

铂钯纳米催化剂界面反应的理论研究

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厦门大学博硕士学位论文摘要库

学校编码: 10384

分类号\_\_\_\_\_密级\_

学号: 20520130153882

UDC \_\_\_\_\_

厦 门 大 学

博 士 学 位 论 文

铂钯纳米催化剂表界面反应的理论研究

Mechanisms for the Surface and Interface Reactions On the

Pt and Pd Based Nanocatalysts: A Theoretical Study

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专业名称: 物理化学

论文提交日期: 2016 年 月

论文答辩日期: 2016 年 月

学位授予日期: 2016 年 月

答辩委员会主席: \_\_\_\_\_

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2016 年 月



**Mechanisms for the Surface and Interface Reactions On the Pt  
and Pd Based Nanocatalysts: A Theoretical Study**

A Dissertation Submitted to the Graduate School in Partial Fulfillment of  
the Requirements for the Degree of Doctor Philosophy

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August, 2016

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中文摘要 .....	I
英文摘要 .....	III
第一章 绪论 .....	1
§1.1  贵金属纳米催化剂表面-概述 .....	1
§1.2  影响贵金属纳米材料性能的主要因素 .....	2
§1.2.1  尺寸效应 .....	2
§1.2.2  形貌效应 .....	4
§1.2.3  界面效应 .....	6
§1.2.3.1  贵金属-金属氧化物界面效应 .....	7
§1.2.3.2  贵金属-配体界面效应 .....	11
§1.2.3.3  界面最大化-单原子催化剂 .....	15
§1.3  反应机理的研究 .....	21
§1.3.1  氢化反应的机理探讨 .....	21
§1.3.1.1  氢和碳无机物修饰 .....	22
§1.3.1.2  胺和醇的配体修饰 .....	24
§1.3.1.3  手性配体修饰 .....	26
§1.3.2  CO氧化的机理研究 .....	27
§1.3.2.1  配位数的影响 .....	27
§1.3.2.2  载体效应的影响 .....	28
§1.3.2.3  金属价态的影响 .....	29
§1.3.2.4  反应气氛的影响 .....	30
§1.4  本论文的选题依据和研究内容 .....	32
§1.5  参考文献 .....	33
第二章 C=C 键催化氢化的晶面效应 .....	47
§2.1  引言 .....	47
§2.2  计算方法和模型 .....	48
§2.3  实验结果与讨论 .....	49
§2.3.1  Pd 纳米颗粒不同形貌的调控及其选择性氢化反应的研究 .....	49
§2.3.2  反式二苯乙烯和苯乙烯在 Pd(111)表面的吸附 .....	51
§2.3.3  反式二苯乙烯和苯乙烯在 Pd(100)表面的吸附 .....	53
§2.3.4  反式二苯乙烯加氢反应的机理研究 .....	54
§2.3.5  苯乙烯加氢反应的机理研究 .....	56
§2.4  本章小结 .....	57
§2.5  参考文献 .....	57
第三章 Fe(III)-OH-Pt 界面催化氧化 CO 的理论研究 .....	62
§3.1  引言 .....	62
§3.2  计算方法和模型 .....	63

§3.2.1	计算方法	63
§3.2.2	模型选取	64
§3.3	结果与讨论	68
§3.3.1	Pt/Fe(OH) <sub>x</sub> 纳米复合材料的制备、表征和催化性能	68
§3.3.2	CO 与 O <sub>2</sub> 在 Fe(OH) <sub>x</sub> /Pt 界面上的竞争吸附	69
§3.3.3	界面上第一个 CO 的氧化	73
§3.3.4	CO 与 O <sub>2</sub> 在界面氧空位上的竞争吸附	76
§3.3.5	界面上第二个 CO 的氧化	77
§3.4	本章小结	79
§3.5	参考文献	80
第四章	单原子分散钯催化剂及其氢化反应中的机理研究	85
§4.1	引言	85
§4.2	计算方法和模型	86
§4.3	实验结果与讨论	88
§4.3.1	Pd <sub>1</sub> /TiO <sub>2</sub> 单原子催化剂的制备及其催化性能研究	88
§4.3.2	乙二醇调控 TiO <sub>2</sub> (B) 的厚度	90
§4.3.3	探索单原子催化剂 Pd <sub>1</sub> /TiO <sub>2</sub> 的形成过程	93
§4.3.4	苯乙烯在 Pd <sub>1</sub> /TiO <sub>2</sub> 催化剂上加氢反应的机理研究	99
§4.3.4	苯甲醛在 Pd <sub>1</sub> /TiO <sub>2</sub> 催化剂上加氢反应的机理研究	103
§4.4	本章小结	106
§4.5	参考文献	107
第五章	单原子分散钯催化剂催化 CO 氧化的理论研究	112
§5.1	引言	112
§5.2	计算方法和模型	113
§5.3	实验结果与讨论	114
§5.3.1	Pd <sub>1</sub> /TiO <sub>2</sub> -c 催化剂催化 CO 氧化的反应性能研究	114
§5.3.2	Pd <sub>1</sub> /TiO <sub>2</sub> -c 催化剂催化 CO 氧化	115
§5.3.2.1	CO 与 O <sub>2</sub> 的吸附研究	115
§5.3.2.2	CO 氧化机理的研究	117
§5.4	本章小结	119
§5.5	参考文献	120
第六章	结论与展望	125
附录	博士期间取得的科研成果	128
	致谢	130

