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**CO₂ 加氢合成甲醇用 Co 修饰碳纳米管促进
CuO-ZnO-ZrO₂ 催化剂的研究**

**Study of Co-decorated MWCNTs-promoted CuO-ZnO-ZrO₂
Catalyst for Methanol Synthesis from CO₂ Hydrogenation**

刘 志 铭

指导教师姓名: 张鸿斌 教授

专 业 名 称: 工 业 催 化

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摘 要

为了改善气候条件并解决碳资源问题，需要开发能将 CO₂ 转化为有价值材料的技术。在所考虑的多种选项中，甲醇因其是重要化工原料并可作为石油补充替代合成燃料，因而通过加氢将 CO₂ 转化为甲醇的研究倍受关注。

CO₂ 是最稳定的化合物之一。从 CO₂ 加氢制甲醇 (CO₂ + 3H₂ = CH₃OH + H₂O, ΔG_{523 K} = 46.5 kJ/mol) 较之从 CO 加氢制甲醇 (CO + 2H₂ = CH₃OH, ΔG_{523 K} = 26.9 kJ/mol) 在热力学上不利得多。在工业上要求的反应温度 (523 K) 下 CO₂ 加氢的平衡转化率相当低。因此，开发能在高原料气空速条件下操作的高效催化剂 (以便实现高的单程甲醇时空产率)，不失为克服该过程“低平衡转化率”之不足提供一条行之有效的技术途径。近 20 年来有关 CO₂ 加氢制甲醇用催化剂文献已有所报道，但从实用角度着眼，现有 CO₂ 加氢制甲醇用催化剂 (主要是 CuO-基催化剂) 的活性和选择性都较低 (5 ~ 8 MPa 和 523 K 的反应条件下甲醇的单程时空产率多在 200 ~ 350 mg·h⁻¹·g⁻¹)。研发更加有效的 CO₂ 加氢制甲醇用催化剂是实现该过程工业化的技术瓶颈。

在另一前沿领域，多壁碳纳米管 (MWCNTs, 下文简称为 CNTs) 基纳米复合材料作为高效新型的加氢催化剂的载体或促进剂已日益引起国际催化学界的关注。本文用一种 Co 修饰 CNT-基复合材料作为促进剂，研发出一种 Co 修饰 CNT-促进的共沉淀型 CuO-ZnO-ZrO₂ 催化剂，该催化剂对 CO₂ 加氢制甲醇兼具高的活性和选择性，能在高的原料气空速条件下操作，获得较高的甲醇时空产率；利用多种物化检测技术 (TEM, SEM, XRD, XPS, H₂-TPD 等) 对催化剂进行表征，初步弄清 CNT-基添加剂的促进作用本质。

本论文取得如下兼具理论意义和实用价值的重要进展：

1. CO₂ 加氢制甲醇用 Co 修饰 CNT-促进的 CuO-ZnO-ZrO₂ 基催化剂的研制

用 Co 修饰 CNT-基复合材料 (y%Co/CNTs) 作为添加剂，研制出一类 Co 修饰 CNT-促进的共沉淀型 CuO-ZnO-ZrO₂ 催化剂，记为 Cu₇Zn_jZr_{k-x}% (y%Co/CNTs) (x% 和 y% 均为质量百分数)。实验结果表明，适当添加少量 Co 修饰 CNTs 于共沉淀型 CuO-ZnO-ZrO₂ 基质中能明显地提高其催化 CO₂ 加氢生成甲醇的活性。在组成

经优化的 $\text{Cu}_8\text{Zn}_2\text{Zr}_5\text{-10\%(4.5\%Co/CNTs)}$ 催化剂上, 5.0 MPa, 523 K, $V(\text{H}_2)/V(\text{CO}_2)/V(\text{N}_2) = 69/23/8$, $\text{GHSV} = 25\ 000\ \text{ml}_{\text{STP}}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ 的反应条件下, CO_2 加氢的转化频率 (TOF, 即单位时间(s)内在单个表面活性金属 Cu^0 位上 CO_2 加氢转化的分子数) 达 $4.99\times 10^{-3}\ \text{s}^{-1}$, 分别比相同条件下非促进的原基质 $\text{Cu}_8\text{Zn}_2\text{Zr}_5$ 和单纯 CNT-促进的对应物 $\text{Cu}_8\text{Zn}_2\text{Zr}_5\text{-10\%CNTs}$ 上的相应值 ($4.31\times 10^{-3}\ \text{s}^{-1}$ 和 $4.64\times 10^{-3}\ \text{s}^{-1}$) 提高 16% 和 8%。在 CO_2 加氢产物中甲醇的 C-基选择性达 97.9%, 相应的单程时空产率为 $699\ \text{mg}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, 较大幅度地超过迄今国内外文献报道同类或相关催化剂的水平, 具有实用前景。

