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催化剂的制备研究

Study on highly active and stable catalysts for methanol/
higher alcohols synthesis from syngas

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**Study on highly active and stable
catalysts for methanol/higher alcohols
synthesis from syngas**

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摘 要.....	I
Abstract.....	III
第一章 绪论.....	1
1.1 课题研究背景及意义.....	1
1.2 合成气制低碳混合醇研究现状.....	3
1.2.1 国内外合成低碳醇工艺及对比.....	3
1.2.2 低碳混合醇反应热力学.....	5
1.2.3 催化剂体系分类.....	8
1.2.3.1 贵金属系催化剂.....	8
1.2.3.2 改性甲醇合成催化剂.....	9
1.2.3.3 Mo 基催化剂.....	10
1.2.3.4 改性 F-T 合成催化剂.....	11
1.2.4 铜钴基催化剂合成低碳醇反应机理.....	13
1.2.5 铜钴基催化剂活性相的探讨.....	15
1.3 新型高稳定性甲醇/二甲醚催化体系的研究.....	17
1.3.1 传统的基于铜基的甲醇/二甲醚催化体系.....	17
1.3.2 PdZn 催化体系.....	18
1.3.3 反应条件对甲醇/二甲醚合成反应的影响.....	19
1.4 本文选题依据及研究内容.....	21
参 考 文 献.....	23
第二章 实验部分.....	31
2.1 实验原料与仪器.....	31
2.1.1 实验试剂与气体.....	31
2.1.2 实验仪器.....	32
2.2 催化剂的制备.....	32

2.2.1 浸渍法制备 CuCo/Mo-SBA-15 催化剂.....	32
2.2.1.1 载体短孔道 SBA-15 的制备.....	32
2.2.1.2 两步浸渍法制备 CuCo/Mo-SBA-15 催化剂.....	33
2.2.2 水热法制备 CuCo ₂ O ₄ 尖晶石相催化剂.....	33
2.3 催化剂的活性评价.....	34
2.3.1 催化剂评价装置.....	34
2.3.2 产物分析与计算.....	35
2.4 催化剂表征手段.....	36
2.4.1 X 射线粉末衍射 (XRD)	36
2.4.2 X 射线荧光光谱 (XRF)	36
2.4.3 比表面积测定 (BET)	36
2.4.4 程序升温还原 (H ₂ -TPR)	37
2.4.5 扫描电镜 (SEM)	37
2.4.6 透射电镜 (TEM)	37
2.4.7 程序升温脱附 (NH ₃ -TPD)	37
参 考 文 献.....	38
第三章 助剂和制备方法对 CuCo 基催化剂性能的影响.....	39
3.1 引言.....	39
3.2 20wt%CuCo/Mo-SBA-15 催化剂性能评价.....	40
3.2.1 助剂 Mo 对催化剂性能的影响.....	40
3.2.2 助剂 Mo 对载体 SBA-15 的影响.....	40
3.2.3 不同 Co/Cu 摩尔比对催化剂性能的影响.....	42
3.2.4 不同 Co/Cu 摩尔比对催化剂结构的影响.....	43
3.2.4.1 XRD 表征结果.....	43
3.2.4.2 H ₂ -TPR 表征结果.....	44
3.3 CuCo₂O₄ 催化剂性能评价.....	45
3.3.1 不同反应温度对催化剂性能的影响.....	45
3.3.2 CuCo ₂ O ₄ 尖晶石相制备条件的探索.....	46
3.3.2.1 CuCo ₂ O ₄ 催化剂的 XRD 表征.....	46
3.3.2.2 Co/Cu 摩尔比的影响.....	48
3.3.2.3 水热温度的影响.....	48

