



# 二氧化碳加氢制甲酸的研究进展

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**摘要** 化石能源的大量使用促进了经济社会的快速发展,但也导致二氧化碳(CO<sub>2</sub>)大量释放.截至2023年,全球CO<sub>2</sub>排放超过374亿吨.大气中CO<sub>2</sub>含量的急剧增加造成了严重的温室效应和海水酸化等问题,但CO<sub>2</sub>反过来是一种含量多且清洁无毒的碳资源.通过催化加氢,可有效将CO<sub>2</sub>转化生成多种高附加值烃类及含氧化合物.其中,甲酸是良好的储氢载体,可直接用于甲酸燃料电池,也有利于解决氢的储运问题.因此,CO<sub>2</sub>加氢制甲酸不仅可以有效减轻CO<sub>2</sub>大量排放造成的全球温室效应,而且也开辟了制备甲酸的新途径.本文综述了当前CO<sub>2</sub>加氢制甲酸的研究进展,着重探讨了CO<sub>2</sub>加氢制甲酸不同催化体系的优缺点及反应性能,深入认识了金属-载体间的相互作用及载体限域效应对金属物种结构、分散度及催化性能的影响机制.

**关键词** CO<sub>2</sub>加氢, 甲酸, 非均相催化剂, 金属-载体相互作用, 限域效应

2023年,全球二氧化碳(CO<sub>2</sub>)排放量超374亿吨,其中与煤炭相关的CO<sub>2</sub>排放量增长了2.66亿吨(<https://www.iea.org/reports/co2-emissions-in-2023>).过量的CO<sub>2</sub>排放造成了严重的温室效应和全球气候变化等问题.截至2023年9月,全球平均气温较工业化前水平高出1.8℃(<https://wedocs.unep.org/20.500.11822/43922>).因此,减少CO<sub>2</sub>的过度排放、降低大气中的CO<sub>2</sub>含量,已成为当前全球面临的重大挑战,是制约经济和社会发展的主要影响因素.

目前,减缓CO<sub>2</sub>排放、控制CO<sub>2</sub>含量的有效方法是CO<sub>2</sub>捕获、封存及利用(capture, utilization, storage, 简称CCUS)技术<sup>[1]</sup>.CO<sub>2</sub>是一种丰富、清洁、无毒的碳资源<sup>[2,3]</sup>,通过加氢可合成大宗化学品和精细化学品,与封存相比,经济上更可行<sup>[4]</sup>.因而,将CO<sub>2</sub>定向转化为高值化学品是目前研究的热点<sup>[5]</sup>.但CO<sub>2</sub>分子高度稳定,是化石能源利用的终极产品,CO<sub>2</sub>的化学转化利用是一个

高能耗过程.考虑到CO<sub>2</sub>较高的键能(806 kJ mol<sup>-1</sup>)和第一电离能(13.79 eV),通过引入高活性分子和向CO<sub>2</sub>传输电子,促进C=O键活化断裂是实现CO<sub>2</sub>催化转化的主要方式.在“双碳”背景下,氢气(H<sub>2</sub>)作为清洁能源受到了高度重视<sup>[6,7]</sup>.将CO<sub>2</sub>和H<sub>2</sub>定向转化为高值燃料和化学品不仅可以有效减排CO<sub>2</sub>、减轻温室效应,同时也开辟了制备化学品的新路线,有助于推动国家能源结构调整<sup>[8,9]</sup>.

CO<sub>2</sub>加氢可转化为甲烷<sup>[10,11]</sup>、低碳烯烃、芳烃、液化石油气和汽柴油等烃类化合物及甲酸<sup>[5,12,13]</sup>、甲醇<sup>[14,15]</sup>和低碳醇等含氧化合物<sup>[4,16]</sup>.其中,甲酸是一种重要的化工原料,广泛应用于制革、医药、纺织印染、农业、造纸和化工等领域<sup>[17,18]</sup>.同时,甲酸也是良好的氢能存储载体,体积氢存储量达到53 g<sub>H<sub>2</sub></sub> L<sup>-1</sup><sup>[19]</sup>.目前,技术上相对成熟的氢气储运方式是高压储罐和管道运输,存在高成本和危险系数大的问题,而甲酸不仅

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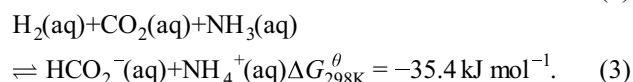
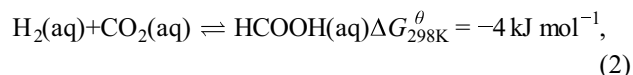
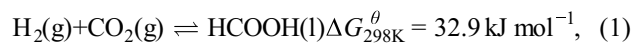
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可以在温和的条件下实现氢气的有效存储和释放,也实现了CO<sub>2</sub>的循环利用<sup>[20,21]</sup>.例如山东大学邓伟侨团队<sup>[22]</sup>构筑了一种2,6-二氯苯酚-共价三嗪框架材料(2,6-DCP-CTF)负载的双单原子钯(Pd)催化剂,在30℃, 1 bar (1 bar=10<sup>5</sup> Pa)的反应条件下催化剂转化频率(TOF)高达13.46 h<sup>-1</sup>,从而实现了常温、常压下CO<sub>2</sub>加氢制甲酸.该结果也说明以甲酸为媒介,在温和条件下进行氢气的有效存储和释放是可行的.

