

学校编号: 10384
学 号: 19120051403093

分类号 _____ 密级 _____
UDC _____

厦 门 大 学

博 士 学 位 论 文

**CO₂ 加氢制甲醇用 Pd-修饰 MWCNT-促进
高效新型 Pd-ZnO 催化剂的研究**

**Study of Pd-decorated MWCNT-promoted Pd-ZnO
Catalysts for CO₂ Hydrogenation to Methanol**

梁雪莲

指导教师姓名: 张鸿斌 教授

专 业 名 称: 物 理 化 学

论文提交日期: 2009 年 2 月

论文答辩日期: 2009 年 3 月

学位授予日期: 2009 年 6 月

答辩委员会主席: _____

评 阅 人: _____

2009 年 2 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下，独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为（）课题（组）的研究成果，获得（）课题（组）经费或实验室的资助，在（）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

年 月 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

1. 经厦门大学保密委员会审查核定的保密学位论文，
于 年 月 日解密，解密后适用上述授权。

2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月 日

扩展式摘要

温室效应对我们这个星球的环境和人类社会的生存发展已构成越来越严重的威胁,减少主要温室气体之一的 CO_2 的排放已成为一个紧迫的问题. 通过加氢转化,将 CO_2 加工为有价值的燃料或化学品被认为是现时固定大量排放的 CO_2 的较好方法. 在诸多 CO_2 加氢的可能产物中,甲醇因其既是非石油基洁净合成燃料,又是重要化工原料,还可作为燃料电池氢燃料的载体,因而成为首选的目标产物.

催化剂的研制开发是实现该过程实用化的关键. 较早报道可用于催化 CO_2 加氢制甲醇的催化剂是 Cu 基(尤其是 CuO-ZnO-基和 CuO-ZrO₂-基)催化剂;负载型 Pd 催化剂对 CO_2 加氢制甲醇也有相当高的催化活性和选择性,并以 ZnO 负载的 Pd 基体系为佳. 一个具有实用意义的 CO_2 加氢制甲醇的过程要求所使用的催化剂具有高的性能;然而就我们所知,现有 CO_2 加氢制甲醇用催化剂的活性和选择性均比较低,开发兼具高活性高选择性的催化剂是实现该过程实用化的技术瓶颈.

在另一前沿,多壁碳纳米管(MWCNTs)作为一类新型纳米催化材料,近年来引起国际催化学界日益增加的兴趣. 这类纳米碳材料在结构上与中空的石墨纤维相近;它具有纳米级的管腔、由 sp^2 -C 构成的表面,并展现出良好的导电导热性及对 H_2 吸附活化的优异性能;迄今报道的催化应用领域涵盖选择加氢、氢甲酰化、脱氢、氧化、氨合成、F-T 合成、甲醇/低碳醇合成、电催化和燃料电池等,研究结果已展现其作为某些类型催化剂的优良载体或促进剂的应用前景.

本文开展 CO_2 加氢制甲醇用的 MWCNTs 促进的高效新型 Pd-ZnO 基催化剂的开发研究,从负载型 Pd-ZnO 催化剂的应用基础研究入手,在初步弄清 MWCNTs 的促进作用性质的基础上,进而研发出一类金属 Pd 修饰 MWCNTs 促进的高效新型 Pd-ZnO 催化剂,取得如下兼具理论意义和实用价值的重要进展.

