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二氧化硅包裹增强型铜基催化剂的合成及其催化性能的研究

Study on the Synthesis and Catalytic Performance of Silica-Encapsulation Enhanced Copper-Based Nanocatalysts

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Study on the Synthesis and Catalytic Performance of Silica-Encapsulation Enhanced Copper-Based Nanocatalysts

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

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摘要

多相催化剂在化学工业中具有举足轻重的应用，约有 90%的化工过程需要使用催化剂。近年来，人们在多相催化剂的制备方法、结构设计、性质研究等方面做了大量研究，制备出了许多高效的催化剂。但是，催化剂在使用过程中容易发生烧结，导致催化剂催化活性的降低，乃至失活。针对催化剂存在的这一问题，人们采用不同的方法来提高催化剂的抗烧结性能，如，选择不同的载体、改变组分和包裹等策略。其中，包裹的策略最为常用，一般涉及两种结构，yolk-shell 结构和 core-shell 结构。包裹的策略不仅可以稳定核内金属纳米颗粒，也能产生新的金属-载体界面，尤其是 core-shell 结构能实现这种界面的最大化。由于包裹而产生的界面有助于人们研究金属-载体间的相互作用。研究已经表明，金属和载体间的相互作用影响催化剂的催化性能，尤其是金属-载体间的强相互作用（SMSI），且界面在这过程中扮演了重要的角色。金属-载体的强相互作用一般容易在可还原性的载体上（如，TiO_x, MnO_x）发生，而在难还原的氧化物载体（如 SiO_2, Al_2O_3, MgO 和 Sc_2O_3）上则不易发生。SiO_2 作为一种惰性壳层材料，被广泛的应用于 yolk-shell 结构和 core-shell 结构。因而人们的研究主要集中在 SiO_2 与催化剂稳定性的关系，却很少涉及金属-SiO_2 之间的界面作用。本文主要开展了 Cu-SiO_2 界面作用与催化剂催化性质的研究，主要研究结果如下：

第一章：从纳米催化剂出发，简要介绍稳定催化剂的策略，并着重介绍了界面作用的重要性。最后提出本论文的选题依据和研究内容。

第二章：运用二氧化硅包裹的方法我们制备了 Cu_2O@m-SiO_2 催化剂，验证 Cu-SiO_2 界面的增强效应。研究发现，二氧化硅壳层能够增强 Cu_2O 催化剂在草酸二甲酯加氢制乙二醇反应中的催化活性。我们通过分析认为 Cu-SiO_2 界面起了关键作用，Cu-SiO_2 界面能够增强催化剂的催化活性。这种 Cu-SiO_2 界面增强作用在 CuO、C-Cu_2O 和 Cu/SiO_2 催化剂上。

第三章：通过水热法我们制备了具有层状结构的中空多孔硅酸铜纳米球催化剂。利用其层状结构，我们能够高效的构筑 Cu-SiO_2 界面。中空多孔硅酸铜纳米

球催化剂中存在大量的 Cu-SiO_2 界面，并在草酸二甲酯加氢制乙二醇反应中表现出高的活性。

第四章：通过制备方法的改进，我们能够高效的制备硅酸铜纳米管催化剂。硅酸铜纳米管也具有层状结构的特征，因此也同样可以用于构筑 Cu-SiO_2 界面。经过还原处理后，硅酸铜纳米管催化剂中可以形成大量 Cu-SiO_2 界面，其催化性质(草酸二甲酯加氢制乙二醇)优于中空多孔硅酸铜纳米球和 AE-Cu/SiO_2 催化剂。我们发现 Cu-SiO_2 界面能够起到稳定 Cu^+的作用，并且催化剂中 Cu^+的含量越高，催化剂的催化活性也越高。

第五章：通过引入二氧化硅包裹的策略，我们制备了 CS-NT@m-SiO_2 催化剂，成功解决了硅酸铜纳米管催化剂中部分铜纳米颗粒无法用于构筑 Cu-SiO_2 界面的问题。由于 CS-NT@m-SiO_2 催化剂中 Cu^+的比例进一步的提高，该催化剂在草酸二甲酯加氢制乙二醇反应中的催化性能也明显增强。