近年来,转化CO<sub>2</sub>制甲酸已经引起了科研人员的广泛关注.除了采用热催化外,还可以通过光催化或电催化的方式转化CO<sub>2</sub>合成甲酸.例如,天津理工大学鲁统部与张志明团队<sup>[23]</sup>通过在铈-金属有机骨架(Eu-MOF)中引入三联吡啶氯化钐六水合物Ru(bpy)<sub>3</sub>光敏剂和单位点催化剂bpy-CuCl/X(bpy=2,2'-联吡啶, X=Cl或腺嘌呤),构筑出了用于高效催化CO<sub>2</sub>还原制甲酸的催化剂@光敏剂复合光催化体系,甲酸的选择性达到99.7%.中国科学技术大学曾杰团队<sup>[24]</sup>研制了一种铅单原子修饰的铜催化剂(Pb<sub>1</sub>Cu),在电流密度为500 mA cm<sup>-2</sup>下的长期稳定性超过20 h,甲酸的法拉第效率平均为90%,且在电流密度为100 mA cm<sup>-2</sup>下连续工作180 h后甲酸的法拉第效率仍保持在85%左右.尽管光催化或电催化CO<sub>2</sub>制甲酸已经取得了非常重要的突破和进展,但反应过程中依然存在甲酸产率和能量利用率低的问题.相比之下,热催化CO<sub>2</sub>加氢制甲酸/甲酸盐则具有更高的转化效率.为此,本文主要介绍了利用传统热催化转化

CO<sub>2</sub>制甲酸的催化体系.

如式(1)<sup>[25]</sup>所示,CO<sub>2</sub>加氢制甲酸涉及到从气相原料变为液相产物,吉布斯自由能(ΔG)为+32.9 kJ mol<sup>-1</sup>,因而该过程受到明显的热力学限制,加入适宜的溶剂可以改变反应热力学<sup>[26,27]</sup>,推动反应向甲酸生成方向移动(式(2)、(3)):



此外,CO<sub>2</sub>加氢制甲酸需要同时活化H<sub>2</sub>和CO<sub>2</sub>两种稳定的气体<sup>[28]</sup>,需要输入大量的能量来推动H-H键解离和C=O键的加氢和裂解.因此,设计有效的催化体系对于降低催化转化过程中氢气解离和CO<sub>2</sub>加氢的高能垒至关重要.目前,用于CO<sub>2</sub>加氢制甲酸的催化剂主要包括均相和非均相两类体系,如图1所示.

## 1 均相催化剂

1976年,日本的井上明久等人<sup>[29]</sup>首次报道了过渡金属Ru(钌)和磷化氢组成的络合物催化剂,在以苯作为溶剂、有机胺作为碱助剂的条件催化CO<sub>2</sub>加氢生成甲酸.自此之后,研究人员针对CO<sub>2</sub>加氢制甲酸过程进行了大量研究,相继报道了贵金属Ru<sup>[30-32]</sup>、Rh

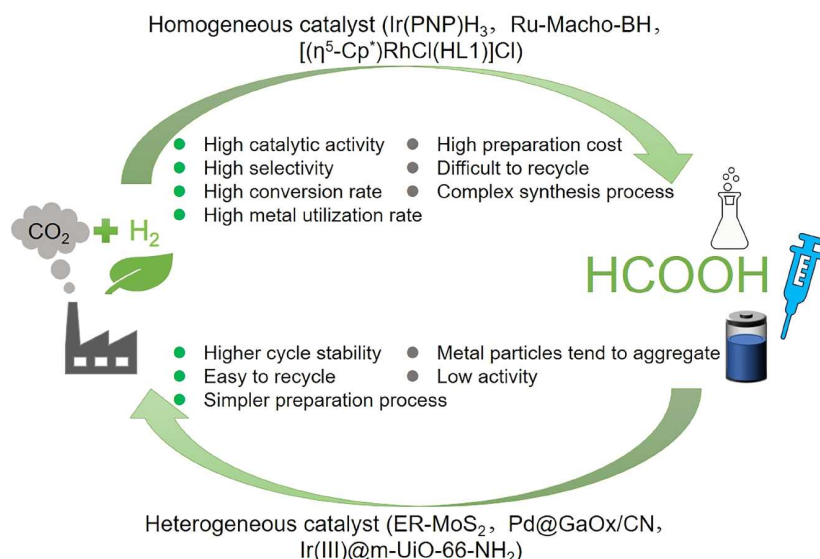


图1 (网络版彩色)CO<sub>2</sub>加氢制甲酸过程示意图

Figure 1 (Color online) Schematic diagram of the CO<sub>2</sub> hydrogenation process to formic acid

(铑)<sup>[33]</sup>和Ir(铱)<sup>[34,35]</sup>等均相络合物催化剂。例如, Kyoko等人<sup>[34]</sup>将Ir(PNP)H<sub>3</sub>(PNP钳形配合物偶联铱(III)三氢化物)作为催化剂用于CO<sub>2</sub>加氢制甲酸, 在CO<sub>2</sub>/H<sub>2</sub>=30/30 bar, 120℃的条件下反应48 h后, 甲酸的转换频率(turn-over frequency, TOF)可达73000 h<sup>-1</sup>。Evgeny等人<sup>[30]</sup>将Ir替换成Ru, 所制备的Ru-PNP催化剂可将甲酸TOF进一步提高到1100000 h<sup>-1</sup>。在均相催化CO<sub>2</sub>加氢反应过程中, H<sub>2</sub>首先与金属位点相互作用形成金属氢化物(M-H), 随后, CO<sub>2</sub>插入到金属氢化物中形成甲酸盐(HCOO\*), 并经过进一步加氢生成甲酸(HCOOH)。通常来说, 促进H<sub>2</sub>活化形成金属氢化物, 提高M-H的稳定性是提升CO<sub>2</sub>加氢制甲酸反应性能的关键。