3.3.2.4 水热时间的影响.....	49
3.3.3 还原态 CuCo_2O_4 催化剂的 XRD 图.....	50
3.3.4 CuCo_2O_4 催化剂的 H_2 -TPR 表征.....	50
3.4 本章小结.....	51
参 考 文 献.....	53
第四章 $\text{Pd}/\text{ZnAl}_2\text{O}_4$ 催化剂上 CO 加氢生成甲醇和 DME 的研究.....	54
4.1 引言.....	54
4.2 催化剂的制备.....	55
4.2.1 $\text{Pd}/\text{ZnAl}_2\text{O}_4$ 催化剂的制备.....	55
4.2.2 $\text{Pd}/\text{ZnO}/\text{Al}_2\text{O}_3$ 催化剂的制备.....	55
4.3 $\text{Pd}/\text{ZnAl}_2\text{O}_4$ 催化剂的活性评价.....	55
4.3.1 反应条件对 $\text{Pd}/\text{ZnAl}_2\text{O}_4$ 催化剂性能的影响.....	56
4.3.2 还原温度对 $\text{Pd}/\text{ZnAl}_2\text{O}_4$ 催化剂性能的影响.....	61
4.3.3 Pd 负载量对催化剂性能的影响.....	65
4.3.3.1 催化剂还原温度为 350°C 条件下.....	66
4.3.3.2 催化剂还原温度为 500°C 条件下.....	67
4.4 $\text{Pd}/\text{ZnAl}_2\text{O}_4$ 催化剂的物化性能表征.....	69
4.4.1 催化剂的物理性质表征.....	70
4.4.2 催化剂的 XRD 表征.....	71
4.4.3 催化剂的 H_2 -TPR 表征.....	74
4.4.4 催化剂的 NH_3 -TPD 表征.....	75
4.4.5 催化剂的 TEM 表征.....	76
4.5 本章小结.....	78
参 考 文 献.....	80
第五章 $\text{Pd}/\text{ZnAl}_2\text{O}_4$ 催化剂与 $\text{Pd}/\text{ZnO}/\text{Al}_2\text{O}_3$ 催化剂性能对比.....	81
5.1 引言.....	81
5.2 $2.0\text{wt}\%\text{Pd}/\text{ZnAl}_2\text{O}_4$ 与 $2.0\text{wt}\%\text{Pd}/\text{ZnO}/\text{Al}_2\text{O}_3$ 催化剂性能对比.....	81
5.2.1 催化剂还原温度为 350°C	82
5.2.2 催化剂还原温度为 500°C	83

5.3 7.5wt%Pd/ZnAl ₂ O ₄ 与 7.5wt%Pd/ZnO/Al ₂ O ₃ 催化剂性能对比.....	84
5.4 Pd/ZnAl ₂ O ₄ 与 Pd/ZnO/Al ₂ O ₃ 物性表征对比.....	85
5.4.1 两者催化剂 XRD 表征.....	85
5.4.2 两者催化剂 H ₂ -TPR 表征.....	87
5.4.3 两者催化剂 NH ₃ -TPD 表征.....	88
5.5 本章小结.....	89
参 考 文 献.....	90
第六章 结论与建议.....	91
硕士期间发表论文.....	93
致 谢.....	94

厦门大学博硕士论文摘要库

Table of Contents

Abstract in Chinese.....	I
Abstract in English.....	III
Chapter 1 Preface.....	1
1.1 Background and significance of the study.....	1
1.2 Research status of higher alcohol synthesis.....	3
1.2.1 Higher alcohols synthesis process at home and abroad.....	3
1.2.2 Thermodynamics of higher alcohols synthesis.....	5
1.2.3 Catalysts for higher alcohols synthesis.....	8
1.2.3.1 Noble metals-based catalysts.....	8
1.2.3.2 Modified methanol synthesis catalysts.....	9
1.2.3.3 Mo-based catalysts.....	10
1.2.3.4 Modified F-T synthesis catalysts.....	11
1.2.4 Reaction mechanism of higher alcohols synthesis over CuCo-based catalysts.....	13
1.2.5 Discussion of active sites over CuCo-based catalysts.....	15
1.3 Study of highly stable catalytic system of methanol/DME synthesis.....	17
1.3.1 Traditional Cu-based catalysts for methanol/DME synthesis.....	17
1.3.2 PdZn-based catalysts.....	18
1.3.3 Effect of reaction conditions on methanol/DME synthesis.....	19
1.4 Basis and study content of the thesis.....	21
References.....	23
Chapter 2 Experimental section.....	31
2.1 Reagents and Instruments.....	31
2.1.1 Reagents and gases.....	31