1. CO_2 加氢制甲醇用的 MWCNTs 负载 Pd-Zn 催化剂的研究

1.1 MWCNTs 负载 Pd-Zn 催化剂的性能

用一类自行制备的“鱼骨型 (Herringbone-type)” MWCNT (记为 MWCNTs (*h-type*) 或 MWCNTs) 作为载体, 由分步等容浸渍法制备 MWCNTs-负载的 Pd-ZnO 催化剂 (记为 $x\%Pd_iZn_j/MWCNTs$, $x\%$ 为质量百分数), 在加压固定床连续流动反应系统, 评价其对 CO_2 加氢制甲醇的催化性能, 并与常规载体 $\gamma-Al_2O_3$, 活性炭 (AC), 以及“平行型 (Parallel-type)” MWCNTs (记为 MWCNTs(*p-type*)) 分别负载的体系作比较. 结果表明, 在组成经优化的 $16\%Pd_{0.100}Zn_1/MWCNTs$ (*h-type*) 催化剂上, 在 3.0 MPa, 523 K, $V(H_2):V(CO_2):V(N_2) = 69:23:8$ 和 GHSV = $1800 ml_{STP}/(g \cdot h)$ 的反应条件下, 所观测 CO_2 加氢的转化率达 6.30%, 相应的转化频率 (TOF, 即在单位时间 (s)、单个表面 Pd^0 -活性位上 CO_2 加氢转化的分子数) 为 $1.15 \times 10^{-2} s^{-1}$. 这个 TOF 值是相同反应条件下 3 种各具最佳 $Pd_{0.100}Zn_1$ 负载量的参比催化剂, $22\%Pd_{0.100}Zn_1/MWCNTs(p-type)$ 、 $35\%Pd_{0.100}Zn_1/AC$ 和 $20\%Pd_{0.100}Zn_1/\gamma-Al_2O_3$ 上的相应 TOF 观测值 (1.08×10^{-2} , 0.98×10^{-2} 和 $0.97 \times 10^{-2} (s^{-1})$) 分别的 1.06, 1.17 和 1.18 倍.

1.2 MWCNTs 负载 Pd-Zn 催化剂的表征

表观活化能 (E_a) 的测量及催化剂的 XRD、XPS 和 H_2 -TPD 比较表征研究揭示, 用 MWCNTs 代替 AC 或 $\gamma-Al_2O_3$ 作为催化剂载体并不引起 CO_2 加氢反应的 E_a 发生明显变化, 但导致工作态催化剂表面以 PdZn 合金形态存在的 Pd^0 -物种 (一类与甲醇的生成密切相关的表面催化活性物种) 的摩尔分率明显上升. 在另一方面, MWCNTs-负载的 Pd-ZnO 催化剂在从室温至 623 K 温度范围能可逆地吸附大量的 H_2 , 这一特点有助于在工作态催化剂表面营造较高稳态浓度活泼氢吸附物种的表面反应氛围, 于是提高了表面加氢反应的速率. 与常规载体 AC 或 $\gamma-Al_2O_3$ 不同, MWCNTs 起着作为催化剂的载体和促进剂的双重作用. 与 MWCNTs (*p-type*) 管壁表面 C 原子属于类石墨平面内原子的情形不同, MWCNTs(*h-type*) 的管壁表面 C 原子属于类石墨平面边沿原子, 有较多的表面悬键, 化学活性较高, 因而对 H_2 有较强的吸附活化能力, 其促进作用较 MWCNTs(*p-type*) 显著.

2. CO_2 加氢制甲醇用 Pd-修饰 MWCNTs 促进的高效新型 Pd-Zn 催化剂的研发

2.1 Pd 修饰 MWCNTs-基纳米材料的研制

以自行制备的MWCNTs作为基质，用微波助多元醇化学还原沉积法制备一类金属Pd-修饰的MWCNTs，记为 $y\%Pd/MWCNTs$ ($y\%$ 为质量百分数， $2\% \leq y\% \leq 8\%$)。所制得的复合材料的TEM/SEM观测结果显示，金属Pd颗粒相当均匀地负载/分散在MWCNTs表面，从TEM/SEM和XRD的图像可估计其粒径在10 nm以下。组成为5.0%Pd/MWCNT的试样的EDX分析证实，C和Pd是该试样表面仅有的两种元素，其原子分率分别为 99.4% 和 0.6%。H₂-TPD测试揭示，适量金属Pd对MWCNTs表面的修饰导致其对H₂的吸附容量显著增加，以组成为5.0%Pd/MWCNTs的试样对H₂吸附容量的增幅最大，达~85%（所作对比观测两试样的H₂-TPD曲线在273~723 K温度范围的相对面积强度比为： $A_{5.0\%Pd/MWCNTs}/A_{MWCNTs} = 100/54$ ）。