2. CO_2 加氢制甲醇用 Co 修饰 CNT-促进的 CuO-ZnO-ZrO_2 基催化剂的表征

(1) 反应后催化剂的 XRD 测量结果显示, 在工作态催化剂中, Cu 组分的存在形式主要是: 金属 Cu (Cu_x^0) ($2\theta = 43.4^\circ, 50.4^\circ$ 和 74.1°); ZrO_2 组分以微晶相存在的可能性并不排除; ZnO 组分则高度分散, 其微晶相含量在 XRD 检测极限以下。在另一方面值得注意的是, 与不含 ZnO 的二元 CuO-ZrO_2 体系不同, 在添加 ZnO 的三元 CuO-ZnO-ZrO_2 体系中观测到 XRD-可检测量的 Cu_2O 微晶相; 这很可能缘于所谓“离子掺杂-价态补偿效应”, 即在共沉淀法制得的 CuO-ZnO-ZrO_2 三元体系中, ZnO 晶格可溶解入一定量离子半径与 Zn^{2+} (0.074 nm) 相近但价态较 Zn^{2+} 高的 Zr^{4+} 离子 (离子半径为 0.077 nm), 同时诱生出相应价量的正离子缺位, 后者可扩散迁移到 ZnO 晶格表面, 并可通过装填入等价量的低价金属 Cu^+ 离子以达到价态和电荷的补偿, 于是有助于 Cu_2O 界面相的生成。有趣的是, 在 CuO-ZnO-ZrO_2 三元体系中适当添加 Co-修饰 CNTs 导致 Cu_2O 微晶相的含量明显增加 (已知表面 Cu^+ -位能吸附和解离活化 H_2)。

(2) 反应后催化剂的 XPS 观测结果表明, 添加 Co-修饰 CNTs 的体系与不含 CNT-基添加剂的原基质催化剂相比, 它们的 Zn(2p)和 Zr(3d) 的 XPS 谱峰的位置及形状无明显差别, 分别属于 Zn^{2+} 和 Zr^{4+} 物种的特征, 但它们的 Cu(2p)-XPS 谱峰的位置和形状则稍有不同。解谱结果显示, 工作态催化剂表面 Cu 物种的存在形式主要是 Cu^0 和 Cu^+ , 三种催化剂表面 Cu^0 物种在相应总表面 Cu 物种中所占摩尔分率比为: $\text{Cu}_8\text{Zn}_2\text{Zr}_5\text{-10\%(4.5\%Co/CNTs)} : \text{Cu}_8\text{Zn}_2\text{Zr}_5\text{-10\%CNTs} : \text{Cu}_8\text{Zn}_2\text{Zr}_5 = 72 : 69 : 66$ 。这个顺序与由 N_2O 氧化-还原法测定的活性 Cu 表面

积作为计算基准的这些催化剂上 CO_2 加氢的转化频率实验值的高低顺序相一致。这个结果也为“表面 Cu^0 是负责 CO_2 加氢的主要催化活性 Cu 物种”的论断提供实验支持。

- (3) H_2 预还原催化剂的 H_2 -TPD 测试结果显示, 添加适量 Co-修饰 CNTs 于 $\text{Cu}_8\text{Zn}_2\text{Zr}_5$ 基质催化剂中能显著地提高其对 H_2 的吸附能力。在本文 CO_2 加氢制甲醇的反应温度范围 (463 ~ 543 K), 三种预还原催化剂的 H_2 -TPD 峰的相对面积强度比为 $S_{\text{Cu}_8\text{Zn}_2\text{Zr}_5-10\%(4.5\%\text{Co}/\text{CNTs})} : S_{\text{Cu}_8\text{Zn}_2\text{Zr}_5-10\%\text{CNTs}} : S_{\text{Cu}_8\text{Zn}_2\text{Zr}_5} = 100 : 87 : 60$; 这个顺序与 3 种催化剂上 CO_2 加氢的转化频率实验值的高低顺序相一致。

