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碳载钯基催化剂的合成及相关  
氢化反应的应用研究

Synthesis of carbon supported Pd-based catalyst and  
the application in hydrogenation

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**Synthesis of carbon supported Pd-based catalyst and the  
application in hydrogenation**

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## 摘要

氢化反应作为化工产业的主要反应之一，通过合成高性能的催化剂来提高氢化反应的选择性一直以来都是科学家们研究的重点内容。碳载钯基催化剂是工业上进行氢化反应所使用最广泛的催化剂，特别是在精细化工领域。因此必要对高活性、高选择性、高稳定性的碳载钯基催化剂进行研究，使其能够应用于精细化工中的催化氢化工艺。

本论文的工作集中在制备有工业应用价值的碳载钯基催化剂，考察了其在多种实用氢化反应中的催化性能，并研究了间硝基苯胺的催化加氢合成工艺，具体内容如下：

第一章：概述了芳胺类中间体的合成工艺，选择性氢化的重要性，提高催化剂选择性的策略以及工业上氯化亚锡的回收工艺，最后阐述了本论文的选题依据和研究内容。

第二章：以  $\text{CO}$ 、 $\text{H}_2\text{O}$  混合气作为还原剂在不同条件下合成了  $\text{Pd/C}$  催化剂，并以苯乙烯的氢化为探针反应，考察催化剂在氢化反应中的催化性能，筛选出了最优的  $\text{Pd/C}$  催化剂制备条件，还将所制备的  $\text{Pd/C}$  催化剂成功应用于催化加氢回收氯化亚锡的工艺中，并表现出优异的催化性能。

第三章：将  $\text{Ru}$  引入到  $\text{Pd/C}$  催化剂中制备了  $\text{Pd-Ru}$  双金属催化剂。通过共沉淀法合成出不同负载量和不同钯钌摩尔比的双金属催化剂，并研究了其在硝基苯和邻硝基苯胺氢化过程中的催化性能，结果表明  $\text{Pd}$  负载量为 1%， $\text{Ru}$  负载量为 4% 时催化剂对硝基的氢化表现出最优的催化效果，性能远远高于商用的  $\text{Pd/C}$  催化剂。另外， $\text{Pd}_1\text{Ru}_4/\text{C}$  催化剂在氢化松香的合成中也有良好的催化性能。

第四章：发展了一种间二硝基苯选择性氢化合成间硝基苯胺的工艺路线，通过选用合适的催化剂、催化助剂以及合理的终点控制，使间硝基苯胺产品的收率达到了 90% 以上，优于传统的硫化碱还原工艺。这一结果为工业上间硝基苯胺绿色合成工艺的开发带来了新的机遇。

第五章：对本论文的研究工作进行了总结，并在碳载钯基催化剂的机理和应用拓展等方面提出了展望。

关键词：Pd/C 催化剂；钯钌双金属催化剂；选择性氢化；间硝基苯胺

厦门大学博硕士学位论文摘要库

## Abstract

Hydrogenations are one of the pillars of the chemical industry. Synthesis of high performance catalysts to improve the selectivity of the hydrogenation reaction has always been the core content of scientists' research. Carbon supported Pd-based catalysts are the most widely used catalysts in industrial hydrogenations, especially in the field of fine chemicals. Therefore, it is necessary to study the carbon supported Pd-based catalysts with high activity, selectivity and stability for fine chemical industrial application.

This work focuses on the preparation of carbon-supported palladium-based catalysts which can be applied in industry, and the catalytic performance in varieties practical hydrogenation reactions. In addition, the synthesis process of m-nitroaniline by catalytic hydrogenation was studied.

Main research findings have been summarized as following:

Chapter 1: Summarized the synthesis process of aromatic amine intermediates and the importance of selective hydrogenation. Strategies of improving hydrogenation selectivity and the recovery process of stannous chloride in industry were also introduced. The meanings and content of this thesis were listed.

Chapter 2: CO and H<sub>2</sub>O are used as reductant to synthesize Pd/C catalyst under different conditions. And the performance of the catalysts in the hydrogenation reaction were investigated by the hydrogenation of styrene as the probe. The optimum preparation condition of Pd/C was screened out and the prepared Pd/C catalyst was successfully applied into the recovery process of stannous chloride by catalytic hydrogenation.

Chapter 3: A bimetallic catalyst was prepared by introducing Ru into Pd/C catalyst. The bimetallic catalysts with different loading and different molar ratios of palladium and ruthenium were synthesized by coprecipitation method, and their

catalytic performance in hydrogenation of nitrobenzene and o-nitroaniline was studied. The result showed that the catalyst with 1% Pd loading and 4% Ru loading has favorable performance in the hydrogenation of nitro group, which was superior to commercial Pd/C catalysts. In addition, the prepared Pd<sub>1</sub>Ru<sub>4</sub>/C catalyst also has a good performance in the synthesis of hydrogenated rosin.

Chapter 4: A process route for the preparation of m-nitroaniline by selective hydrogenation of m-dinitrobenzene was developed. The yield of m-nitroaniline products reached more than 90% through controlling the end point of reaction and selecting the appropriate catalyst and catalytic additives, was superior to traditional synthesis process. This result brings new opportunities for the industrial green synthesis processes of m-nitroaniline.

Chapter 5: Conclusions and prospects of the mechanism and application of carbon-supported palladium-based catalysts are given.

Keywords: Pd/C catalyst; Pd-Ru bimetallic catalyst; Selective hydrogenation ; M-nitroaniline



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