2.2 Pd 修饰 MWCNTs 促进的共沉淀型 Pd-Zn 催化剂的性能

用上述制备的金属Pd-修饰的MWCNTs ($y\%Pd/MWCNT$) 作为促进剂，制备 $y\%Pd/MWCNTs$ -促进的共沉淀型 Pd-ZnO 催化剂，记为 Pd_iZn_j- $x\%$ ($y\%Pd/MWCNTs$) ($x\%$ 和 $y\%$ 均为质量百分数)；在加压固定床连续流动反应系统，评价其对CO₂加氢制甲醇的催化性能，并与不含促进剂的原基质 Pd_iZn_j和添加等量纯MWCNTs的参比体系作比较。结果表明，在组成经优化的 Pd_{0.100}Zn₁-9.6%(5.0%Pd/MWCNTs)催化剂上，在5.0 MPa, 543 K, 15000 ml_{STP}/(h·g) 和 $V(H_2)/V(CO_2)/V(N_2) = 69/23/8$ 的反应条件下，CO₂加氢的转化率达6.98%，相应的TOF为 $6.68 \times 10^{-2} \text{ s}^{-1}$ ，这个TOF值是相同反应条件下两种参比催化剂，Pd_{0.100}Zn₁和Pd_{0.100}Zn₁-9.6%MWCNTs，的相应观测值 (4.22×10^{-2} 和 $5.40 \times 10^{-2} \text{ (s}^{-1}\text{)}$) 分别的和1.58和1.24倍；前者的甲醇时空产率达343 mg/(h·g)，是后两者的相应值(202和307 mg/(h·g)) 分别的1.70和1.12倍，也大幅度超过迄今文献报道的同类或可比的Pd-基催化剂(Pd-ZnO、Pd-Ga₂O₃等)或Cu-基催化剂(CuO/ZnO、CuO/ZrO₂等)的水平。这些结果表明，MWCNTs，尤其是Pd修饰的MWCNTs，确实可作为CO₂加氢制甲醇用的Pd-ZnO催化剂的高效促进剂。

2.3 Pd 修饰 MWCNTs 促进的共沉淀型 Pd-Zn 催化剂的表征

TEM/SEM、N₂-BET和CO化学吸附的联合表征结果显示，含促进剂的催化

剂 ($\text{Pd}_{0.100}\text{Zn}_{1-9.6\%}(5.0\%\text{Pd}/\text{MWCNTs})$ 和 $\text{Pd}_{0.100}\text{Zn}_{1-9.6\%}\text{MWCNTs}$) 的粒度较小、分散度较高, 而不含促进剂的原基质催化剂 ($\text{Pd}_{0.100}\text{Zn}_1$) 的粒度较大、比面较小. 3 种催化剂的氧化态 N_2 -BET 比表面(SSA)依次为 15.64, 19.05, 4.05 (m^2/g); 相应工作态的金属 Pd 表面 (SA_{Pd}) 分别为 2.120、2.346、1.975 (m^2/g).

实验发现, 催化剂的最高还原温度对其催化性能有显著影响, 以经受 538 K、 H_2 -还原的催化剂的活性为佳; XRD 观测证实, 经适当高温还原的催化剂金属 Pd 组分绝大部分以 Pd-Zn 合金相的形态存在; 这些实验事实表明 Pd-Zn 合金微晶相是与 CO_2 加氢制甲醇更加密切相关的催化活性相. 3 种催化剂 ($\text{Pd}_{0.100}\text{Zn}_{1-9.6\%}(5.0\%\text{Pd}/\text{MWCNTs})$, $\text{Pd}_{0.100}\text{Zn}_{1-9.6\%}\text{MWCNTs}$ 和 $\text{Pd}_{0.100}\text{Zn}_1$) 的反应后试样的 XPS 分析显示, 其表面 Pd^0 物种在总表面 Pd 量中的摩尔分率分别为 57.3, 52.6, 48.6 (mol%), 前者是后两者分别的 1.09 和 1.18 倍; 这个顺序与 3 种催化剂上 CO_2 加氢制甲醇的反应活性高低顺序相一致.

H_2 -TPD 测试结果表明, MWCNT, 尤其是 5.0%Pd/MWCNTs, 促进的 $\text{Pd}_{0.100}\text{Zn}_{1-9.6\%}$ -基体系对 H_2 有更强的吸附/活化能力; 所作对比观测 3 种试样的 H_2 -TPD 曲线的相对面积强度比为: $A_{\text{Pd}_{0.100}\text{Zn}_{1-9.6\%}(5.0\%\text{Pd}/\text{MWCNTs})} / A_{\text{Pd}_{0.100}\text{Zn}_{1-9.6\%}\text{MWCNTs}} / A_{\text{Pd}_{0.100}\text{Zn}_1} = 100/86/81$ (在 293~773 K 温度范围) 或 100/87/75 (在 473~773 K 温度范围), 这个顺序与这 3 种催化剂上 CO_2 加氢制甲醇的反应活性高低顺序相一致.