均相催化剂因具有较大的接触面积以及简单的金属活性位点结构, 从而在CO<sub>2</sub>加氢制甲酸过程中展现出高的催化活性和甲酸产率, 但由于其合成过程复杂、需要使用昂贵的有机配合物, 并且存在反应后催化剂难以回收等问题, 造成了极高的运行成本, 给工业化应用带来许多困难和挑战。表1汇总了几种常见的CO<sub>2</sub>加氢制甲酸均相催化剂的反应性能结果。

## 2 非均相催化剂

相较于均相催化剂的高成本, 非均相催化剂因制备容易、稳定性好、易分离回收等优势受到了更为广泛的关注。Adkins等人<sup>[36]</sup>在1935年使用雷尼镍(Raney-Ni)作为催化剂, 在80℃和有机胺存在的条件下反应1 h, 甲酸产率达55%。尽管该过程需要极高的压力, 但是开创了非均相催化CO<sub>2</sub>加氢制甲酸的先河。

到目前为止, 研究人员相继研制了多种用于CO<sub>2</sub>加氢制甲酸的非均相催化剂。其中, 金属负载型催化剂最为常见。但在反应过程中, 由于金属纳米粒子的团聚和

流失, 造成催化剂活性快速下降, 往往表现出较低的稳定性。因此, 选取适宜的载体<sup>[37]</sup>, 并通过调控载体的结构<sup>[38,39]</sup>、形貌和暴露晶面<sup>[40]</sup>等来提高金属位点的分散度以及金属与载体间的相互作用强度, 从而增强金属位点的抗烧结能力, 是解决其稳定性较低问题的有效方式。目前, 分子筛、介孔二氧化硅、金属有机骨架和金属氧化物等已相继被用于负载金属纳米颗粒。表2汇总了不同金属负载型催化剂用于CO<sub>2</sub>加氢制甲酸的反应性能。本文也将主要介绍通过改变载体种类、表面几何和电子结构等方式对CO<sub>2</sub>加氢制甲酸催化性能产生的影响。

### 2.1 分子筛

分子筛由于具有规整的孔道结构、可调的酸碱性质以及较高的热稳定性, 在石油化工、煤化工、生物质转化、CO<sub>2</sub>捕获和利用以及气体污染物消除等领域得到广泛的应用<sup>[52]</sup>。通过负载、封装、离子交换或机械混合将适宜的金属物种引入到分子筛孔道或笼内, 实现了金属位点与Brønsted酸位点的协同催化, 将极大拓展分子筛在煤化工、石油化工和精细化学品合成方面的应用。最近, 研究人员通过在分子筛孔道内限域亚纳米金属/双金属位点<sup>[53,54]</sup>的方式, 大幅提高了CO<sub>2</sub>加氢制甲酸活性。例如, 新加坡国立大学颜宁课题组和吉林大学于吉红课题组<sup>[41]</sup>采用一步水热法构筑了全硅沸石限域亚纳米Pd-Mn双金属催化剂(PdMn@S-1), 在25℃, 2 mL 1.5 mol L<sup>-1</sup> NaOH水溶液, 原料气H<sub>2</sub>/CO<sub>2</sub>=20/20 bar的反应条件下, 甲酸盐的产率达526 mol<sub>formate</sub> mol<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup>, 当反应温度升高到80℃时, 甲酸盐生成速率可以进一步提升到2151 mol<sub>formate</sub> mol<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup>, 并且在25℃, 2 mL 1.5 mol L<sup>-1</sup> NEt<sub>3</sub>水溶液, 原料气H<sub>2</sub>/

表1 几种常见的二氧化碳加氢制甲酸均相催化剂及其反应性能

Table 1 Catalytic performance of several common homogeneous catalysts for carbon dioxide hydrogenation to formic acid

| 催化剂                                                                       | 溶剂             | 添加剂                                 | 温度(℃) | 原料气P(CO <sub>2</sub> /H <sub>2</sub> )<br>(bar) | 时间(h) | TOF(h <sup>-1</sup> ) | TON     | 文献   |
|---------------------------------------------------------------------------|----------------|-------------------------------------|-------|-------------------------------------------------|-------|-----------------------|---------|------|
| Ir(PNP)H <sub>3</sub>                                                     | 水              | 氢氧化钾(-)                             | 120   | 30/30                                           | 48    | 73000                 | 3500000 | [34] |
| Ru PNP-<br>钳形配合物                                                          | N,N-二甲基甲<br>酰胺 | 1,8-二氮杂二环[5.4.0]<br>十一碳-7-烯(-)      | 120   | 10/30                                           |       | 1100000               |         | [30] |
| Ru-Macho-BH <sup>a)</sup>                                                 | 水              | 四甲基胍(-)                             | 55    | 0/50                                            | 20    |                       | 7375    | [31] |
| Ru(Acriphos)(PPh <sub>3</sub> )<br>(Cl)(PhCO <sub>2</sub> ) <sup>b)</sup> | 二甲基亚砷/水        | 醋酸缓冲液<br>(4.0 mol L <sup>-1</sup> ) | 60    | 40/80                                           | 16    |                       | 16310   | [32] |
| [(η <sup>5</sup> -Cp*)RhCl(HL1)]Cl <sup>c)</sup>                          | 水              | 氢氧化钾<br>(0.1 mol L <sup>-1</sup> )  | 80    | 5/5                                             | 8     |                       | 5991    | [33] |

a) Ru-Macho-BH=氢化羰基(四氢化硼)[双(2-二苯基膦基乙基)氨基]钌(II); b) Acriphos=4,5-bis(diphenylphosphino)acridine, 4,5-双二苯基膦吖啶; c) HL1,8-氨基喹啉