## Table of Contents

Abstract (Chinese) .....	I
Abstract (English) .....	III
Chapter 1 Introduction .....	1
§1.1 Surface and Interface of noble-metal nanocatalysts: Introduction .....	1
§1.2 Factors affecting the catalytic activity of noble-metal nanocatalysts .....	2
§1.2.1 Effect of size .....	2
§1.2.2 Effect of shape .....	4
§1.2.3 Effect of interface .....	6
§1.2.3.1 Metal-metal oxide interfacial effect .....	7
§1.2.3.2 Metal-ligand interfacial effect .....	11
§1.2.3.3 Atomically dispersed catalysts .....	15
§1.3 Mechanisms of common reactions .....	21
§1.3.1 Mechanism of hydrogenation reactions .....	21
§1.3.1.1 H and C coverage effect .....	22
§1.3.1.3 Thioalcohol and amine modification .....	24
§1.3.2.3 Chiral molecule modification .....	26
§1.3.2 Mechanism of CO oxidation .....	27
§1.3.2.1 The effect of coordination number .....	27
§1.3.3.3 The effect of support .....	28
§1.3.2.3 The effect of metallic valance .....	29
§1.3.2.4 The effect of reaction gases .....	30
§1.4 Objectives and contents of this thesis .....	32
§1.5 References .....	33
Chapter 2 Origin of the facet dependence in the hydrogenation catalysis of olefins .....	47
§2.1 Introduction .....	47
§2.2 Computational methods and models .....	48
§2.3 Results and discussion .....	49
§2.3.1 Shape-controlled Pd nanocrystals and their catalytic property .....	49
§2.3.2 Trans-stilbene and styrene adsorption on Pd{111} surfaces .....	51
§2.3.3 Trans-stilbene and styrene adsorption on Pd{100} surfaces .....	53
§2.3.4 The reaction mechanism of the trans-stilbene hydrogenation .....	54
§2.3.5 The reaction mechanism of the styrene hydrogenation .....	56
§2.4 Summary .....	57
§2.5 References .....	57



