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多组分纳米催化剂的构建及其催化性能研究

Fabrication of Nanocatalysts with Multi-component and
Their Catalytic Performance

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Their Catalytic Performance**

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摘要

贵金属纳米材料因其独特的性能在很多催化反应中得到了广泛的应用，如 CO 氧化、有机污染物降解、选择性加氢、电催化等。然而贵金属资源有限、价格昂贵等因素制约其更为广泛的催化应用。因此进一步优化贵金属纳米材料的催化性能和发展非贵金属可替代型催化材料是很有必要的。本论文通过制备方法的优化，有效地构建了几类多组分多界面的贵金属型和非贵金属型纳米催化剂，详细研究了这些纳米催化剂结构与催化性能的关系，以期为其他纳米催化剂的制备提供参考。

本论文的研究内容概括如下：

一、发展了一种氨水辅助水热法制备过渡金属掺杂 TiO_2 载体的策略。采用 XRD、Raman、TEM、氮气吸脱附、ICP-OES 和 EPR 等手段对载体的结构、形貌和组成进行了表征。结果表明，这种掺杂型 TiO_2 载体 (M-TiO_2) 表面存在大量的结构缺陷，氨水在表面缺陷的构建中起到了关键作用。进一步通过溶剂浸渍法，制备了 M-TiO_2 负载的 Pd 催化剂。以 CO 氧化为探针反应，详细考察了催化剂活化程度、Cu 掺杂量和掺杂元素与催化剂的催化性能的关系。发现当 Cu/Ti 比为 1/10 时，即 Pd/Cu-TiO-1 催化剂，经过低温活化 15 min 即可实现 CO 的 100% 转化。通过 HAADF-STEM、 H_2 -TPR 和 XPS 等表征发现，金属 Pd 与载体 Cu-TiO-1 存在协同催化效应。

二、以氨水辅助水热法制备的二氧化钛 (TiO_2 -N) 为载体，通过引入 Bi 助剂，共浸渍法制备了一系列 Pd&Bi/ TiO_2 -N 催化剂。详细考察了不同制备方法、活化程度、负载量和焙烧温度对 Pd&Bi/ TiO_2 -N 催化剂 CO 氧化活性的影响。进一步通过不同助剂、不同载体和稳定性考察发现，氧化铋对 Pd 基催化剂的 CO 氧化具有明显的促进作用。通过 XRD、Raman、TEM 和 HAADF-STEM 等表征发现，金属 Pd 和助剂 Bi 在载体表面形成了高度分散的复合型粒子； H_2 -TPR 表征发现，金属 Pd、助剂 Bi 和载体 TiO_2 -N 之间存在协同效应；XPS 表征发现，在 Pd&Bi/ TiO_2 -N 催化剂中存在多种金属和金属氧化物形态。值得一提的是，这种多组分多界面的纳米催化剂可以通过共浸渍法一步即可大量合成，为其他催化剂的制备提供了借鉴。

三、采用 6-氨基己酸为形貌调控剂，水热法合成了一系列的 CuCe 双金属氧化物。详细考察了不同水热温度、水热时间、投料比和碱量对 CuCe 双金属氧化物的形貌、Cu 掺杂量、比表面积和暴露面的影响。以 CO 氧化为探针反应，进一步考察了这系列 CuCe 双金属氧化物的催化性能。与 CuCe-w1（不加入 6-氨基己酸）和 5% Cu/CeO₂-c 负载型催化剂相比（相同的 Cu 含量），线网络结构的 CuCe-10 催化剂具有更优的催化活性和稳定性，在 80 °C 下连续反应 60 h，其活性无衰减。通过 XRD、Raman、TEM、HAADF-STEM、H₂-TPR 和 XPS 等表征发现，与氧空位有关的表面缺陷是催化活性的关键位。另外，也说明在催化剂制备中采用小分子作为调控剂是可行有效的。

四、以 Na₄EDTA 为结构调控剂和稳定剂，发展了一种简单有效制备合金纳米线的方法，即在冰水浴中，将所需阴阳离子和 Na₄EDTA 混合，硼氢化钠还原即可得到宽度为 6 nm 左右的合金纳米线。通过改变阴阳离子的不同组合（阳离子包括 Co²⁺、Mn²⁺、Ni²⁺、Cu²⁺、Fe³⁺、Ag⁺，阴离子包括 PdCl₄²⁻、PtCl₄²⁻、AuCl₄⁻），可以有效制备不同组分的合金纳米线。另外，通过原位置换反应，进一步可以构建多金属纳米线（如 PdCuAu）。以 4-硝基苯酚加氢为探针反应，相比无配体或其他配体辅助合成的 PdCu 纳米结构，EDTA⁴⁻辅助合成的 PdCu 纳米线具有较优的催化性能和稳定性，表明 EDTA⁴⁻在合金纳米线的制备和催化中扮演了重要的角色。另外，在 EDTA⁴⁻辅助合成的系列合金纳米线中，PdAg 纳米线呈现了更优的催化活性和稳定性。