表 2 几种常见的二氧化碳加氢制甲酸非均相催化剂

Table 2 Catalytic performance of several common heterogeneous catalysts for the hydrogenation of carbon dioxide to formic acid

| 催化剂                                | 溶剂   | 添加剂                                | 温度(℃) | 原料气<br>P(CO <sub>2</sub> /H <sub>2</sub> )(bar) | 时间(h) | TOF<br>(h <sup>-1</sup> ) <sup>a)</sup> | TON  | 文献   |
|------------------------------------|------|------------------------------------|-------|-------------------------------------------------|-------|-----------------------------------------|------|------|
| PdMn <sub>0.6</sub> @S-1           | 水    | 氢氧化钠<br>(1.5 mol L <sup>-1</sup> ) | 25    | 20/20                                           |       | 526                                     |      | [41] |
|                                    |      |                                    | 80    |                                                 |       | 2151                                    |      |      |
| PdCe <sub>0.2</sub> /SP-S-1        | 水    | 碳酸氢钾<br>(2.0 mol L <sup>-1</sup> ) | 50    | 10/10                                           |       | 536                                     |      | [42] |
| PdAg/SBA-15                        | 水    | 碳酸氢钠<br>(1.0 mol L <sup>-1</sup> ) | 100   | 10/10                                           | 24    | 36                                      | 874  | [43] |
| Pd-Co@MSN                          | 水    | 碳酸氢钠<br>(1.0 mol L <sup>-1</sup> ) | 100   | 0/20                                            |       | 408                                     |      | [38] |
| Ru@MCM-41                          | 水    | 三乙胺(-)                             | 110   | 30/20                                           | 15    | 182                                     | 2729 | [44] |
| RuCl <sub>3</sub> @ZIF-8-Mtz(0.29) | 乙醇/水 | 三乙胺(-)                             | 120   | 40/40                                           | 2     |                                         | 1008 | [45] |
| PdAg@MIL-101-PEI-50                | 水    | 碳酸氢钠<br>(1.0 mol L <sup>-1</sup> ) | 120   | 40/40                                           | 2     |                                         | 4968 | [46] |
| 2%Pd/CeO <sub>2</sub>              | 水    | 碳酸氢钠(-)                            | 100   | 0/20                                            | 1     | 366 <sup>b)</sup>                       |      | [37] |
| 2%Pd/ZnO                           |      |                                    |       |                                                 |       | 68 <sup>b)</sup>                        |      |      |
| Pd/p-CeO <sub>2</sub>              | 水    | 碳酸氢钠(-)                            | 40    | 10/10                                           | 1     | 746 <sup>b)</sup>                       |      | [39] |
| Pd/TiO <sub>2</sub>                | 水    | 碳酸氢钠(-)                            | 40    | 10/10                                           | 1     | 1369 <sup>b)</sup>                      |      | [40] |
| Ni/TiO <sub>2</sub>                | 水    | 碳酸钠(-)                             | 190   | 0/30 <sup>c)</sup>                              | 3     | 3.51 <sup>d)</sup>                      |      | [47] |
| ER-MoS <sub>2</sub>                | 水    | 碳酸氢钾<br>(0.5 mol L <sup>-1</sup> ) | 200   | 11.25/33.75                                     | 10    | 780.7                                   |      | [48] |
|                                    |      |                                    | 200   | 6.25/18.75                                      | 10    | 598.9                                   |      |      |
|                                    |      |                                    | 160   | 6.25/18.75                                      | 10    | 218.8                                   |      |      |
| Pd@GaOx/CN                         | 水    | 碳酸氢钠<br>(1.0 mol L <sup>-1</sup> ) | 100   | 10/10                                           | 6     | 105                                     | 629  | [49] |
| PdAg-NMHCS                         | 水    | 碳酸氢钠<br>(1.0 mol L <sup>-1</sup> ) | 100   | 10/10                                           | 2     |                                         | 640  | [50] |
| Ir(III)@m-UiO-66-NH <sub>2</sub>   | 水    | 碳酸钾(-)                             | 140   | 10/40                                           | 24    |                                         | 3313 | [51] |

a) 用活性金属总原子计算甲酸的TOF(mol<sub>FA</sub> mol<sub>total</sub><sup>-1</sup> h<sup>-1</sup>); b) 用催化剂表面活性金属的原子数计算甲酸的TOF(mol<sub>FA</sub> mol<sub>surf</sub><sup>-1</sup> h<sup>-1</sup>); c) 90% H<sub>2</sub>/Ar; d) 质量活性( $r_{FA+CH_4+C_2}$ , m<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>)

CO<sub>2</sub>=20/20 bar的反应条件下经过5次循环后, 甲酸盐的TOF依然可维持在360 h<sup>-1</sup>以上. 结合HRTEM、XANES/EXAFS和XRD等表征结果证实, 分子筛的孔道结构有效防止了反应过程中Pd和Mn位点的团聚, 从而提高了催化剂稳定性. 此外, 原位DRIFTS测试表明, Pd与Mn形成的合金结构促进了H<sub>2</sub>解离以及CO<sub>2</sub>加氢经碳酸盐、碳酸氢盐生成甲酸盐的过程.

近期于吉红课题组<sup>[42]</sup>通过初湿浸渍法将活性金属负载在自支撑沸石纳米片(SP-S-1)上, 构筑了一系列Pd基双金属纳米催化剂. 其中PdCe<sub>0.2</sub>/SP-S-1样品在2.0 mol L<sup>-1</sup> KHCO<sub>3</sub>水溶液, 10 bar H<sub>2</sub> and 10 bar CO<sub>2</sub>原料气和50℃的反应条件下, 甲酸盐生成速率达到536 mol<sub>formate</sub> mol<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup>. 针对SP-S-1的研究证明具有自支撑纳米片结构的分子筛载体拥有高比表面积和丰富的孤立硅羟基基团, 有利于锚定金属物种并提高金属

位点的分散性. 同时, DFT计算表明, 引入氧化铈可与Pd物质产生协同效应, 从而显著降低CO<sub>2</sub>加氢的活化能垒, 提高甲酸生成活性.