2.1.2 Experimental instruments.....	32
2.2 Preparation of catalysts.....	32
2.2.1 Preparation of CuCo/Mo-SBA-15 catalyst by wet impregnation.....	32
2.2.1.1 Preparation of short SBA-15 support.....	32
2.2.1.2 Preparation of 20wt%CuCo/Mo-SBA-15 catalyst by step wet impregnation.....	33
2.2.2 Preparation of CuCo ₂ O ₄ spinel catalyst by hydrothermal method.....	33
2.3 Evaluation of catalytic activity.....	34
2.3.1 Catalyst test apparatus.....	34
2.3.2 Analysis and calculation of products.....	35
2.4 Characterization of catalysts.....	36
2.4.1 X-ray powder diffraction (XRD)	36
2.4.2 X-ray fluorescence spectrum (XRF)	36
2.4.3 Surface area measurement (BET)	36
2.4.4 Temperature programmed reduction (H ₂ -TPR)	37
2.4.5 Scanning electron microscope (SEM)	37
2.4.6 Transmission electron microscope (TEM)	37
2.4.7 Temperature programmed desorption(NH ₃ -TPD).....	37
References.....	38
Chapter 3 Effect of promoter and preparation method on CuCo-based catalytic performance.....	39
3.1 Introduction.....	39
3.2 Evaluation of 20wt%CuCo/Mo-SBA-15 catalyst.....	40
3.2.1 Effect of promoter Mo on catalytic performance.....	40
3.2.2 Effect of promoter Mo on SBA-15 support.....	40
3.2.3 Effect of Co/Cu on catalytic performance.....	42
3.2.4 Effect of Co/Cu on catalyst properties.....	43
3.2.4.1 XRD measurement.....	43
3.2.4.2 H ₂ -TPR measurement.....	44
3.3 Evaluation of CuCo₂O₄ catalyst.....	45
3.3.1 Effect of reaction temperature on catalytic performance.....	45

3.3.2 Exploration of preparation condition of CuCo_2O_4	46
3.3.2.1 XRD measurement of CuCo_2O_4	46
3.3.2.2 Effect of Co/Cu molar ratio.....	48
3.3.2.3 Effect of hydrothermal temperature.....	48
3.3.2.4 Effect of hydrothermal time.....	49
3.3.3 XRD measurement of reduced catalyst.....	50
3.3.4 H_2 -TPR measurement of calcined catalyst.....	50
3.4 Summary.....	51
References.....	53
Chapter 4 Study of CO hydrogenation to methanol/DME over	
$\text{Pd/ZnAl}_2\text{O}_4$ catalyst.....	54
4.1 Introduction.....	54
4.2 Preparation of catalysts.....	55
4.2.1 Preparation of $\text{Pd/ZnAl}_2\text{O}_4$	55
4.2.2 Preparation of $\text{Pd/ZnO/Al}_2\text{O}_3$	55
4.3 Evaluation of $\text{Pd/ZnAl}_2\text{O}_4$ catalyst.....	55
4.3.1 Effect of reaction condition on $\text{Pd/ZnAl}_2\text{O}_4$ catalyst performance.....	56
4.3.2 Effect of reaction temperature on $\text{Pd/ZnAl}_2\text{O}_4$ catalyst performance....	61
4.3.3 Effect of Pd loading on catalyst performance.....	65
4.3.3.1 Reduction temperature of 350°C	66
4.3.3.2 Reduction temperature of 500°C	67
4.4 Characterization of $\text{Pd/ZnAl}_2\text{O}_4$ catalyst.....	69
4.4.1 Physical properties measurement.....	70
4.4.2 XRD measurement.....	71
4.4.3 H_2 -TPR measurement.....	74
4.4.4 NH_3 -TPD measurement.....	75
4.4.5 TEM measurement.....	76
4.5 Summary.....	78
References.....	80

Chapter 5 Performance comparison between Pd/ZnAl₂O₄ and Pd/ZnO/Al₂O₃.....	81
5.1 Introduction.....	81
5.2 Performance comparison between 2.0wt%Pd/ZnAl₂O₄ and 2.0wt%Pd/ZnO/Al₂O₃.....	81
5.2.1 Reduction temperature of 350°C	82
5.2.2 Reduction temperature of 500°C	83
5.3 Performance comparison between 7.5wt%Pd/ZnAl₂O₄ and 7.5wt%Pd/ZnO/Al₂O₃.....	84
5.4 Characterization comparison of Pd/ZnAl₂O₄ with Pd/ZnO/Al₂O₃.....	85
5.4.1 XRD measurements in comparison.....	85
5.4.2 H ₂ -TPR measurements in comparison.....	87
5.4.3 NH ₃ -TPD measurements in comparison.....	88
5.5 Summary.....	89
References.....	90
Chapter 6 Conclusions and suggests.....	91
Publication.....	93
Acknowledgements.....	94