<b>Chapter 3 Mechanisms for CO oxidation on Fe(III)–OH–Pt interface</b>	<b>62</b>
§3.1 Introduction	62
§3.2 Computational methods and models	63
§3.2.1 Computational methods	63
§3.2.2 Computational models	64
§3.3 Results and discussion	68
§3.3.1 Synthesis and Characterization of Pt-Fe(III)(OH) <sub>x</sub> Interfaces and Catalytic Performance Study	68
§3.3.2 Competitive adsorption of CO and O <sub>2</sub> on Fe(OH) <sub>x</sub> /Pt interfaces	69
§3.3.3 The first CO oxidation on Fe(OH) <sub>x</sub> /Pt interfaces	73
§3.3.4 Competitive adsorption of CO and O <sub>2</sub> on Fe–□–Pt	76
§3.3.5 Mechanism of the second CO oxidation	77
§3.4 Summary	79
§3.5 References	80
<b>Chapter 4 atomically dispersed palladium–titanium oxide catalyst in hydrogenation C=C and C=O</b>	<b>85</b>
§4.1 Introduction	85
§4.2 Computational methods and models	86
§4.3 Results and discussion	88
§4.3.1 Synthesis atomically dispersed Pd catalyst (Pd <sub>1</sub> /TiO <sub>2</sub> ) and their catalytic property	88
§4.3.2 The thickness of TiO <sub>2</sub> (B)-EG	90
§4.3.3 The stepwise preparation mechanism of Pd <sub>1</sub> /TiO <sub>2</sub>	93
§4.3.4 The mechanism of the styrene hydrogenation	99
§4.3.5 The mechanism of the benzaldehyde hydrogenation	103
§4.4 Summary	106
§4.5 References	107
<b>Chapter 5 Mechanisms for CO oxidation on Pd<sub>1</sub>/TiO<sub>2</sub> catalyst</b>	<b>112</b>
§5.1 Introduction	112
§5.2 Computational methods and models	113
§5.3 Results and discussion	114
§5.3.1 Preparation and characterization of Pd <sub>1</sub> /TiO <sub>2</sub> -c and their catalytic performance	114
§ 5.3.3 CO oxidation on Pd <sub>1</sub> /TiO <sub>2</sub> -c catalyst	115
§ 5.3.3.1 Adsorption of CO and O <sub>2</sub> on Pd <sub>1</sub> /TiO <sub>2</sub> -c catalysts	115
§ 5.3.3.2 Mechanism of the CO oxidation	117

§5.4	Summary .....	119
§5.5	References .....	120
Chapter 6	summary and Outlook .....	125
	Publications of Ph.D. Study.....	128
	Acknowledgements .....	130

厦门大学博硕士论文摘要库

## 摘要

贵金属催化剂被广泛应用于能源、环保、食品加工等重要化工领域。各种尺寸可控、形貌可控和组成可控的纳米催化材料的成功合成为研究催化反应的构效关系提供了丰富的素材。研究纳米材料的形貌调控，探明纳米材料的尺度、表面微观结构与催化活性和选择性之间的关联是当前催化研究中最活跃也最具挑战的方向之一。

本论文主要从三个方向进行研究：1) 研究 Pd 低米勒指数面在催化加氢反应中的晶面效应；2) 考察了 Pt-Fe(OH)<sub>x</sub> 界面催化氧化 CO 的反应机理。3) 探讨了单原子分散 Pd<sub>1</sub>/TiO<sub>2</sub> 催化剂的形成机理及其催化加氢和 CO 氧化的过程。全文共分为五章，各章内容概括如下：

第一章，阐述了纳米催化剂中的表界面结构及其在催化加氢和 CO 氧化反应机理中的重要作用，提出了本文的选题依据。

第二章，贵金属钯暴露不同的晶面，催化加氢的反应活性不同。应用密度泛函理论(DFT)考察了不同氢覆盖度下钯表面对 C=C 的吸附反应行为。研究表明，当表面氢为饱和覆盖 ( $\theta_H=1.0$  ML)时，反式二苯乙烯在(111)表面的吸附不稳定，而在(100)表面上弱吸附；苯乙烯在两个表面都能稳定吸附。进一步研究了它们的催化加氢机理，C=C 加氢反应遵循 H-P 反应机理，即分步加氢机理。比较了第一步加氢 Langmuir-Hinshelwood(L-H)和 Eley-Rideal(E-R)机理，发现动力学上更有利的是 E-R 加氢机理；同时发现导致(111)和(100)反应活性的差别可能来源于半氢化中间体(SHI)的稳定性及第二步加氢反应。计算结果表明位阻更小的苯乙烯将有助于 SHI 的稳定，从而有利于整个加氢过程。另一方面，位阻较大的烯烃即反式二苯乙烯，在原子排列紧密(111)面上形成不稳定的 SHI，导致第二步的加氢能垒太高而难以进一步氢化。