## 2.2 介孔二氧化硅

介孔二氧化硅(SiO<sub>2</sub>)因具有较大孔径和较高比表面积的特点, 常被用于锚定金属团簇或过渡金属配合物<sup>[55]</sup>. 新加坡国立大学颜宁等人<sup>[38]</sup>采用十六烷基三甲基溴化铵(CTAB)作为配体保护剂, 通过水热法将Pd和Co同时限域在介孔二氧化硅纳米球中(Pd-Co@MSN). 纳米球丰富的孔道结构可以有效提高Pd-Co合金纳米团簇的分散度. 评价结果表明, 在CO<sub>2</sub>加氢过程中(100℃, 20 bar H<sub>2</sub>, 1.0 mol L<sup>-1</sup> NaHCO<sub>3</sub>溶液), Pd-Co@MSNs催化剂的甲酸盐生成速率可达408 mol<sub>formate</sub> mol<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup>, 高于商业Pd/C, Pd/BaSO<sub>4</sub>和

Pd/Al<sub>2</sub>O<sub>3</sub>的结果。此外, Pd-Co@MSNs的催化性能与Pd/Co的摩尔比密切相关, 引入适量的Co(Pd/Co=4/1)可以显著促进H<sub>2</sub>解离, 生成更多的活性H\*, 有利于随后的CO<sub>2</sub>加氢反应。这是因为Co作为重要的电子助剂可以向Pd传递电子, 提高了Pd的电子密度, 但过高的Co含量会造成Pd位点被覆盖, 导致活性下降。

同样, Ordonsky等人<sup>[44]</sup>以介孔MCM-41为载体, 负载了3.2 wt%的Ru, 评价结果显示, 在110℃, H<sub>2</sub>/CO<sub>2</sub>=20/30 bar原料气反应条件下, 经过15 h的反应后, Ru@MCM-41的TON达到了2000以上。研究发现, 在合成过程中加入适量的CTA<sup>+</sup>可以有效稳定分散在介孔MCM-41孔隙中Ru的位点, 并降低Ru的颗粒尺寸。DFT计算指出, 这些低配位的Ru位点通过异裂解离H<sub>2</sub>, 形成活性Ru-H物种, 并进一步与CO<sub>2</sub>加氢生成甲酸。

## 2.3 金属有机框架

金属有机框架(MOFs)是以金属离子或簇作为无机节点通过与有机连接剂相互作用, 配位而成的具有三维多孔结构的无机-有机骨架材料<sup>[56]</sup>。MOFs材料因其大的比表面积、丰富的金属位点和三维多孔结构而被大量用于吸附、分离和催化反应过程<sup>[57]</sup>。值得注意的是, MOFs材料的热稳定性低于传统分子筛和介孔二氧化硅, 更适合于温和条件的液相催化加氢过程<sup>[55]</sup>。

天津大学马新宾等人<sup>[45]</sup>以3-甲基-1,2,4-三唑(Mtz)为连接体通过水热法一步合成了Ru改性ZIF-8(Ru@-ZIF-8)催化剂。DFT计算结果指出Mtz上的配位不饱和N位点与Ru之间存在强电子相互作用, 不仅能够稳定Ru颗粒, 还可以向其传递电子, 提高Ru的电子密度。在120℃、H<sub>2</sub>/CO<sub>2</sub>=40/40 bar原料气的反应条件下, 经过2 h反应后, 甲酸的TON超过1000, 并且经过5次循环测试后, 依然可以保持93%的初始催化活性。

墨尔本大学李刚等人<sup>[46]</sup>在MIL-101上同时负载Pd和Ag, 并加入聚乙烯亚胺(PEI)来对催化剂进行改性。理论计算结果表明, Ag的引入和PEI的功能化共同降低了催化CO<sub>2</sub>加氢的活化能垒, 从而提高了催化剂的活性。在120℃、H<sub>2</sub>/CO<sub>2</sub>=40/40 bar原料气的条件下经过2 h的反应, 所构筑的PdAg@MIL-101-PEI-50催化剂的TON值高达4968。

## 2.4 金属氧化物催化剂

相较于分子筛、介孔二氧化硅和MOFs等多孔材料, 金属氧化物具有更高的结构稳定性以及耐酸碱特

征, 使其成为CO<sub>2</sub>加氢制甲酸过程中应用最为广泛的载体材料<sup>[49]</sup>。通过改变金属氧化物载体的晶体结构、暴露晶面以及表面缺陷位点等, 可有效调变金属位点的分散度和金属-载体之间的相互作用(metal-support interaction)强度, 进而影响金属活性位点的几何/电子结构和电荷密度, 改变催化剂的活性和循环稳定性<sup>[40]</sup>。

颜宁等人<sup>[37]</sup>采用共沉淀法制备了Pd/CeO<sub>2</sub>和Pd/ZnO两种金属氧化物负载的Pd基催化剂, 并考察了不同载体上CO<sub>2</sub>加氢制甲酸的反应性能差异。在NaHCO<sub>3</sub>作为添加剂, 20 bar H<sub>2</sub>, 100℃的反应条件下, Pd/CeO<sub>2</sub>和Pd/ZnO的甲酸盐TOF分别为366和68 h<sup>-1</sup>。造成催化性能差异的主要原因是CeO<sub>2</sub>载体具有更加丰富的表面碱性位点, 有利于CO<sub>2</sub>吸附形成碳酸盐, 并进一步与金属Pd位点解离的活性H\*相互作用生成甲酸盐, 而ZnO由于缺少碱性位点, 甲酸盐产率较低。因此, 提高金属氧化物载体的碱度, 是提升其反应活性的有效方式。

