-66-NH<sub>2</sub> 和UiO-bdc<sub>3</sub>/(bdc-NH<sub>2</sub>)<sub>3</sub>。利用浸渍法负载Pd NPs，制得Pd-UiO-66、Pd-UiO-66-NH<sub>2</sub> 和Pd-UiO-66-bdc<sub>3</sub>/(bdc-NH<sub>2</sub>)<sub>3</sub>。XRD、IR、SEM、TEM表征结果显示这些MOFs同时含有有Pd NPs、碱性配体bdc-NH<sub>2</sub> (Pd-UiO-66除外) 酸性金属节点。与Pd(z)-UiO-bpydc<sub>x</sub>/bpdc<sub>6-x</sub> MOF一样，Pd NPs可以催化CO<sub>2</sub>加氢还原生成甲酸中间体；酸性金属节点Zr<sub>6</sub>( $\mu_3\text{-O}$ )<sub>4</sub>( $\mu_3\text{-OH}$ )<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub>催化甲酸中间体与溶剂EtOH发生酯化反应生成HCOOEt；碱性配体bdc-NH<sub>2</sub>吸附CO<sub>2</sub>。其中，Pd-UiO-66-NH<sub>2</sub> MOF在4 MPa反应气 ( $\text{CO}_2/\text{H}_2 = 1/3$ )，135 °C条件下反应10 h，HCOOEt的生成速率达到937  $\mu\text{mol}/\text{g}_{\text{cat}}/\text{h}$ ，反应过程中同时伴有甲醇生成，其生成速率为607  $\mu\text{mol}/\text{g}_{\text{cat}}/\text{h}$ 。

关键词：MOFs；CO<sub>2</sub>加氢；串联催化。



## Abstract

Global economy growth, especially in the developing countries, has led to global carbon dioxide (CO<sub>2</sub>) emissions reaching several ten billions of tons per year. To mitigate the concern with greenhouse gas emissions such as CO<sub>2</sub>, sustainable conversion of CO<sub>2</sub> to fuels/chemicals has received increasing attention, especially considering CO<sub>2</sub> is non-toxic, non-flammable, and abundant C<sub>1</sub> resources.

Among the potential products considered from CO<sub>2</sub>, ethyl formate (HCOOEt) is a stable platform chemical, which is widely used in organic synthesis for, pharmaceutical, food and perfume industries. CO<sub>2</sub> can be possibly converted to HCOOEt via tandem steps: (1) hydrogenation of CO<sub>2</sub> to formic acid; (2) esterification of formic acid with ethanol (EtOH). The first step of CO<sub>2</sub> hydrogenation can be catalyzed by metal nanoparticles such as Pd nanoparticles (Pd NPs) and the second step of esterification is typically catalyzed by acid sites. In addition, base or basic sites for CO<sub>2</sub> adsorption can promote the reaction of carbon dioxide hydrogenation.

Metal-organic frameworks (MOFs) are a class of hybrid materials with well-defined structures, which can serve as a suitable platform to arrange multiple and functionally distinct catalytic centers within the same structure. Specifically, metal nodes can act as catalytic active sites for catalytic reactions. Catalytic active sites can be introduced by functionalizing the ligand. Metal nanoparticles in the pores of the MOFs can catalyze the reaction.

The main work of this paper is to use MOFs as a platform to design and synthesize multifunctional catalysts for catalytic tandem hydrogenation and esterification to directly carbon dioxide to ethyl formate. The main research is summarized as follows:

1. The functional ligand H<sub>2</sub>L (H<sub>2</sub>L = PdCl<sub>2</sub> (H<sub>2</sub>bpydc)) was prepared by chelating Pd<sup>2+</sup> with H<sub>2</sub>bpydc (H<sub>2</sub>bpydc = 2, 2'-bipyridine-5, 5'-dicarboxylic acid) ligand. UiO-L<sub>x</sub>/bpydc<sub>6-x</sub> was prepared by solvothermal method with H<sub>2</sub>L and H<sub>2</sub>bpdc (H<sub>2</sub>bpdc = 4,4'-biphenyl dicarboxylic acid). Pd(z)-UiO-bpydc<sub>x</sub>/bpydc<sub>6-x</sub> was prepared after reduction treatment with NaBH<sub>4</sub>. XRD, IR, SEM, TEM, <sup>1</sup>H NMR characterization

results show that this MOF had the same morphology and structure as that of UiO-67 MOF (only H<sub>2</sub>bpdC ligand). Pd NPs as well as basic ligand (bpydc) and acidic metal node owned Pd(z)-UiO-bpydc<sub>x</sub>/bpdc<sub>6-x</sub> can act as catalytic active sites. Pd NPs can catalyze CO<sub>2</sub> hydrogenation to form formic. Acidic metal node [Zr<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub>] catalyze the esterification of formic acid and EtOH to HCOOEt. Basic ligand (bpydc) for adsorbing CO<sub>2</sub> can promote the reaction of CO<sub>2</sub> hydrogenation. The Pd(1)-UiO-bpydc<sub>1</sub>/bpdc<sub>5</sub> exhibited a high activity in converting CO<sub>2</sub> to form HCOOEt with a production rate of 1333 μmol/g<sub>cat</sub>/h at 135 °C and a pressure of 4 Mpa (H<sub>2</sub>/CO<sub>2</sub>= 3/1) for 10 h or a turnover number (TON) of 475.

2、UiO-66, UiO-66-NH<sub>2</sub> and UiO-66-bdc<sub>3</sub>/(bdc-NH<sub>2</sub>)<sub>3</sub> were prepared by solvent thermal method with H<sub>2</sub>bdc (H<sub>2</sub>bdc = terephthalic acid) and H<sub>2</sub>bdc-NH<sub>2</sub> (H<sub>2</sub>bdc-NH<sub>2</sub> = 2-amino terephthalic acid). Pd-UiO-66, Pd-UiO-66-NH<sub>2</sub> and Pd-UiO-66-bdc<sub>3</sub>/(bdc-NH<sub>2</sub>)<sub>3</sub> were prepared by impregnation with H<sub>2</sub>PdCl<sub>4</sub>. XRD, IR, SEM, TEM characterization results show that these MOFs contain Pd NPs, basic ligand (bdc-NH<sub>2</sub>, except Pd-UiO-66) and acidic metal nodes. Similar to Pd(z)-UiO-bpydc<sub>x</sub>/bpdc<sub>6-x</sub>, Pd NPs can catalyze CO<sub>2</sub> hydrogenation to form formic; acidic metal node catalyzes the esterification of formic acid and ethanol (EtOH) to HCOOEt; basic ligand (bdc-NH<sub>2</sub>) for adsorbing CO<sub>2</sub> can promote the reaction of CO<sub>2</sub> hydrogenation. HCOOEt formation rate on Pd-UiO-66-NH<sub>2</sub> reaches 937 μmol/g<sub>cat</sub>/h at 135 °C and a pressure of 4 Mpa (H<sub>2</sub>/CO<sub>2</sub>= 3/1) for 10 h. In addition, methanol was also produced with a formation rate of 607 μmol/g<sub>cat</sub>/h.

Key words: metal-organic frameworks (MOFs); CO<sub>2</sub> hydrogenation; tandem catalysis

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