关键词： 纳米催化；多组分界面；制备方法；CO 氧化；4-硝基苯酚还原

Abstract

Because of their unique physical and chemical properties, noble metal nanomaterials have been widely applied in many catalytic reactions, such as CO oxidation, nitroaromatics reduction, selective hydrogenation, electrocatalysis, and photocatalysis. Quite frankly, limited precious metal resource is a problem. So how to further optimize the catalytic properties of the noble metal nanomaterials or develop the alternative non-noble metal catalyst is worth considering. For the sustainable development, the thesis has effectively prepared a series of multi-component nanocatalysts by different strategies. Then, the relationships between structure and performance of nanocatalysts are studied in detail.

I. Ammonium hydroxide was employed as the precipitant and complexant, and transition metal doped TiO_2 supports (M-TO- x) were synthesized by the strategy of hydrothermal synthesis. The structure, morphology and composition of M-TO- x were characterized by XRD, TEM, EPR, Raman spectroscopy, nitrogen adsorption/desorption, and ICP-OES techniques. The results show that there presents a large number of structure defects on the surface of M-TO- x . Ammonium hydroxide plays a key role in the formation of such surface defect. Pd/M-TO- x catalysts were further prepared by solvent impregnation method. A detailed comparison was made on the basis of their unique doped structures and catalytic behaviors. XPS, H_2 -TPR, and EPR investigations revealed the evolution of surface oxygen vacancies and Cu oxidation state. The catalytic activity and structural characterization results of the Pd/Cu-TO-1 catalyst suggest that both Pd and Cu-doped TiO_2 structural feature can have a synergistic effect on the catalytic behavior of generated multi-interface.

II. Nanostructured titanium dioxide (TiO_2 -N) was prepared by an ammonia-assisted hydrothermal method. Then, a series of multicomponent catalysts were prepared, Pd and Bi co-supported on TiO_2 -N, by using a modified co-impregnation method. The CO oxidation activities of the multicomponent catalysts were detailedly compared by the different preparation methods, H_2 activation, load amounts, calcination temperatures, and supports. Metal Pd and additives Bi are of high dispersion on the

TiO₂-N that was revealed by the XRD, Raman, TEM, and HAADF-STEM. In addition, H₂-TPR analysis proved that the synergistic effect among metal Pd, additives Bi, and TiO₂-N support. The results of XPS showed that multi-interface of the Pd-based catalysts may exist, owing to coexistence of a variety of metal and metal oxides. The catalytic activity and structural characterization results proved that an appropriate amount of Bi species has a clear promoting effect on the Pd-based catalyst. Particularly, the catalyst can be mass-produced conveniently, which may be beneficial for versatile reactions and practical applications.

III. A series of CuCe bimetallic oxides with characteristic morphology had been constructed by using a 6-aminocaproic acid-assisted hydrothermal method, in which different hydrothermal temperature, hydrothermal time, and additives were respectively researched. Compared to CuCe-wl and 5% Cu/CeO₂-c catalyst, the wire-network-like CuCe-10 catalyst exhibits the high catalytic activity and amazing stability in CO oxidation. The characterization results of TEM, XRD, H₂-TPR, XPS and Raman spectra show that surface defects of the oxygen vacancy is the key to the catalytic activity. Moreover, it means that the introduction of 6-aminocaproic acid makes sense for tunable fabrication and enhanced catalytic performance.

IV. A series of alloy nanowires were conveniently synthesized in water using ethylenediaminetetraacetate (EDTA⁴⁻) as a structural controller and stabilizer, which are ultrafine with a width of approximately 6 nm. In the producing process of EDTA⁴⁻ assisted nanowires, different cations (Co²⁺, Mn²⁺, Ni²⁺, Cu²⁺, Fe³⁺, and Ag⁺) and anions (PdCl₄²⁻, PtCl₄²⁻, and AuCl₄⁻) were introduced and studied. The reduction of 4-nitrophenol by NaBH₄ was used to evaluate the activity of the alloy nanowires catalysts. The EDTA⁴⁻ assisted alloy nanowires exhibited excellent activity and stability, outperforming the bare nanowires and sodium citrate assisted nanowires, and indicating the EDTA⁴⁻ has a great influence on the morphology and activity.

Keywords: nano-catalysis, multi-component-interface, preparation method, CO oxidation, 4-nitrophenol reduction

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