此外, 改变载体形貌同样会对反应性能产生重要影响。浙江师范大学的鲁继青等人<sup>[39]</sup>通过沉积-沉淀法合成了具有不同形貌的CeO<sub>2</sub>, 分别为棒状(r-CeO<sub>2</sub>)、立方体(c-CeO<sub>2</sub>)和多面体(p-CeO<sub>2</sub>), 并进一步负载金属Pd, 形成Pd/CeO<sub>2</sub>催化剂(图2)。在CO<sub>2</sub>加氢制甲酸过程中, Pd/p-CeO<sub>2</sub>催化剂的甲酸TOF最高, 为746 h<sup>-1</sup>, 其次是Pd/c-CeO<sub>2</sub>(532 h<sup>-1</sup>)和Pd/r-CeO<sub>2</sub>(425 h<sup>-1</sup>)。研究表明, 金属-载体相互作用强度取决于氧化铈的氧空位浓度, 并且改变金属-载体相互作用强度会导致Pd物种的粒径和电子结构发生变化, 强金属-载体相互作用可以诱导制备更小的金属纳米颗粒, 提高金属位点分散度, 但也导致金属位点难以还原。例如, 在Pd/CeO<sub>2</sub>催化剂中, 氧空位浓度遵循棒状>立方体>多面体的顺序。氧空位浓度最高的r-CeO<sub>2</sub>载体在负载Pd粒子后, 虽然Pd颗粒尺寸更小, 但Pd物种电子密度降低。而Pd/p-CeO<sub>2</sub>氧空位浓度最低, 金属Pd<sup>0</sup>含量最高, 更容易活化H<sub>2</sub>, 表现出更高的加氢活性。

2022年, 中国科学院山西煤炭化学研究所张振华课题组<sup>[40]</sup>利用水热法研制了形貌一致、但暴露不同晶面的锐钛矿型TiO<sub>2</sub>。负载相同含量的金属Pd之后, 对所制备的Pd/TiO<sub>2</sub>-{100}、Pd/TiO<sub>2</sub>-{101}和Pd/TiO<sub>2</sub>-{001}进行了CO<sub>2</sub>加氢制甲酸性能测试。结果发现, 甲酸的生成活性取决于载体暴露晶面。其中Pd/TiO<sub>2</sub>-{100}具有最高的甲酸TOF, 为1369 h<sup>-1</sup>, 其次是Pd/TiO<sub>2</sub>-{101}为1034 h<sup>-1</sup>和Pd/TiO<sub>2</sub>-{001}为323 h<sup>-1</sup>(图3)。结合EPR光谱表征, 作者指出改变TiO<sub>2</sub>载体的暴露晶面, 会对金属Pd

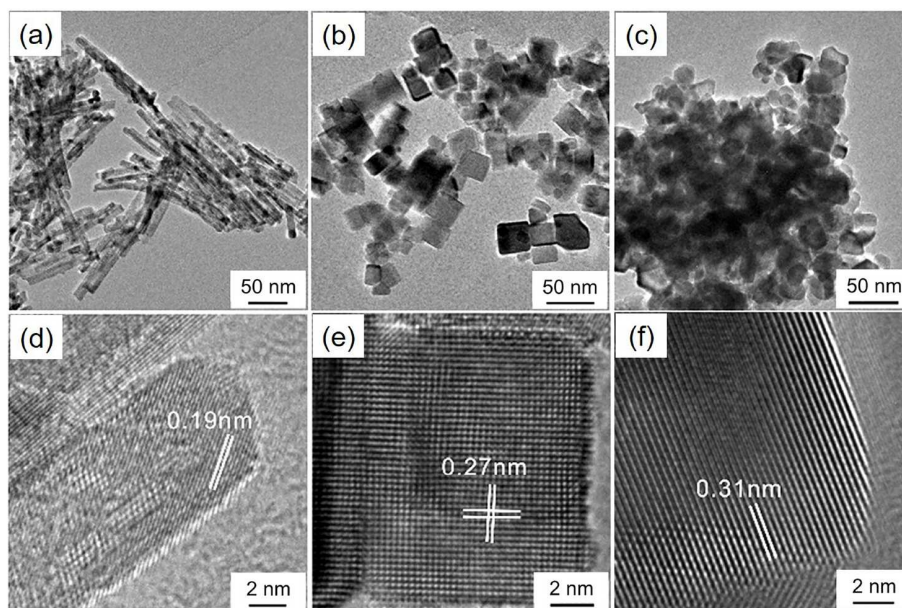


图 2 不同形貌的Pd/CeO<sub>2</sub>催化剂的TEM图和Pd颗粒尺寸分布<sup>[39]</sup>. (a, d) Pd/r-CeO<sub>2</sub>; (b, e) Pd/c-CeO<sub>2</sub>; (c, f) Pd/p-CeO<sub>2</sub>

Figure 2 TEM images and Pd particle size distribution of Pd/CeO<sub>2</sub> catalysts with different morphologies<sup>[39]</sup>. (a, d) Pd/r-CeO<sub>2</sub>; (b, e) Pd/c-CeO<sub>2</sub>; (c, f) Pd/p-CeO<sub>2</sub>