3. Co-修饰 CNT-基添加剂的促进作用本质

本文研究结果表明, 适当添加少量 Co-修饰 CNTs 于 $\text{Cu}_8\text{Zn}_2\text{Zr}_5$ 基质催化剂中并不引起 CO_2 加氢反应的表现活化能发生明显变化, 但却导致工作态催化剂表面催化活性 Cu 物种 (Cu^0) 所占表面 Cu 摩尔分率有所提高。这无疑有助于以单位质量 $\text{Cu}_8\text{Zn}_2\text{Zr}_5$ 组分为计算基准的催化剂比活性 (即 CO_2 加氢比反应速率) 的提高。在另一方面, 与非促进的原基质或单纯 CNT-促进的对应物相比, 添加 (4.5%Co/CNTs) 的催化剂的工作态表面存在较高浓度的可逆吸附氢物种, 营造出具有较高活泼氢稳态浓度的表面氛围。这些活泼氢吸附物种通过氢溢流作用容易传输到 $\text{Cu}_x^0(\text{Cu}^+)-\text{ZnO}-\text{ZrO}_2$ 催化活性位, 于是有助于提高单个表面活性位上 CO_2 加氢的转化频率 (TOF)。以上两方面的促进效应对 (Co 修饰 CNTs)-促进的 $\text{Cu}_8\text{Zn}_2\text{Zr}_5$ 催化剂上 CO_2 加氢反应活性的提高都有不同程度的贡献。

关键词: 多壁碳纳米管; Co 修饰多壁碳纳米管基复合材料;

$\text{Cu}_i\text{Zn}_j\text{Zr}_k-x\%(y\%\text{Co}/\text{MWCNTs})$ 催化剂; CO_2 加氢; 甲醇合成

Abstract

Hydrogenation of carbon dioxide has been considered as one of the most economical and effective ways to chemically fix huge amount of emitted CO₂. In order to improve climate conditions, it is desirable to develop methods to convert CO₂ into valuable chemicals. Among the options considered, catalytic hydrogenation of CO₂ to produce methanol has received much attention.

Since carbon dioxide is one of the most stable compounds, most reactions including CO₂ as a reactant are not favorable thermodynamically. The synthesis of methanol from CO₂ ($\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$, $\Delta G_{523\text{ K}} = 46.5\text{ kJ/mol}$) is less favored compared to that from CO ($\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$, $\Delta G_{523\text{ K}} = 26.9\text{ kJ/mol}$), therefore the equilibrium conversion of CO₂ is extremely low even at a commercially desirable operating temperature around 523 K. Development of highly active catalyst, which is able to operate under the reaction conditions of high space velocity of feed-gas so as to gain high single-pass time-space-yield of methanol, is one of ways to overcome deficiency of low thermodynamic equilibrium conversion of CO₂ hydrogenation to methanol. Nevertheless, the activity of the existing catalysts (mainly CuO-based catalysts) is relatively low in eyes of practicability. Under the typical reaction conditions (of 5 ~ 8 MPa), the reached single-pass time-space yield (STY) of methanol for most systems is in range of 200 ~ 350 mg·h⁻¹·g⁻¹.

To the other front, multi-walled carbon-nanotubes (MWCNTs, simplified as CNTs in next text), as a novel nano-carbon material, have been drawing increasing attention recently. This new form of nano-carbon possesses several unique features, such as graphitized tube-wall, nanometer-sized channel and *sp*²-C-constructed surface. They display high thermal/electrical conductivity 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 this dissertation, a type of Co-decorated CNT-promoted CuO-ZnO-ZrO₂ catalysts was developed. The catalyst displays higher activity and selectivity for CO₂ hydrogenation to methanol, compared to the CNT-free counterpart and to the reference catalyst promoted by the simple CNTs. The results shed some light on understanding

the nature of promoter action by the Co-decorated CNTs and on the design of practicable catalyst for CO₂ hydrogenation to methanol.