第三章，实验表明，Pt 纳米立方块上沉积亚单层的 Fe(OH)<sub>x</sub> 可实现室温下 CO 的 100% 氧化。理论计算结果表明，不同于其它界面的 Fe(II)一开始就活化 O<sub>2</sub> 的反应方式，Fe(III)-OH-Pt 界面并不能活化 O<sub>2</sub>，CO 的吸附依然强于 O<sub>2</sub>；CO 与高活性的界面 OH 耦合形成 CO<sub>2</sub>，脱附后在界面上原位产生的 Fe-□-Pt 负责吸附并活化 O<sub>2</sub>。采用高指数 Pt(332)和 Pt(322)晶面来模拟 Pt 真实纳米催化剂的台阶位，并与 Pt(111)表面进行对比。计算结果表明，CO 的氧化是结构敏感的反应，载体不同暴露面的反应活性很大程度上取决于 Fe-OH 键的作用强度。当 Fe(OH)<sub>x</sub>/Pt(111)界面形成氧空位时，CO 仍抑制 O<sub>2</sub> 的吸附和活化，但 Fe(OH)<sub>x</sub>/Pt(332)和

Pt(322)界面可有效地活化  $O_2$ ，从而增强 CO 低温氧化的活性。研究反应机理时，发现吸附态的  $H_2O$  在氧化过程中扮演着重要的角色，既可通过形成-OOH 来稳定  $O_2$  的吸附，又可促进对 O-O 键的活化。解释了反应一段时间，撤掉水蒸气活性明显降低，补充水蒸汽反应活性又回到 100% 的实验现象。

第四章，应用光化学辅助的方法制备了钯负载量高达 1.5% 的单原子分散  $Pd_1/TiO_2$  催化剂。通过理论计算首次探讨了单原子分散钯催化剂的形成机理。光照可使电子空穴发生分离，电子将  $Ti^{4+}$  还原成  $Ti^{3+}$ ，乙二醇基在空穴的作用下氧化成自由基，从而高效脱除钯( $PdCl_2$ )上的第一个氯，与表面氧形成更多的 Pd-O 键来锚定钯，形成  $PdCl_1/TiO_2$ 。 $H_2$  在  $PdCl_1/TiO_2$  界面上吸附并活化，以 HCl 的形式脱除第二个氯，形成独特的 Pd-乙二醇- $TiO_2$  界面。然后研究了单原子分散钯催化剂能高效催化氢化 C=C 和 C=O 的反应机理， $H_2$  在界面上通过异裂的方式解离，形成  $Pd-H^\delta$  和  $O-H^\delta$  物种；比较了两条可能的加氢路径，能垒较低的路径是  $H^\delta$  先进攻苯乙烯上的端基碳，然后  $H^\delta$  加到苯乙烯的中间碳，O-H 上的质子转移是决速步， $CH_3OD$  同位素交换实验证明了分步加氢反应路径的合理性。对于极性不饱和键加氢，如苯甲醛，反应机理是协同加氢，所要克服的反应能垒只有 0.27 eV。

第五章，单原子催化剂对 CO 氧化是否有活性仍存在争议，理论计算发现  $O_2$  在单原子分散钯催化剂的 Pd-Ti 处形成了 Pd-O-O-Ti 超氧物种；可低温催化 CO 氧化，反应遵循 L-H 机理，即 CO 吸附在钯上， $O_2$  以 Pd-O-O-Ti 的桥式吸附，第一个 CO 氧化可直接形成  $CO_2$ ，反应能垒为 0.77 eV，第二个 CO 与反应后形成的 Pd-O-Ti 容易发生氧化反应，所克服的能垒仅为 0.28 eV。与传统钯催化剂不同的是，载体上  $Ti^{3+}$  与单原子钯形成的界面对 CO 氧化至关重要，所形成的 Pd-O-O-Ti 特殊界面是催化氧化 CO 的活性中心。

**关键词：**催化氢化；CO 氧化；单原子分散催化剂；DFT 计算

## Abstract

Noble metal nanocatalysts are of vital importance in many fields of chemical, food, energy and environmental industry. The development of nanoscience in recent years demonstrated that the catalytic activity and selectivity of noble metal nanocatalyst is strongly dependent on controlled synthesis of noble metal nanocrystals with a specific size, shape and composition. It was very important to gain deeper understanding of structure-activity mechanism on the surfaces in catalysis at the atomic scale. Based the well-defined nanostructures, how to enhance the utilization of noble metal while keeping the catalyst performing efficiently, selectively and stably is the core issues in the development of noble metal catalysts.