摘要

随着对原油消耗的日益关注,发展煤基替代能源成为我国“十二五”规划能源发展的重要战略,其中煤基合成气制低碳醇醚燃料不仅可以减少我国对石油进口的依赖,还能摆脱“石油危机”。醇醚燃料包含甲醇、二甲醚和乙醇等低碳醇组分,不仅可以作为燃油的清洁替代品和添加剂,还是重要的化工原料。合成气可以由煤气化得来,目前低碳醇合成催化剂存在活性差、 C_{2+} 醇选择性低和催化剂易失活等问题,因此开发高活性、高稳定性的催化剂迫在眉睫。本文研究了两类催化剂:1) CuCo 基低碳醇合成催化剂;2) PdZn 基甲醇/二甲醚合成催化剂。本文的目的是分别对这两类催化剂构建其构效关系。

一、CuCo 基催化剂研究结果

分别采用浸渍法和水热法制备了 20wt%CuCo/Mo-SBA-15 催化剂和 $CuCo_2O_4$ 催化剂。我们考察了助剂 Mo 对 20wt%CuCo/Mo-SBA-15 催化剂性能的影响,合成 $CuCo_2O_4$ 催化剂的目的是通过还原 CuCo 尖晶石的方法得到 CuCo 密切协同、高稳定性的双功能催化体系。

实验结果表明 Mo 的引入对催化剂活性和醇类选择性有极大地促进作用。在 $230^{\circ}C$, 5.4MPa, GHSV=3750mL $g^{-1} h^{-1}$ 条件下,当引入 5wt%Mo, 20wt%Cu₁Co₂/SBA-15 催化剂的总醇选择性由 5.7%提高到 45.7%, CO 转化率由 5.5%提高到 11.2%。然而调变 Co/Cu 摩尔比则对总醇选择性几乎没影响,产物仍以甲醇为主。 $CuCo_2O_4$ 催化剂则在 ($270^{\circ}C$, 5.4MPa, GHSV=3750mL $g^{-1} h^{-1}$) 的反应条件下表现出最佳的催化性能,CO 转化率为 31.6%,总醇选择性和 C_{2+} 醇在总醇中的比例分别为 17.8%和 80%。XRD 和 H_2 -TPR 结果表明,催化剂还原过程中 Cu、Co 发生了一定的相分离,但较高的 C_{2+} 醇选择性应该是和还原态催化剂表面 Cu、Co 物种紧密相邻的共存状态有关。

二、Pd/ZnAl₂O₄ 催化剂研究结果

通过异丙醇溶剂诱导水热法和湿法浸渍制备了 Pd/ZnAl₂O₄ 催化剂,考察了反应条件、催化剂还原温度和 Pd 负载量对催化剂性能的影响,最后对比了 ZnAl₂O₄ 作为载体与 γ -Al₂O₃ 的区别。

研究发现，升高反应温度有利于提高催化剂的活性，但降低了产物甲醇和 DME 的总选择性 $S_{\text{el}}(\text{MeOH}+\text{DME})$ ；相同转换率下，随着 Pd 负载量的增加，产物甲醇和 DME 的总选择性逐渐降低，而烷烃的选择性则逐渐增加，副产物 CO_2 选择性一直保持在 10%-40% 之间。

XRD 结果表明，Pd 的负载量越低，在 ZnAl_2O_4 表面更容易形成 PdZn β 相，而高负载量的 Pd/ ZnAl_2O_4 催化剂需要更高的还原温度才能把富含 Pd 的 PdZn α 相合金转变为 PdZn β 相；另外 ZnAl_2O_4 相比 $\gamma\text{-Al}_2\text{O}_3$ ，更倾向于生成 PdZn 合金相。进一步的分析表明，PdZn α 相促进 CO 的解离得到更多的烷烃副产物，而 PdZn β 则可显著抑制烷烃的生成。NH₃-TPD 的结果表明，Pd/ ZnAl_2O_4 催化剂比 Pd/ $\text{ZnO}/\text{Al}_2\text{O}_3$ 酸性位更弱，因此减缓了甲醇的酸催化到二甲醚的反应，这也导致了两者在产物甲醇和 DME 的选择性方面的较大差异。