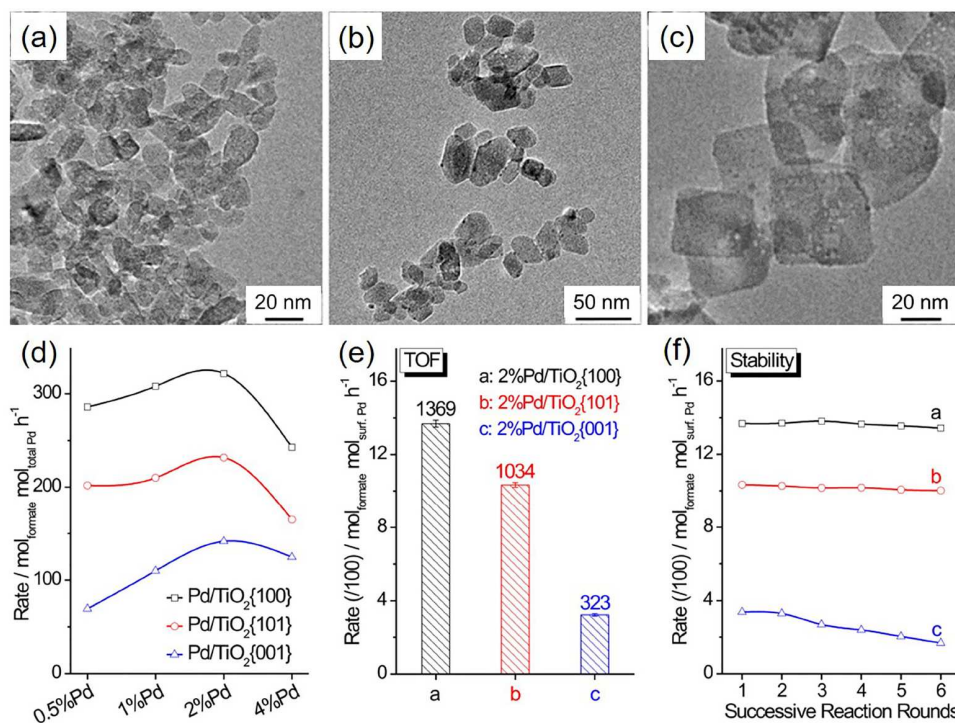


图 3 (网络版彩色)2%Pd/TiO<sub>2</sub>不同暴露晶面的TEM图和反应性能评价结果<sup>[40]</sup>. (a) 2%Pd/TiO<sub>2</sub>-{100}、(b) 2%Pd/TiO<sub>2</sub>-{101}和(c) 2%Pd/TiO<sub>2</sub>-{001}催化剂的TEM图像. (d) 313 K下, 不同暴露晶面的Pd/TiO<sub>2</sub>催化剂甲酸盐生成速率; (e) 313 K时, 不同暴露晶面的2%Pd/TiO<sub>2</sub>的TOF; (f) 不同暴露晶面的Pd/TiO<sub>2</sub>催化剂的循环稳定性

Figure 3 (Color online) TEM and reaction performance evaluation results of different exposed crystal surfaces of 2%Pd/TiO<sub>2</sub><sup>[40]</sup>. TEM images of (a) 2%Pd/TiO<sub>2</sub>-{100}, (b) 2%Pd/TiO<sub>2</sub>-{101}, and (c) 2% Pd/TiO<sub>2</sub>-{001} catalysts. (d) Formate formation rate of Pd/TiO<sub>2</sub> catalyst with different exposed crystal planes at 313 K; (e) TOF value of 2% Pd/TiO<sub>2</sub> with different exposed crystal planes at 313 K; (f) recycle stability of Pd/TiO<sub>2</sub> catalysts with different exposed crystal planes

粒子的形貌产生影响,进而影响了其氢气解离和加氢活性。

载体与金属位点之间的强相互作用同样会对金属位点的价态产生重要影响。北京大学马丁等人<sup>[47]</sup>发现金属Ni<sup>0</sup>在CO<sub>2</sub>加氢制甲酸过程中活性很低,而通过调控合成方法,增强Ni位点与载体TiO<sub>2</sub>的相互作用强度可以诱导部分Ni<sup>2+</sup>的产生,从而显著提高CO<sub>2</sub>转化率和甲酸选择性。作者认为这是由于Ni<sup>0</sup>和Ni<sup>2+</sup>组分之间存在协同作用, Ni<sup>2+</sup>可以促进CO<sub>3</sub><sup>2-</sup>在Ni<sup>0</sup>和TiO<sub>2</sub>上的吸附,同时, H<sub>2</sub>在金属Ni位点解离形成活性H\*,随后溢流到Ni-TiO<sub>2</sub>的界面,并与在此吸附的碳酸盐反应生成甲酸盐。

除上述所介绍的催化剂外,一些新兴的催化体系也值得关注。例如,离子液体(IL)配位金属催化剂作为均相催化剂的绿色替代品,在CO<sub>2</sub>转化过程中表现出优异的反应性能<sup>[58]</sup>。英国诺丁汉大学的Sans等人<sup>[28]</sup>利用IL作为缓冲剂,配合Ru基催化剂和路易斯酸催化剂用于催化CO<sub>2</sub>制甲酸,其生成甲酸的TOF和TON分别可达 $2.1 \times 10^4 \text{ h}^{-1}$ 和 $8 \times 10^5$ 。这说明离子液体催化剂在CO<sub>2</sub>加氢制甲酸过程中同样具有较大的应用潜力。

### 3 总结与展望

以CO<sub>2</sub>为原材料,经过催化转化制备高价值的化学品,既能解决因CO<sub>2</sub>大量排放引发的环境问题,同时又可以在一定程度上缓解不可再生化石能源枯竭的压力,具有重要的经济效益和战略意义。在CO<sub>2</sub>的化学利用中,CO<sub>2</sub>加氢还原制甲酸操作简便,具有100%的原子利用率;在实现温室气体CO<sub>2</sub>转化的同时,还能将H<sub>2</sub>转化