The obtained progress in the present study was briefly described as follows:

1. Co-decorated CNT-promoted CuO-ZnO-ZrO₂ based catalyst for CO₂ hydrogenation to CH₃OH

With Co-decorated CNTs as promoter, a type of Co-decorated CNT-promoted CuO-ZnO-ZrO₂ catalysts was developed. The catalyst displays excellent performance for CO₂ hydrogenation to methanol. Over a Cu₈Zn₂Zr₅-10%(4.5%Co/CNTs) catalyst under the reaction conditions of 5.0 MPa, 523 K, $V(\text{H}_2) : V(\text{CO}_2) : V(\text{N}_2) = 69 : 23 : 8$ and GHSV = 25 000 ml_{STP}·h⁻¹·g⁻¹, the observed turnover frequency (TOF) of CO₂ hydrogenation reached 4.99×10⁻³ s⁻¹. This value was 1.16 and 1.08 times that (4.31×10⁻³ s⁻¹ and 4.64×10⁻³ s⁻¹) of the CNT-free substrate Cu₈Zn₂Zr₅ and the simple CNT-promoted counterpart Cu₈Zn₂Zr₅-10%CNTs, respectively, under the same reaction conditions. The selectivity of CH₃OH in the CO₂ hydrogenation products reached 97.9%, with the corresponding STY reaching 699 mg_{-CH₃OH}·h⁻¹·g_{-catal.}⁻¹, markedly higher than the level of the similar or related catalysts reported in the literature.

2. Characterization of Co-decorated CNT-promoted CuO-ZnO-ZrO₂ based catalyst

The XRD measurements disclosed that, in the functioning catalysts, the metal Cu component existed mainly in the forms of Cu_x⁰ ($2\theta = 43.4^\circ, 50.4^\circ, 74.1^\circ$), and the presence of crystallite phase of ZrO₂ could not be excluded, while the content of ZnO-phase was under the XRD-detection limit. It is worth noting that, being different from the ZnO-free binary system CuO-ZrO₂, a XRD-observable amount of Cu₂O crystallite phase ($2\theta = 36.4^\circ$) was detected in the ZnO-containing ternary system CuO-ZnO-ZrO₂, which most probably resulted from the so-called “effect of ion-doping-valence-compensation”. It is interesting that appropriate addition of an amount of Co-decorated CNTs to the ternary CuO-ZnO-ZrO₂ system led to a marked increase of the content of Cu₂O crystallite phase.

XPS post-analysis of the tested catalysts showed that little marked difference in the Zn(2p)-XPS and Zr(3d)-XPS spectra but a certain difference in the Cu(2p)-XPS spectra

existed among the three tested catalysts in the position and shape as well as relative intensity of the XPS peaks associated with the Zn, Zr and Cu species, respectively. The results of analysis-fitting of those XPS spectra showed that, at the surface of functioning catalysts, the observed Zn-species all were +2 valence-state, with the corresponding binding energy (*B.E.*) of $\text{Zn}^{2+}(2p_{3/2})$ at 1022.5 eV, and Zr-species all were +4 valence-state, with the corresponding *B. E.* of $\text{Zr}^{4+}(3d_{5/2, 3/2})$ at 182.8/185.2 eV, while the dominant Cu-species were Cu^0 , secondary Cu^+ , with the corresponding *B.E.* of $\text{Cu}^0(2p_{3/2, 1/2})$ and $\text{Cu}^+(2p_{3/2, 1/2})$ at 932.5/952.5 and 931.8/951.8 eV, respectively. The ratio of the molar percentage of Cu^0 -species in the total Cu-amount at the surface of the three tested catalysts was $\text{Cu}_8\text{Zn}_2\text{Zr}_5\text{-10\%(4.5\%Co/CNTs)} : \text{Cu}_8\text{Zn}_2\text{Zr}_5\text{-10\%CNTs} : \text{Cu}_8\text{Zn}_2\text{Zr}_5 = 72 : 69 : 66$, this sequence being in line with the sequence of turn-over frequency (TOF) of CO_2 hydrogenation over the three catalysts. This result also provided a strong support to the suggestion that the surface Cu^0 was the catalytically active Cu-species responsible for CO_2 hydrogenation.