In this thesis, following projects will be studied and discussed in detail: 1) Well-defined Pd nanoparticles for the study the facet dependence in the hydrogenation catalysis of olefins; 2) Mechanisms for CO oxidation on Pt-Fe(OH)<sub>x</sub> interfaces was studied by using periodic density functional calculations.; 3) The formation mechanism of atomically dispersed palladium–titanium oxide catalyst was investigated by theoretical calculation. And hydrogenation mechanisms of C=C and C=O and CO oxidation was explored. This will be divided into five chapters, with the main research results summarized as follows:

**Chapter 1.** Briefly review on the surface and interfacial structure and catalytic performance on hydrogenation and CO oxidation in catalysis. My research signigance and research project during the Ph. D. period are also demonstrated.

**Chapter 2.** Different exposed facets have various atom arrangements, resulting in different adsorption and activation energies for various substrates. Our calculations revealed that under hydrogen pre-saturated condition, Pd(111) facets exhibit no activity for trans-stilbene with the  $\pi$  bonded mode, while Pd(100) facets show high activity for trans-stilbene. The hydrogenation of C=C bond still follows the stepwise mechanism, i.e. Horiuti-Polanyi mechanism. For the first hydrogenation step, the E-R type mechanism preferentially occurs such that both facets exhibit similar barriers towards a given substrate. The difference in reactivity between {111} and {100} might originate from the stability of SHI and its subsequent hydrogenation. A more open surface as well as the olefin with a smaller steric hindrance would help to stabilize SHI, thus facilitating the

whole hydrogenation. On the other hand, the bulky olefin, i.e. trans-stilbene, forms unstable SHI over the compact {111} facet so that the barrier of the second hydrogenation becomes hard to be conquered.

**Chapter 3.** The sub-5 nm iron hydroxide-platinum hybrid nanoparticles are highly efficient for CO oxidation. Our calculations show that The Fe(III)-OH-Pt interfaces are preferentially occupied by CO, inhibiting the activation of O<sub>2</sub>. CO oxidation could begin with the coupling between CO and OH. This indicates that OH present in Fe(III)-OH-Pt is active and liable to oxidizing CO into CO<sub>2</sub>. The created interfacial vacancies Fe-□-Pt favor the adsorption and activation of O<sub>2</sub> and exhibit low activity for CO oxidation under room temperature. CO oxidation is found to be a structure sensitive reaction. A weak Fe(III)-OH bond at the Fe(OH)<sub>x</sub>/Pt(111) interface results in a high activity towards the CO + OH reaction; however, it renders the interfacial vacancy preferentially occupied by CO, inhibiting the activation of O<sub>2</sub>. On the other hand, Fe(OH)<sub>x</sub> together with the Pt(332) or (322) is able to effectively activate both CO and O<sub>2</sub>, thus enhancing the low-temperature reactivity of CO oxidation. The roles that the adsorbed water plays in adsorption and activation of O<sub>2</sub> have been considered. On one hand, it can stabilize O<sub>2</sub> adsorption by forming OOH species; on the other hand, the O-O bond breaking can be facilitated by the coexistence of water.

**Chapter 4.** Atomically dispersed Pd catalyst (Pd<sub>1</sub>/TiO<sub>2</sub>) on ultrathin TiO<sub>2</sub> nanosheets with Pd loading up to 1.5% were fabricated with a room-temperature photochemical strategy. The formation mechanism of atomically dispersed palladium-titanium oxide catalyst was first investigated by theoretical calculation. Once exposed to UV, electron-hole pairs were generated on TiO<sub>2</sub>(B) nanosheets. Electrons were trapped in Ti-3d orbitals to form Ti<sup>3+</sup> sites, and holes broke Ti-O bonds between glycolate and TiO<sub>2</sub>, leading to the formation of -OCH<sub>2</sub>CH<sub>2</sub>O• radicals. the OH group in -OCH<sub>2</sub>•CHOH attacked its nearby Pd site by replacing one Cl<sup>-</sup>, leading to the formation of PdCl<sub>1</sub>/TiO<sub>2</sub> intermediate, The remaining Cl<sup>-</sup> on PdCl<sub>1</sub>/TiO<sub>2</sub> could be easily removed by using H<sub>2</sub> treatment, giving rise to H<sup>+</sup> and Cl<sup>-</sup>. Different from homolytic dissociation to H atoms, Pd<sub>1</sub>/TiO<sub>2</sub> activate H<sub>2</sub> in a heterolytic way. One of the H atoms moved to nearby oxygen on EG to yield O-H<sup>δ+</sup>, leaving the other H atom with Pd as Pd-H<sup>δ-</sup>. Two possible pathways beginning with either H<sup>δ-</sup> or H<sup>δ+</sup> transfer were considered. The favorable pathway beginning with H<sup>δ-</sup> transfer from Pd to C=C, only 0.47 eV barrier was required for the H<sup>δ-</sup> transfer from Pd to the terminal CH<sub>2</sub> to make the half-