成不易燃液体产品甲酸,既可以缓解温室效应,又能够实现H<sub>2</sub>的安全储存和运输。

用于CO<sub>2</sub>加氢制甲酸的催化剂种类繁多,包括了均相和非均相两类催化体系。其中,均相催化剂具有活性高,选择性好的优势,但其制备成本高昂,且存在回收和循环利用方面的困难。相比之下,非均相催化剂因制备容易、稳定性好、易分离回收等优势受到了更为广泛的关注。其中,金属负载型催化剂是最为常用的非均相CO<sub>2</sub>加氢制甲酸催化体系。但在反应过程中,由于金属纳米粒子的团聚和流失,造成催化剂活性快速下降、活性组分稳定性较差。此外,金属负载型催化剂的催化性能与载体的种类和结构密切相关。通过调控载体的晶体结构、微观形貌、暴露晶面以及缺陷位点浓度等,可以有效改变金属位点的颗粒尺寸、分散度和电子密度,从而影响了氢气解离和CO<sub>2</sub>加氢活性。

当前,分子筛、介孔二氧化硅、金属有机骨架和金属氧化物等已相继被用于负载金属纳米颗粒,并在CO<sub>2</sub>加氢制甲酸过程中展现出优异的反应性能。尽管取得了重要进展,但这些研制的金属负载型催化剂依然存在甲酸产率低、循环稳定性差以及需要高浓度碱作为溶剂等问题。因此,设计和研制新型金属负载型催化剂,通过引入额外的助剂或改变金属-载体相互作用强度来调控金属位点的电荷密度、几何/电子结构和局域配位环境,从而增强其氢气解离和C=O键加氢活化能力,是进一步提升其CO<sub>2</sub>加氢制甲酸反应性能的有效途径。此外,利用分子筛、金属有机框架或介孔材料的空间限域效应,构筑核壳型金属@载体催化剂,将有效防止金属位点的团聚和流失,从而大幅提高催化剂稳定性。

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Summary for “二氧化碳加氢制甲酸的研究进展”

# Recent advances in carbon dioxide hydrogenation to formic acid

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The massive utilization of fossil resources, such as coal, petroleum and natural gas, has spurred rapid societal advancement, however, it has also led to excessive carbon dioxide (CO<sub>2</sub>) emissions. In 2022, global atmospheric CO<sub>2</sub> concentrations reached 417.9±0.2 ppm, and marking a new record high over the past two million years. This substantial in CO<sub>2</sub> levels contributes to intensified greenhouse effects and widespread environmental issues. By 2023, the annual average temperature increased to 1.45±0.12°C above pre-industrial levels, further approaching the 1.5°C temperature control target set by the Paris Agreement, resulting in notable significant negative economic and social consequences. Mitigating CO<sub>2</sub> emissions and controlling atmospheric CO<sub>2</sub> levels have thus become urgent global priorities. Given that CO<sub>2</sub> is a clean abundant carbon resource, it can be catalytically hydrogenated into valuable C<sub>1</sub> compounds, such as methane (CH<sub>4</sub>), methanol (CH<sub>3</sub>OH), formic acid (HCOOH) and carbon monoxide (CO), as well as C<sub>2+</sub> products, such as like alkenes, aromatics, gasoline, diesel and liquefied petroleum gas (LPG) etc. The conversion of CO<sub>2</sub> into value-added products helps reduce atmospheric CO<sub>2</sub> content and provides a sustainable pathway for producing essential chemicals. Amongst these products, formic acid stands out as a fundamental organic chemical feedstock with extensive applications in leather production, pharmaceutical, textile printing, dyeing, agriculture, paper manufacturing and chemical industries. In addition, formic acid serves as a crucial hydrogen energy, carrier with a hydrogen storage capacity of up to 53 g L<sup>-1</sup>. It exhibits low toxicity and flammability, making it safe and practical for storage and transportation. Consequently, the selective conversion of CO<sub>2</sub> to formic acid holds promise for mitigating the global greenhouse effect, while enabling synthesis of valuable chemical precursors. Nevertheless, this reaction has a significant challenge that cannot be overlooked, the hydrogenation of CO<sub>2</sub> to formic acid necessitates simultaneous activation of two stable gas molecules-H<sub>2</sub> and CO<sub>2</sub>, which is subject to obvious thermodynamic limitations and usually requires reaction conditions of high temperature and pressure. Therefore, designing an effective catalytic system is critical to lower the substantial energy barrier involved in hydrogen dissociation and C=O bond hydrogenation. Current catalytic approaches for CO<sub>2</sub> hydrogenation to formic acid mainly include both homogeneous and heterogeneous systems. Although homogeneous catalysts demonstrate exceptional catalytic activity for formic acid/formate production, their practical application is limited by the high costs of organic ligands and challenges associated with separating and recycling metal complexes, making industrialization difficult. Conversely, heterogeneous catalysts are particularly appealing owing to their low preparation costs, good stability and ease of separation and recycling. Among these, metal-supported catalysts are the most commonly utilised heterogeneous catalysts for CO<sub>2</sub> hydrogenation to formic acid/formate reaction. However, the activity of such catalysts rapidly decreases during reactions, primarily due to metal site agglomeration and loss. To enhance the catalytic stability of metal-supported catalysts, strengthening the metal-support interaction is essential. This can be achieved by tailoring the surface geometry and electronic structure of the support material. In this review, we present a comprehensive evaluation of the catalytic performance of various metal-supported catalysts, including zeolites, mesoporous silicas, metal-organic frameworks and metal oxides, for CO<sub>2</sub> hydrogenation to formic acid/formate. In addition, we assess the impact of support structure, morphology and exposed crystal surfaces on the activity in formic acid/formate formation. We hope this work may provide some guidance for the design of high-performance catalysts for CO<sub>2</sub> hydrogenation to formic acid.

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