H_2 -TPD tests of the pre-reduced catalysts revealed that the CNTs(especially Co-decorated CNTs)-containing catalysts could adsorb considerably greater amount of hydrogen than the CNTs-free substrate. The ratio of relative area-intensities of the H_2 -TPD profiles taken on the three H_2 -prereduced catalysts in the temperature region of 463 ~ 543 K was: $S_{\text{Cu}_8\text{Zn}_2\text{Zr}_5\text{-10\%(4.5\%Co/CNTs)}} : S_{\text{Cu}_8\text{Zn}_2\text{Zr}_5\text{-10\%CNTs}} : S_{\text{Cu}_8\text{Zn}_2\text{Zr}_5} = 100 : 87 : 60$. This sequence was in line with the sequence of reactivity of CO_2 hydrogenation to methanol over these catalysts.

3. Nature of the promoter action by CNTs-based additives

It was experimentally found that appropriate incorporation of a minor amount of the CNTs or the Co-decorated CNTs into the CuO-ZnO-ZrO_2 host catalyst did not cause a marked change in the apparent activation energy (E_a) for CO_2 hydrogenation to CH_3OH , implying that the addition of a minor amount of the CNTs or the Co-decorated CNTs to the CuO-ZnO-ZrO_2 did not alter the major reaction pathway of CO_2 hydrogenation to CH_3OH . It is quite evident that the considerably better performance of the CNT-containing catalysts for CO_2 hydrogenation to CH_3OH is closely related to the properties of the CNTs or the Co-decorated CNTs as promoter. The results of the present study demonstrated that the action by the CNT-based promoters (CNTs or Co-decorated CNTs) was mainly in increasing the concentration of surface-species (Cu^0) active

catalytically via affecting the chemical states of catalyst and in improving the capability of catalyst for adsorbing and activating H₂ (one of the reactants). Both the factors are in favor of increasing the reaction rate of CO₂ hydrogenation to CH₃OH.

Key words: MWCNTs; Co-decorated MWCNT-based composite material;
Cu_iZn_jZr_{k-x%}(y%Co/MWCNTs) catalysts; CO₂ hydrogenation; methanol synthesis

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厦门大学博硕士学位论文摘要库

第一章 绪 论

1.1 CO₂加氢合成甲醇

煤、石油和天然气通常被称为矿物燃料,它们是自然经过亿万年演变而形成。相对于人类的时间尺度而言是不可再生的,因此矿物燃料会由于过度使用而逐渐耗尽。自工业革命以来,煤炭成为了工业生产和人类生活主要能源,而进入 20 世纪后石油和天然气也逐渐成为主要能源。据分析,目前可获得的石油和天然气储备可能只能维持到 21 世纪末,而煤炭资源储备也仅可以供人类再使用一至两个世纪。因此,急需为未来能源寻找新的解决途径。

1.1.1 CO₂加氢合成甲醇的研究背景

近年来,人类为了更高效地利用现有的石油和天然气资源,不断的探索和研究新的可行的方法,以摆脱对煤、石油和天然气等矿物燃料的依赖。甲醇本身就是一种优秀燃料,可用于未来的内燃机或燃料电池。空气与石油和天然气截然不同,地球上每个人都可以轻易获得空气,而空气中的 CO₂ 组分属于一类取之不竭,可以循环使用的碳资源。通过利用目前可获得的矿物燃料资源以及对二氧化碳进行加氢还原来生产甲醇,意义将显得十分重大。从长远来看,对空气中的二氧化碳进行俘获和回收利用将成为可能。

甲醇也能很容易经由脱水生成乙烯和丙烯,从而转化为合成烃及它们的衍生产物,因此甲醇可以作为解决人类对正在不断减少的石油和天然气(甚至煤)资源的平台分子。此外,通过对过量排放的 CO₂ 气体的回收循环利用进行合成甲醇,可以减轻或消除温室效应的影响。

从长远来看,在 CO₂ 催化加氢合成甲醇工艺过程中,通过大规模、低成本、高收益地电解水生产氢气将是关键所在。电解水生产氢气是一种开发成熟且简单的工艺,即通过在插入某些电解质的水中的电极间通入电流来实现。目前所生产的电能大部分是从矿物燃料衍生而来的,将来为了实现可持续和合乎环境要求的大规模电解水所需的电能应该从原子能(裂变和以后如果证明在技术上和商业上可行的聚变)和包括水能、太阳能、风能、波浪能以及潮汐能的任何可再生能源资源获得^[1]。

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