hydrogenated intermediate. Then the half-hydrogenated intermediate added  $H^{\delta+}$  from nearby O-H group. Isotopic experiments were conducted to prove the mechanism. Due to the unique  $H_2$  activation pathway,  $Pd_1/TiO_2$  also performed well in the catalytic hydrogenation of aldehydes.

**Chapter 5.** Whether atomically dispersed catalysts are active or not in CO oxidation is still a debate. It may be critical to expose  $Ti^{3+}$  sites adjacent to Pd atoms. The Ti-Pd site prefers to bond to  $O_2$  over CO. Electron transfer reaction between  $Ti^{3+}$  and  $O_2$  formed superoxide ions ( $O_2^-$ ), CO then bonds with the  $O_2^-$  species and forms  $CO_2$  by overcoming a barrier of 0.77 eV, leaving an oxygen atom on  $Ti^{3+}$ -Pd site. This occur via a Langmuir–Hinshelwood scheme (L–H scheme). The second CO easily reacts with the resulting Ti-O-Pd, with a small activation barrier of 0.28 eV.

**Key words:** Catalytic hydrogenation; CO oxidation; Atomically dispersed catalysts; Density functional theory calculation

# 第一章 绪论

## § 1.1 贵金属纳米催化剂的表界面-概述

随着纳米科技的发展,纳米材料在石油化工、精细化工合成、能源与环境保护和生物学等领域的应用中已有举足轻重的地位。纳米材料(nanomaterials)是尺寸至少在一个维度上位于 1~100 nm 之间或以它们为基本单元所构成的材料。它处在原子簇和宏观尺寸材料的过渡区域,使它具有与宏观材料所迥异的特殊效应,如小尺寸效应、表面与界面效应、量子尺寸效应、宏观量子隧道效应和介电限域效应。

周期表中,目前只有八种金属可称为贵金属,分别是金(Au)、铂(Pt)、银(Ag)、钌(Ru)、锇(Os)、铑(Rh)、铱(Ir)、钯(Pd),是有色金属的重要组成部分。当贵金属达到纳米尺寸(直径)时,在电化学、选择性加氢、催化氧化等方面均表现出优异的特性<sup>1</sup>。如金纳米颗粒会产生表面等离子体共振和对多种反应底物均表现出催化活性和选择性,如不饱和烃类选择性氢化、水煤气反应(WGS)、富氢气氛下一氧化碳选择氧化(PROX)和醇的液相氧化以及精细化工中的反应<sup>2-10</sup>;铂纳米颗粒是优异的燃料电池催化剂,电催化氧化<sup>11-15</sup>;钯纳米颗粒在直接甲酸燃料电池中的应用以及是优异的选择性加氢催化剂<sup>16-22</sup>。由此可见,贵金属纳米催化剂在催化和实际生产应用中的优异性<sup>23</sup>。

贵金属纳米催化剂一般以固体的形式存在,如何定义表界面?物理化学教材上,界面是相与相之间的交界面,两相接触的约几个原子或分子厚度的过渡区域。如贵金属表面修饰有机分子形成金属-有机界面、贵金属与金属氧化物形成金属-氧化物界面和与其他金属形成金属-金属界面等。当界面两相中有一相是气相,此时的界面也即为表面。如裸露的二维超薄纳米片、超细线和贵金属立方块与气相反应物作用时,与气相吸附和反应的场所就是表面。

表面等离子共振、催化、分子识别、电荷转移以及其他化学反应过程都是发生在催化剂的表面和界面;工业生产如石油裂化、费托合成和合成氨等<sup>21</sup>,也是在多相催化剂的表界面发生。综上所述,纳米材料的催化性质明显地依赖对表面(尺寸、形貌、组成和晶相)和界面结构。对贵金属纳米材料的控制合成是调控其物理和化学性质的主要手段,下面主要就贵金属纳米晶体尺寸、形貌和界面三方



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