2.4 Pd-修饰 MWCNTs-基纳米材料的促进作用本质

上述催化剂评价结果显示, 适当添加少量 5.0%Pd/MWCNTs 到 $\text{Pd}_{0.100}\text{Zn}_1$ 基质催化剂中导致 CO_2 加氢转化率和甲醇产率大幅度增加; 然而表观活化能 (E_a) 的测量结果显示, 少量 MWCNTs-基纳米材料促进剂的加入并不引起 CO_2 加氢转化的 E_a 发生明显变化, 这可能暗示 CO_2 加氢反应速率决定步骤的反应途径并不因少量 MWCNTs-基促进剂的加入而有所改变.

在另一方面, 所观测催化活性表面 Pd-物种的摩尔分率的增加无疑有助于催化剂比活性 (即单位质量催化剂的活性) 的提高, 然而所观测 CO_2 加氢转化率高达 70% 的增幅 (6.98% vs. 4.11% 对于 $\text{Pd}_{0.100}\text{Zn}_{1-9.6\%}(5.0\%\text{Pd}/\text{MWCNTs})$ 和 $\text{Pd}_{0.100}\text{Zn}_1$) 很难单纯归因于活性金属 Pd 表面的增加 (2.120 vs. 1.975 (m^2/g), 增幅仅为 7.3%) 所贡献; 此外, 从活性金属 Pd 表面积增加的角度出发也无法解释单

个表面Pd⁰-活性位上CO₂加氢的转化频率（即TOF）的显著差别（ $6.68 \times 10^{-2} \text{ s}^{-1}$ vs. $4.22 \times 10^{-2} \text{ s}^{-1}$ ，增幅达58%）。

因此在我们看来，在Pd修饰MWCNTs促进的Pd-ZnO催化剂上CO₂加氢高的活性与作为促进剂的MWCNTs-基纳米材料对H₂优良的吸附性能也密切相关。根据上述H₂-TPD结果，能够推断：在CO₂加氢的反应条件下，在工作态Pd_{0.100}Zn_{1-9.6%}(5.0%Pd/MWCNTs)催化剂表面存在着大量的氢吸附物种，营造具有较高稳态浓度活泼氢吸附物种的表面反应氛围，于是提高了表面加氢反应的速率。

3. 结论

- Pd修饰MWCNTs能够作为CO₂加氢制甲醇用的Pd-Zn催化剂的高效促进剂；
- 作为助剂的MWCNTs-基纳米材料的促进效应主要表现在：1) 通过影响催化剂的化学态使表面催化活性钯（Pd⁰）的表面积有所增加；2) 提高了催化剂对H₂（反应物之一）的吸附活化能力。

4. 本文的创新点

- 研发出一种金属Pd修饰MWCNTs促进的高效新型Pd-ZnO催化剂，其对CO₂加氢制甲醇的催化活性和选择性高而稳定，CO₂加氢转化率及甲醇时空产率明显高于现有文献报道同类催化剂的水平，具有明显创新性。
- 初步弄清作为助剂的MWCNTs-基纳米材料的促进作用机理，对于增进对MWCNTs-基纳米材料催化特性的认识具有重要理论意义。

关键词：多壁碳纳米管；Pd-修饰碳纳米管；Pd-ZnO 催化剂；CO₂加氢；甲醇合成。

Extended Abstract

The greenhouse effect of carbon dioxide has been recognized to be one of the most serious problems in the world and a number of countermeasures have been proposed so far. Catalytic hydrogenation of carbon dioxide to produce various kinds of chemicals and fuels has received much attention. Among the options considered, methanol synthesis by CO₂ hydrogenation has been also considered to play a role in the transportation of hydrogen energy produced from natural such as solar energy, hydropower and so on.

