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硕士学位论文

负载型Au纳米催化剂及其催化活性研究

Supported gold nanoparticle catalyst and its catalytic activity

卫巍

指导教师：李海燕

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摘 要

纳米尺寸的金（Au纳米粒子，Au NPs），因其优异的物理化学特性，有望成为组装高活性催化剂的重要单元，由此引发的“淘金热”催生了催化领域系列前沿研究课题。本文工作致力于负载型金催化剂及其催化选择性加氢/脱氢反应的研究，论文分为两部分：

I．高效合成Au/碳纳米管复合材料及其催化选择性加氢。

通过壳聚糖(CHIT)功能化的碳纳米管(CNTs)自发还原负于其上的Au3+，开发出一类Au纳米粒子修饰的CNTs复合材料。利用循环伏安法，结合其他谱学表征技术，如SEM/HETEM，XRD和XPS等技术，对Au/CHIT-CNTs合成过程中壳聚糖和碳纳米管的协同作用进行了探讨。研究结果表明，壳聚糖不仅提高了碳纳米管在水溶液中的分散性和稳定性，锚定Au纳米粒子于碳纳米管载体表面以防止他们迁移/聚结，更重要的是，其还能够通过降低碳纳米管的还原电势来促进Au3+的自发还原。

受上述研究结果的启发，将工作扩展至非贵金属/CNTs复合材料的研究，开发出一种在室温，氨水溶液中，快速、高效合成Cu、Co和Ni修饰的CNTs复合材料的新方法。表征结果显示，超小粒径（约3 nm）的Cu、Co和Ni颗粒均匀地分布于CNTs表面；氨水是促进CHIT-CNTs自发还原非贵金属离子的关键。

进一步，以水溶液中NaBH4还原对硝基苯酚（4-NP）制对氨基苯酚（4-AP）为探针反应，前述所得纳米复合材料对该反应均表现出高效催化选择加氢性能。

II．单分散高比表面纳米孔SiO2的制备及其负载的Au催化剂催化选择性脱氢。

首次采用界面缩聚，在没有模板剂存在条件下合成出BET比表面积高达530~900 m2/g，孔容为0.3~0.6 cm3/g以及窄孔径分布（4~6 nm）的单分散纳米孔SiO2。以此为载体合成的负载型Au催化剂对甲酸选择性分解制氢反应表现出极其优异的催化性能。在363K，1.32wt%Au/SiO2催化剂上，甲酸分解反应的转化频率（TOF）高达1356 h-1，是相同条件下商品SiO2负载的Au催化剂活性（TOF为55 h-1）的33倍。显然，这种首创的界面法制备的SiO2作为Au催化剂的载体有其独特的优越性及有效性。

关键词：Au纳米粒子；碳纳米管；二氧化硅；选择性催化加氢；选择性催化脱氢

Abstract

Gold particles with the nanoscale size (gold nanoparticles, Au NPs) are expected to be the key building blocks for extraordinary active catalysis. The “gold rush” has generated a considerable variety of research topic in the frontier of catalysis. Herein, our work focuses on the supported Au NPs for selective hydrogenation / dehydrogenation. The paper is composed of two parts:

One is highly effective synthesis of gold-carbon nanotube nanohybrid and its performance for selective hydrogenation reaction.

The novel synthesis of AuNPs nanoparticles(NPs) decorated multiwalled carbon nanotubes(CNTs) nanobrids, via the spontaneous reduction of Cu ions with chitosan functionalized CNTs, has been developed. The synergistic effect of chitosan and carbon nanotube in synthesis of gold-carbon nanotube nanohybrids were investigated by cyclic voltammograms measurement, combined with various characteristic techniques, such as SEM/HETEM, XRD and XPS. The present results reveal that the role of chitosan is not only just to disperse CNTs steadily in aqueous solution as well as to anchor Au NPs preventing them from migrating/agglomerating on the carbon nanotubes support, but also to adjust carbon nanotubes’ reduction potential improving spontaneous deposition of gold ions.

Inspired by those results, extending work to synthesize non-precious metal nanoparticles, such as Cu, Ni and Co, decorated CNTs in the presence of ammonia has successfully done. Characterization of the nanohybrids reveal that the ultra-small Cu, Ni and Co nanoparticles (approx. 3 nm) were well uniformly loaded on the surface of CNTs. The addition of ammonia to the suspension (or dispersed solution) to adjust the pH is responsible for the reduction of Cu ions. Moreover, reduction of 4-nitrophenol by sodium borohydride in aqueous solution was chosen as probe reaction, these nanohybrids have shown highly effective

catalytic performance.

Another part is preparation of high surface area monodispersed nanoporous silica and its supported gold catalyst for selective dehydrogenation reaction .

A facile template-free synthetic approach for monodispersed nanoporous silica nanoparticles via interfacial condensation has been developed for the first time. The particles synthesized in this work possess a surface area of ca. 530–900m2/g, pore volume of ca. 0.3–0.6 cm3/g, and 4~6nm narrow pore size distribution.

such nanoporous silica supported gold nanoparticle catalysts display excellent catalytic performance for the dehydrogenation of formic acid (FA). Under 363K, Over 1.32wt%Au/SiO2 catalyst, the initial turnover frequency (TOF) for the decomposition of FA can reach the highest value of 1356 h-1, almost 33 times the corresponding value (55 h-1) of commercial silica supported gold catalyst, clearly, our home made silica is quite unique and effective as support for gold catalysts.

Keywords: Au nanoparticles; Carbon nanotubes; Silica; Selectivly catalytic hydrogenation; Selectivly catalytic dehydrogenation

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