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博士学位论文

高分散、抗烧结、粒径可控 Pd/SiO_2 催化剂的浸渍法制备及其制备机理和催化性能研究

Studies on the Well-dispersed, Sinter-resistant and Size-controlled Pd/SiO_2 Catalysts Prepared by Impregnation Method

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Studies on the Formation Mechanism and Catalytic Performance of Well-dispersed and Sinter-resistant Pd/SiO_2 Catalysts Prepared by Impregnation Method

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摘 要

本文的主要目的是探索一种通过简单的浸渍步骤制备高分散、抗烧结且粒径可控Pd/SiO_2催化剂的方法，并对催化剂的制备机理进行考察，为研制粒径可控且具有良好抗高温烧结性能的负载型纳米金属催化剂提供科学基础。

在论文的第一部分工作中，通过浸渍法制备了一系列以不同 Pd 化合物（$PdCl_2$，$(NH_4)_2PdCl_4$，$Pd(NO_3)_2$，$(NH_3)_4Pd(NO_3)_2$，$Pd(OAc)_2$和$Pd(acac)_2$）为前驱体的 Pd/SiO_2 催化剂。采用 BET、XRD、O_2和 CO 化学吸附、TEM 等实验技术对相关催化剂进行了表征，并采用原位 XRD、原位 Raman 光谱以及 TPD-MS 等实验技术对不同Pd前驱体制备的催化剂在空气及H_2/Ar和Ar气氛中的焙烧分解过程进行了在线跟踪。实验结果表明：以乙酰丙酮钯[$Pd(acac)_2$]为前驱体制备的 Pd/SiO_2 催化剂经空气中 800 ^oC 焙烧和 H_2 中 600 °C 还原后，Pd 的平均粒径仍可保持在~ 3 nm。这是因为硅胶（SiO_2）载体表面羟基上的H^+可与$Pd(acac)_2$的$acac^-$反应，生成高度分散于 SiO_2 表面的$(O_s)_2Pd$物种。在空气中升温至~ 200 °C 时，伴随着乙酰丙酮配体的氧化，$(O_s)_2Pd$ 物种被快速还原成高分散的金属 Pd 纳米粒子，这些步骤是保证 SiO_2 上负载的 Pd 物种具有良好的抗烧结性能的关键。进一步的研究表明，只要载体表面能提供足够多的羟基，均可保证最终制备的Pd/SiO_2上 Pd 的平均粒径（~ 3 nm）基本不随其负载量（0.5 ~ 5 wt%）和焙烧温度（200 ~ 800 °C）的改变而变化。基于上述实验结果，在论文的第二部分我们进一步通过改变SiO_2的焙烧温度以及使用H_2O_2和γ-氨丙基-3-乙氧基硅烷对SiO_2进行预处理等方法调变载体表面的羟基密度（12.6 ~ 0.02 个/100 $Å^2$），并进而实现对 Pd/SiO_2 上 Pd 粒径（2.5 ~ 6.8 nm）的调控。在论文第三部分工作中选取了CO 氧化、苯甲醇有氧氧化和甲烷部分氧化（POM）制合成气等反应，对所制备Pd/SiO_2 的催化性能进行了评价。实验结果表明：与大颗粒的 Pd 相比，小颗粒Pd 具有更高的 CO 氧化活性；对苯甲醇有氧氧化反应，平均粒径为 3.3 ~ 3.7 nm的 Pd 颗粒具有最高的 TOF，Pd 粒径过小或过大均会导致 TOF 的降低；与其他前驱体制备的Pd/SiO_2相比，以$Pd(acac)_2$为前驱体制备的催化剂具有较高的 POM催化活性，良好的稳定性和抗烧结性能。

论文第四部分以高分散抗烧结Pd/SiO_2催化剂为基础，比较考察了不同前驱体制备的Pd/SiO_2催化剂在不同温度下的POM反应性能，并采用原位XRD、原位Raman和脉冲反应等实验技术对Pd/SiO_2催化剂上POM反应的机理进行探究。实验结果表明，在POM反应起燃以前，催化剂床层前部（氧化区）的Pd物种处于氧化态，只能催化甲烷的燃烧反应；伴随着POM反应的起燃，Pd物种被还原。在氧化区内甲烷的直接氧化和重整反应对合成气的生成均有一定贡献。

关键词：浸渍法；Pd/SiO_2；乙酰丙酮钯；粒径调控；制备机理；CO氧化；苯甲醇有氧氧化；甲烷部分氧化；反应机理

Abstract

This thesis focuses on the studies of the technique that can be used to prepare sinter-resistant and well-dispersed Pd/SiO_2 catalysts with controllable particle size by simple impregnation steps and the formation mechanisms of the catalysts in order to provide the scientific foundation for developing thus palladium nanocatalysts.