第六章：对本论文的研究工作进行总结，并对未来的工作进行展望。

关键词：Cu/SiO_2 催化剂、Cu-SiO_2 界面、草酸二甲酯、选择性加氢、乙二醇。

Abstract

Heterogenous catalysts have important applications in modern chemical industry and are used in ninety percent of chemical reactions in chemical industry. In recent years, many researches are mainly focused on the design, the preparation and the performance of catalysts. Catalysts are easily sintered during heterogeneous catalysis, which leads to the decrease of surface area of the catalytically active mental nanoparticals and thus the reduced life time and catalytic performance of the catalysts. Researchers have proposed many approaches to solve this problem including using appropriate supports, change structure and the encapsulated strategy. Among these strategies, the encapsulated strategy is most commonly used. This encapsulation strategy generally includes the formation of two different structures, core-shell structure and yolk-shell structure. Besides stabilizing the metal cores, core-shell structure is an ideal case to study metal-support interactions. Researches have shown that metal-support interactions,strong metal support interactions (SMSI) in particular, play an important role in catalytic reactions and could affect the catalytic performance of the catalysts,. The SMSI effects are usually observed when reducible metal oxides are used as supports. Metal oxides, such as SiO_2, Al_2O_3, MgO and Sc_2O_3, with weak reducibility are typically considered as the inert supports to induce SMSI for promoting catalysis. SiO_2 is considered as the inert shell material and has been widely used to fabricate yolk-shell and core-shell metal nanocatalysts, which makes it possible to study themetal-SiO_2 interfacial effect on the metal@SiO_2 core-shell catalysts. This thesis is mainly focus on the relationship between Cu-SiO_2 interfacial effect and the catalytic performance of catalysts, the mainly research results are as follow:

Chapter 1: Considering the significance of the stability of nanocatalyst, this chapter briefly introduces the stabilizing strategy of nanocatalyst and illustrates the

importance of interface interaction, followed by the objectives and contents of this thesis.

Chapter 2: The catalyst of Cu_2O@m-SiO_2 was prepared by silica-encapsulated method to verified the enhanced effect of Cu-SiO_2 interface . The research had shown that silica-encapsulation can enhance the catalytic performance of Cu_2O catalysts in the selective hydrogenation of dimethyl oxalate (DMO) to ethylene glycol (EG). the results reveal that the Cu-SiO_2 interface plays a key role in catalytic reactions and enhance the catalytic performance of Cu_2O catalysts. The Cu-SiO_2 interface interaction was also verified in CuO, C-Cu_2O and Cu/SiO_2 catalysts.

Chapter 3: Hollow porous copper silicate nanospheres were prepared by hydrothermal method. Because of the lamellar structure of copper silicate nanospheres, the Cu-SiO_2 interfaces were produced efficiently. The hollow porous copper silicate nanospheres enjoy abundant Cu-SiO_2 interfaces and showed excellent catalytic performances in the selective hydrogenation of DMO to EG.

Chapter 4: The copper silicate nanotubes with high yield were prepared by the improved method. The copper silicate nanotubes with abundant Cu-SiO_2 interfaces showed higher catalytic performance than hollow porous copper silicate nanospheres and AE-Cu/SiO_2 catalysts. We found that the Cu-SiO_2 interface serves as a Cu^+ stabilizer and the catalytic performance of catalyst improves with the increasing content of Cu^+.

Chapter 5: The CS-NT@m-SiO_2 catalysts were prepared by silica-encapsulated method. The CS-NT@m-SiO_2 catalysts make full use of the copper nanoparticles to creat the Cu-SiO2 interface on CS-NT catalysts. For the increasing amount of Cu^+ the CS-NT@m-SiO_2 catalysts exhibited better catalytic performance than CS-NT catalysts in the selective hydrogenation of DMO to EG..

Chapter 6: The summary of this thesis and the future planning are given.

Keywords: Cu/SiO_2 catalyst, $Cu\text{-}SiO_2$ interface, Enhanced, Dimethyl oxalate, Ethylene glycol, Hydrogenation.