A number of Cu-based catalysts, especially CuO-ZnO and CuO-ZrO₂ based catalysts, have been found to exhibit interesting properties for synthesis of methanol from CO₂/H₂ feedstock. Supported Pd catalysts have also been found to display certain activity for hydrogenation of CO₂ to methanol. Nevertheless, a practical methanol synthesis process from CO₂ hydrogenation requires a high performance catalyst, and to our best knowledge, the activity and selectivity of the existing catalysts for CO₂ hydrogenation to methanol were still relatively low. Development of catalysts with high efficiency and selectivity has been one of the key objectives for R&D efforts.

To the other front, multi-walled carbon-nanotubes (symbolized as MWCNTs in later text), as a novel nano-carbon material, have been drawing increasing attention recently. This new form of carbon is structurally close to hollow graphite fiber, except that it has a much higher degree of structural perfection. MWCNTs possess several unique features, such as graphitized tube-wall, nanometer-sized channel and *sp*²-C-constructed surface. They display high thermal/electrical conductivity, medium to high specific surface areas, and excellent performance for adsorption of hydrogen, all of which render this kind of nanostructured carbon materials full of promise as a novel catalyst support and/or promoter.

In the present work, a series of supported and promoted Pd-ZnO catalysts by MWCNTs or Pd-decorated MWCNTs, noted as *x*%Pd_{*i*}Zn_{*j*}/MWCNTs and Pd_{*i*}Zn_{*j*}-*x*% (MWCNTs or *y*%Pd/MWCNTs), respectively, (where *x*% and *y*% both represented mass percentage) were prepared by methods of conventional impregnation or co-precipitation. Their catalytic performance for CO₂ hydrogenation to methanol was evaluated, and compared with the related reference systems. The results should shed

light on the understanding of the nature of promoter action by the MWCNTs-based nano-material and on the design of practical catalyst for CO₂ hydrogenation to methanol. The progresses obtained in the present work were briefly described as follows.

1. Study of MWCNTs-supported Pd-Zn catalyst for hydrogenation of CO₂ to methanol

1.1 Performance of MWCNTs-supported Pd-Zn catalyst

Using a kind of home-made “Herringbone-type” MWCNTs (noted as MWCNTs(*h-type*) in later text) as support, a type of MWCNTs(*h-type*)-supported Pd-ZnO catalysts were prepared by a stepwise incipient wetness method, and their catalytic activity for CO₂ hydrogenation to methanol was evaluated, and compared to that of the reference systems supported on activated carbon (AC) or γ -Al₂O₃. The results showed that over the composition-optimized catalyst, 16%Pd_{0.100}Zn₁/MWCNTs(*h-type*), under the reaction condition of 3.0 MPa, 523 K, $V(\text{H}_2):V(\text{CO}_2):V(\text{N}_2) = 69:23:8$ and GHSV = 1800 ml_{STP}/(g•h), the observed conversion of CO₂-hydrogenation reached 6.30%, with the corresponding turnover frequency (TOF, i.e., the number of CO₂-molecule hydrogenated on unit site of exposed Pd⁰ per second (s⁻¹)) being $1.15 \times 10^{-2} \text{ s}^{-1}$. This value of TOF was 1.06 or 1.17 or 1.18 times that (1.08×10^{-2} or 0.98×10^{-2} or $0.97 \times 10^{-2} \text{ (s}^{-1}\text{)}$ under the same reaction condition) of the catalyst of 22%Pd_{0.100}Zn₁/MWCNTs(*p-type*) or 35%Pd_{0.100}Zn₁/AC or 20%Pd_{0.100}Zn₁/ γ -Al₂O₃, all prepared by the same method with the respective optimal Pd_{0.100}Zn₁-loading.

1.2 Characterizations of MWCNTs-supported Pd-Zn catalyst

The measurement of the apparent activation energy (E_a) and the comparative characterization-study of the catalysts by XRD, XPS and H₂-TPD et al. demonstrated that using the MWCNTs in place of AC or γ -Al₂O₃ as the catalyst support displayed little change in the E_a for CO₂ hydrogenation, but led to an increase of surface concentration of the Pd⁰-species in the form of PdZn alloys, a kind of catalytically

active Pd⁰-species closely associated with the methanol generation. On the other hand, the MWCNTs-supported Pd-ZnO catalyst could reversibly adsorb a greater amount of hydrogen at temperatures ranging from room temperature to 623 K. This unique feature would help to generate a micro-environment with higher concentration of active H-adspecies at the surface of the functioning catalyst, thus increasing the rate of surface hydrogenation reactions. It is evident that the MWCNTs played dual roles as support and promoter. The “Herringbone type” MWCNTs possess more active surface (with more dangling bonds), and thus, higher capacity for adsorbing H₂, which make their promoting action more remarkable, compared to the “Parallel-type” MWCNTs.