In the first part of the thesis, a serial of Pd/SiO_2 catalysts were prepared from different Pd precursors such as $PdCl_2$, $(NH_4)_2PdCl_4$, $Pd(NO_3)_2$, $(NH_3)_4Pd(NO_3)_2$, $Pd(OAc)_2$ and $Pd(acac)_2$, and further characterized by using BET, XRD, O_2 and CO chemisorption and TEM techniques. Meanwhile, the thermal decompositions of these catalysts under the different atmospheres (air, H_2/Ar or Ar) were explored by using *in situ* XRD, *in situ* microprobe Raman spectroscopy and TPD-MS techniques. It was found that the mean size of Pd particles over the Pd/SiO_2 catalyst prepared by palladium bis-acetylacetonate [$Pd(acac)_2$] maintained at approximately 3 nm even after the catalyst was calcined at 800 ^{o}C in air and subsequently reduced by hydrogen at 600 ^{o}C. This can be explained by the formation of $(O_s)_2Pd$ intermediates highly dispersed on the surface of SiO_2 due to the H-transfer from surface hydroxyls to the acac ligand. These $(O_s)_2Pd$ intermediates can thereby be rapidly reduced into highly dispersed metallic Pd nanoparticles by the oxidation of the acac ligand at the temperature was elevated to about 200 °C in air, which was key for the generation of these Pd species with excellent sinter-resistance. The results of further studies revealed that the mean size of Pd particles (~ 3 nm) was slightly influenced by Pd loadings with 0.5 ~ 5 wt% and calcination temperature of 200 ~ 800 °C in case of the support containing enough amount of surface hydroxyls.

In the second part of the thesis, therefore, we studied the alteration in the density of surface hydroxyls of SiO_2 by changing calcination temperature of SiO_2 and different pretreatment using H_2O_2 or γ-aminopropyl-3-silane, which was found to be adjusted in the range of 12.6 ~ 0.02/100 $Å^2$, resulting in the controllable size of Pd particles with 2.5 ~ 6.8 nm over the Pd/SiO_2 catalyst. In addition, the catalytic activities of the Pd/SiO_2 catalysts prepared by different palladium precursors were evaluated in detail by using CO and benzyl alcohol oxidation as well as the POM reaction to synthesis gas in the third part of the thesis. Lower light-off temperature for CO oxidation was found in smaller Pd particle, while that in larger particle was higher. It was also found that the turnover frequency (TOF) for the aerobic oxidation of benzyl alcohol reached the highest on the Pd particles with mean size of 3.3 ~ 4.5 nm and decreased on those smaller or larger particles. Notably, the Pd/SiO_2 catalyst prepared by Pd(acac)$_2$ exhibited higher catalytic activity, better thermal stability and superior resistance against sintering for POM reaction in comparison with the Pd/SiO_2 catalysts prepared by other palladium precursors.

In the end of the thesis, the catalytic performance at different reaction temperatures of the sinter-resistant and well-dispersed Pd/SiO_2 catalysts prepared by different palladium precursors were investigated in detail for the POM reaction and the reaction pathways were also probed by using *in situ* XRD, *in situ* microprobe Raman spectroscopy and pulsed reaction techniques. The results indicated that Pd species in oxidation zone were present in the oxidation state and only catalyzed the combustion of methane prior to the ignition of the POM reaction, and subsequently would be reduced during the ignition process. In the oxidation zone, the direct oxidation and reforming of methane played a certain role in the formation of synthesis gas.

Keywords: Impregnation; Pd/SiO_2; Pd(acac)$_2$; controllable particle size; formation mechanism; CO oxidation; aerobic oxidation of benzyl alcohol; methane partial oxidation; reaction pathway

目 录

Catalogue