关键词：低碳醇；二甲醚；CuCo 催化剂； ZnAl_2O_4 ；PdZn 合金

Abstract

Along with the increased concerns on the depleting crude oils, the development of clean coal-based alternative process for fuel productions became the important strategy during National “12th five-year plan”. The low carbon alcohol-ether fuels synthesis from coal-based syngas can reduce our dependence on oil imports and break away from the “oil crisis” in the future. The low carbon alcohol ether fuels contain methanol, DME and ethanol as well other higher alcohol components, which not only can be used as the clean alternative fuel and additives, but also as the important chemical raw materials. Syngas can be readily obtained from coal gasification. The current catalysts for higher alcohols synthesis from syngas have the problems of low activity and poor selectivity for C_{2+} alcohols as well as catalyst deactivation. Therefore development of highly active and stable catalysts is highly desired. In this work, two classes of catalysts were studied: 1) Cu-Co catalysts for higher alcohols synthesis; and 2) PdZn catalysts for methanol/DME synthesis. We attempted to establish the structure-activity relationship of these two classes of catalysts.

一、Research results for CuCo-based catalysts

A wet impregnation and a hydrothermal method were used to prepare 20wt%CuCo/Mo-SBA-15 and $CuCo_2O_4$ catalysts respectively. The influence of promoter Mo on the catalytic performance of 20wt%CuCo/Mo-SBA-15 catalyst over CO hydrogenation was studied. The purpose of synthesizing $CuCo_2O_4$ catalyst is to obtain a CuCo bifunctional system containing strong synergistic effect with high stability through reducing $CuCo_2O_4$ spinel. The main conclusions are summarized as follows:

It was experimentally demonstrated that the addition of Mo has significant effect on the reactivity and selectivity of alcohols. After introducing 5wt% Mo, over the 20wt% Cu_1Co_2 /SBA-15 catalyst under 503K, 5.4MPa, GHSV=3750mL $g^{-1} h^{-1}$, the CO conversion increases from 5.5% to 11.2%, the selectivity of total alcohols increases

from 5.7% to 45.7%. While the Co/Cu molar ratio has no significant influence on the selectivity of total alcohols, methanol is still the major product in alcohols. For the CuCo_2O_4 catalyst, it was experimentally confirmed that under the optimum reaction conditions (543K, 5.4MPa, GHSV=3750mL g⁻¹ h⁻¹), catalyst exhibits CO conversion of 31.6% with the selectivity to total alcohols and the proportion of C₂₊ alcohols in total alcohols of 17.8%、80% respectively. The results of XRD and H₂-TPR revealed that Cu and Co phase segregation occurs to some extent during the catalyst reduction process. The higher C₂₊ alcohols selectivity may be associated with the coexist of Cu species and Co species on the surface of reduced catalyst.

二、 Research results for Pd/ZnAl₂O₄ catalysts

Pd/ZnAl₂O₄ catalysts were synthesized by isopropanol-mediated controlled hydrolysis method and wet impregnation method. The influence of reaction condition、reduction temperature of catalyst and the loading of Pd on the CO hydrogenation was studied. The difference between ZnAl₂O₄ and γ -Al₂O₃ as support for PdZn-based catalysts was conducted.

Higher reaction temperature was found to favor the activity of catalyst, but also reduce the total selectivity of methanol and DME(Sel(MeOH+DME)). Under the conditions that all the catalysts have similar CO conversion, the Sel(MeOH+DME) gradually decreases with increasing Pd loading, while the selectivity of alkane gradually increases, meanwhile the CO₂ selectivity remains between 10% to 40%.

The XRD characterizations of reduced catalysts indicate that PdZn β phase formation on surface of ZnAl₂O₄ support is facile at a low Pd loading, while for the catalysts containing higher Pd loadings, the Pd-rich PdZn α phase can be transformed to PdZn β phase under higher reduction temperature. ZnAl₂O₄ is superior to γ -Al₂O₃ as a support with respect to the formation of PdZn alloy. Further analysis showed that PdZn α phase can facilitate the dissociation of CO to form more alkane byproducts, while PdZn β phase suppresses the formation of alkane. NH₃-TPD studies suggest that compared to Pd/ZnO/Al₂O₃ catalyst, Pd/ZnAl₂O₄ has weaker acid sites over reduced catalyst, which reduces the rate of MTD reaction (methanol to DME) over acid sites, leading to the different selectivity to methanol and DME.

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