2. Development of Pd-decorated MWCNTs-promoted co-precipitated Pd-Zn catalyst for hydrogenation of CO₂ to methanol

2.1 Preparation and characterization of metallic Pd-decorated MWCNTs

With the home-made MWCNTs(*h-type*) as substrate material, a type of metallic Pd-decorated CNTs, noted as *y*%Pd/MWCNTs ($2 \text{ mass\%} \leq y\% \leq 8 \text{ mass\%}$), was prepared using an intermittent microwave irradiation-assisted polyol-reduction/deposition method. The TEM and SEM observations of the synthesized materials showed that metallic Pd-particles were quite uniform in shape and size and well dispersed on the MWCNTs surface, with the Pd-particle diameters being below 10 nm, as estimated from the corresponding XRD patterns. The EDX analysis demonstrated that carbon and palladium were the only two elements at the surface of 5.0%Pd/MWCNTs, with atomic percentage of 99.4% and 0.6%, respectively. The H₂-TPD investigation revealed that the modification of an appropriate amount of metallic palladium to the MWCNTs led to a significant increase in their hydrogen-adsorbing capacity, with the material of 5.0%Pd/MWCNTs composition reaching a maximum increment of 85% (i.e., the ratio of relative area-intensity of the observed H₂-TPD profiles $A_{5.0\%Pd/MWCNTs}/A_{MWCNTs} = 100/54$) in the temperature range of 273~723 K.

2.2 Performance of Pd-decorated MWCNTs-promoted co-precipitated Pd-Zn catalysts

Using the CNTs or 5.0%Pd/MWCNTs as promoter, a type of co-precipitated

Pd-ZnO catalysts, noted as Pd_iZn_j-x%(MWCNTs or y%Co/MWCNTs), for hydrogenation of CO₂ to methanol was developed. It was experimentally shown that the CNTs, especially the Pd-decorated MWCNTs, promoted catalyst displayed high activity for CO₂ hydrogenation and excellent selectivity for methanol formation. Over the composition-optimized Pd_{0.100}Zn₁-9.6%(5.0%Pd/MWCNTs) catalyst under reaction condition of 5.0 MPa, 543 K, $V(\text{H}_2)/V(\text{CO}_2)/V(\text{N}_2) = 69/23/8$ and GHSV = 15000 ml_{STP}/(h•g), the observed conversion of CO₂ hydrogenation reached 6.98%, with the corresponding TOF being $6.68 \times 10^{-2} \text{ s}^{-1}$. This TOF value was 1.58 and 1.24 times that (4.22×10^{-2} and $5.40 \times 10^{-2} \text{ (s}^{-1}\text{)}$) of the two reference systems, Pd_{0.100}Zn₁ and Pd_{0.100}Zn₁-9.6%MWCNTs, respectively, under the same reaction condition. The former's methanol-STY reached 343 mg/(h•g), which was 1.70 and 1.12 times that (202 mg/(h•g) and 307 mg/(h•g)) of the latter two systems, successively, showing the remarkable promoter effect by the metallic Pd-decorated MWCNTs-material.

2.3 Characterizations of Pd-decorated MWCNTs-promoted co-precipitated Pd-Zn catalysts

It was experimentally found that the temperature for the reduction of catalyst precursor has a marked effect on the performance of the catalyst, with the performance of catalyst undergoing H₂-reduction at 538 K being optimal. On the other hand, the post XRD analysis of the tested three catalysts revealed that most of the Pd-component existed in the form of PdZn-alloy in the catalysts undergoing the H₂-reduction at 538 K. This strongly implied that it was the PdZn-alloy crystallite phase that was closely associated with the selective formation of methanol. Nevertheless, it was also experimentally shown that the H₂-reduction at the temperatures higher than 538 K lead to increasing particle-diameter of PdZn-alloy crystallites and decreasing the metallic Pd exposed area.

Post XPS-analysis of the tested catalysts revealed that appropriate incorporation of a minor amount of the x%Pd/MWCNTs into the Pd_{0.100}Zn₁ host catalyst led to a marked increase of surface concentration of metallic palladium species (Pd⁰), a kind of catalytically active Pd-species closely associated with the methanol generation. The observed relative content (mol%) of the surface Pd⁰-species in the total Pd-amount at the surface of the three catalysts, Pd_{0.100}Zn₁-9.6%(5.0%Pd/MWCNTs), Pd_{0.100}Zn₁-

9.6%MWCNTs and Pd_{0.100}Zn₁, was 57.3, 52.6 and 48.6 (mol%), successively. This sequence was in line with the sequence of the specific activity of the three catalysts for CO₂ hydrogenation.

H₂-TPD measurements showed that appropriate addition of a minor amount of the *x*%Pd/MWCNTs into the Pd_{0.100}Zn₁ host catalyst could improve the capacity of the catalyst for adsorbing hydrogen to a greater extent. The relative area-intensity ratio of the H₂-TPD profiles taken on the three catalysts pre-reduced by hydrogen was estimated to be $A_{\text{Pd}_{0.100}\text{Zn}_1-9.6\%(5\%\text{Pd/MWCNTs})} / A_{\text{Pd}_{0.100}\text{Zn}_1-9.6\%\text{MWCNTs}} / A_{\text{Pd}_{0.100}\text{Zn}_1} = 100/87/75$ in the temperature region of 473~773 K. This was expected to also be the sequence of increase in concentration of hydrogen ad-species at the surface of functioning catalysts, in line with the activity sequence observed on the corresponding three catalysts for hydrogenation of CO₂ to methanol.

2.4 Nature of the promoter action by MWCNTs-based nano-materials

The aforementioned results of the catalyst evaluation showed that appropriate incorporation of a minor amount of the 5.0%Pd/MWCNTs into the Pd_{0.100}Zn₁ host catalyst led to a significant increase in conversion of CO₂ hydrogenation and yield of methanol. Yet the result of measurement of apparent activation energy (E_a) indicated that the addition of a minor amount of the MWCNTs-based promoter into the Pd_{0.100}Zn₁ host catalyst did not cause a marked change in the E_a for CO₂ hydrogenation-conversion, most likely implying that the addition of a minor amount of the MWCNTs-based promoter to the Pd_{0.100}Zn₁ did not alter the reaction pathway of rate-determining step of the CO₂ hydrogenation reaction.

On the other hand, the increment of the catalytically active surface Pd-species, observed by the XPS, was undoubtedly in favour of enhancing the specific activity of the catalysts (i.e., activity of unit mass of catalyst). Nevertheless, it would be difficult to believe that the observed large-sized increase of CO₂ hydrogenation-conversion over the catalyst promoted by the 5.0%Pd/MWCNTs was solely attributed to the difference in their specific active Pd surface-area. Besides, the difference in the active Pd surface-area could hardly justify the increase of the observed TOF.

It appears that the high reactivity of CO₂ hydrogenation over the 5.0%Pd/MWCNTs promoted Pd_{0.100}Zn₁ catalyst was closely related to the peculiar properties of this kind of MWCNTs, especially their excellent performance for adsorption

/activation of H₂. Based upon the above H₂-TPD results, it could be suggested that, under the reaction conditions of the CO₂ hydrogenation, there existed a considerably larger amount of reversibly adsorbed H-species on the functioning Pd_{0.100}Zn₁-9.6% (5.0%Pd/MWCNTs) catalyst, which would generate a surface micro-environment with high stationary-state concentration of H-adspecies on the catalyst, thus increase the rate of a series of surface hydrogenation reactions in the CO₂ hydrogenation-conversion.

3. Concluding Remarks

The present work showed that the MWCNTs, especially the metallic Pd-decorated MWCNTs, could serve as an excellent promoter of the Pd-ZnO catalyst for CO₂ hydrogenation to methanol. The developed Pd_{0.100}Zn₁-9.6%(5.0%Pd/MWCNTs) catalyst achieved high single-pass-yield of methanol from CO₂ hydrogenation, and demonstrated great potential in commercial use for converting CO₂ into valuable chemicals. The results also shed some light on the understanding of the promoter action by the transition metal-decorated MWCNTs-additive and on the design of practical catalyst for CO₂ hydrogenation to methanol. For better understanding of mechanism of the promoter action by the MWCNTs-based additives, further studies, especially *in-situ* characterization of reaction intermediates under the actual reaction condition, would be desirable.

Keywords: MWCNTs; Pd-decorated MWCNTs; Pd-ZnO catalyst; CO₂ hydrogenation; methanol synthesis.

目录

| | |
|--------------------------------|----|
| 第一章 绪论..... | 1 |
| 1.1 二氧化碳加氢..... | 1 |
| 1.1.1 温室效应..... | 1 |
| 1.1.2 二氧化碳的减排..... | 2 |
| 1.1.3 二氧化碳的直接利用..... | 3 |
| 1.1.4 二氧化碳的转化..... | 3 |
| 1.2 甲醇合成..... | 12 |
| 1.2.1 甲醇的重要性..... | 12 |
| 1.2.2 二氧化碳加氢合成甲醇的热力学分析..... | 13 |
| 1.2.3 二氧化碳加氢合成甲醇的催化剂体系..... | 13 |
| 1.2.4 二氧化碳加氢合成甲醇的机理研究..... | 16 |
| 1.3 碳纳米管..... | 17 |
| 1.3.1 简介..... | 17 |
| 1.3.2 碳纳米管的制备方法概述..... | 18 |
| 1.3.3 碳纳米管在催化研究中的应用和进展..... | 20 |
| 参考文献..... | 23 |
| 第二章 实验部分..... | 33 |
| 2.1 主要试剂及气体..... | 33 |
| 2.2 催化剂制备..... | 33 |
| 2.2.1 碳纳米管的制备..... | 33 |
| 2.2.2 负载型催化剂的制备..... | 34 |
| 2.2.3. Pd 修饰 MWCNTs 的制备..... | 34 |
| 2.2.4. 共沉淀催化剂的制备..... | 34 |
| 2.3 催化剂的活性评价..... | 35 |
| 2.4 产物分析计算方法..... | 35 |
| 2.5 催化剂物化性能表征..... | 36 |
| 2.5.1 H ₂ -TPR..... | 36 |

| | |
|---|----|
| 2.5.2 H ₂ -TPD | 37 |
| 2.5.3 XRD 衍射 | 37 |
| 2.5.4 XPS | 38 |
| 2.5.5 TEM、SEM、EDS | 38 |
| 2.5.6 BET、化学吸附 | 38 |
| 参考文献 | 39 |
| 第三章 MWCNTs 负载 Pd-Zn 催化剂 CO ₂ 加氢制甲醇的研究 | 40 |
| 3.1 前言 | 40 |
| 3.2 催化剂制备参数的优化 | 42 |
| 3.2.1 Zn(NO ₃) ₂ 的分解温度的研究 | 42 |
| 3.2.2 x%Pd _{0.085} Zn ₁ /MWCNTs(<i>h-type</i>)催化剂上 Pd-Zn 负载量的优化 | 44 |
| 3.2.3 15.5%Pd _i Zn _j /MWCNTs(<i>h-type</i>)催化剂上 Pd-Zn 比例的优化 | 46 |
| 3.2.4 灼烧温度的优化 | 49 |
| 3.2.5 MWCNTs(<i>h-type</i>)不同处理方法的优化 | 51 |
| 3.2.6 Pd/Zn 浸渍顺序的优化 | 54 |
| 3.2.7 不同载体的催化剂上 PdZn 负载量的优化 | 57 |
| 3.3 催化剂反应条件的优化 | 61 |
| 3.3.1 反应温度的优化 | 61 |
| 3.3.2 压力条件的优化 | 63 |
| 3.3.3 空速条件的优化 | 66 |
| 3.3.4 还原温度的优化 | 67 |
| 3.4 3.0 MPa 下催化剂与相应体系催化剂活性的比较 | 71 |
| 3.4.1 不同载体相同负载量催化剂的活性对比研究 | 71 |
| 3.4.2 不同载体最佳负载量催化剂的对比研究 | 75 |
| 3.5 催化剂的表征 | 79 |
| 3.5.1 TEM 表征研究 | 79 |
| 3.5.2 SEM 和 EDS 的联合表征研究 | 81 |
| 3.5.3 XRD | 83 |
| 3.5.4 BET | 87 |

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士学位论文摘要库