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高活性碳化钨催化材料的 制备、表征及电化学性能研究

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- 专业：材料学
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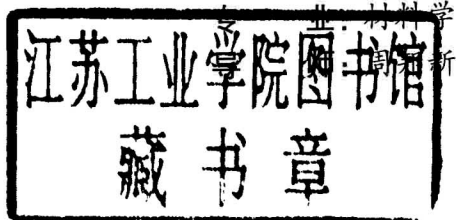


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Shanghai University Doctoral Dissertation (2005)

**Preparation, Characterization and
Electrochemical Properties of
Catalytic Materials of High
Activity Tungsten Carbide**

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Major: Materials

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答辩委员会对论文的评语

碳化钨类铂催化材料是材料、化学与化工领域中的一个研究热点。制备高活性碳化钨电催化材料的研究工作,选题具有重要的学术价值和良好的应用前景。

论文通过对连续式和间歇式高活性碳化钨粉体制备工艺的研究,成功建立了喷雾干燥-固定床还原碳化法制备纳米碳化钨粉末的实验装置及工艺技术。应用 SEM、XRD、AES、XPS、TG、DTA 及 BET 等多种分析手段观察研究了碳化钨粉末制备过程中物相的形貌和结构的变化,探索反应过程的机理。同时,采用恒电流阳极充电法、线性极化、循环伏安等电化学实验方法深入研究了碳化钨在不同电解液中的电化学稳定性及对析氢反应、氢氧化反应、芳香族硝基化合物电还原反应的电催化活性,主要取得了以下创新性的结果:

采用气固反应合成了高活性 WC 粉体,在合成工艺上有创新。

在国内外首次成功制备了具有介孔结构空心球状的碳化钨粉体材料,发现碳化温度和冷却速度对碳化钨粉末的表面形貌有显著影响,提出了介孔结构空心球状碳化钨颗粒的形成机理。

首次采用恒电流阳极充电法对碳化钨催化剂在不同电解液中的电氧化行为和稳定性进行了全面系统的研究,并采用气体扩散电极和粉末微电极技术研究了不同物相组成的

碳化钨对析氢反应、氢氧化反应和芳香族硝基化合物电还原反应的催化活性.这方面的研究结果为碳化钨在燃料电池、有机电化学及化学催化等领域的应用提供了实验和理论依据.

论文的研究思路清晰、实验方法合理、数据翔实可靠、分析严谨、行文流畅、结论可靠,表明作者具有扎实的理论基础和熟练的实验技术,有较强的独立科研能力和科研素质.在论文答辩过程中叙述流畅,回答问题正确.论文已达到材料学专业博士学位论文要求的水平,是一篇优秀的博士论文.

答辩委员会表决结果

经答辩委员会表决,全票同意通过马淳安同志的博士学位论文答辩,建议授予工学博士学位.

答辩委员会主席: **郑小明**

2005年5月26日

摘 要

本文全面综述了国内外在碳化钨(WC)催化材料制备、性能及应用方面的研究进展,系统分析了影响碳化钨催化活性的各种影响因素及碳化钨制备过程中的反应历程.在此基础上,从制备高活性电催化材料出发,开展了碳化钨粉末材料的制备、表征、形成机理、化学和电化学稳定性及电催化活性等方面的研究工作.

论文首先考察了以黄色钨酸和偏钨酸铵为钨源、CO/CO₂为碳源,采用连续式和间歇式两种方法制备高活性碳化钨粉体的工艺.研究表明,碳化钨制备过程包括焙解、还原、渗碳三个阶段;制备工艺对碳化钨的物相组成、表面结构和比表面积等具有十分重要的影响.间歇式法制备碳化钨的最佳工艺条件为:CO流量480 mL/h·g H₂WO₄,CO₂48 mL/h·g H₂WO₄;在制备过程中含钨原料首先在500℃条件下保温1 h,以除去其中的结晶水,然后升温至750℃,恒温反应12 h,即可获得WC样品.连续式法制备碳化钨的最佳工艺条件为:CO流量1.5~3 m³/h,固相物料停留时间9~12 h,物料入口处温度400~500℃,中部壁温(850±20)℃,反应区入口气体400~600℃,按此条件可连续制得WC粉体材料.

在上述实验基础上,成功地构建了喷雾干燥-固定床法制备纳米碳化钨的实验室装置,在国内外首先制备了具有介孔结构空心球状的碳化钨粉体.这种 WC 粉体由许多长 100~800 nm、宽 50~150 nm 的柱状体构成,柱状体之间存在介孔孔隙.进一步研究发现,在制备过程中碳化温度和冷却速度对碳化钨粉末的表面形貌与结构具有很大的影响,通过急冷技术处理得到的碳化钨颗粒具有多孔结构,其中物相组成以六方结构 WC 相为主,主要化学成分为 W、C 和 O, W 与 (C + O) 的原子比为 0.977,这种结构的 WC 具有良好的电催化活性.

采用原位 XRD 和 SEM 技术深入研究了 WC 制备中的物相转变及其形貌变化过程,对介孔结构空心球状 WC 颗粒的形成机理进行了探讨.研究表明,偏钨酸铵在 CO/CO₂ 气氛中进行还原碳化时,物相转变过程与还原碳化时的温度和升温速率密切相关.缓慢升温时,样品遵循 AMT→WO₃→WO₂→W₂C→WC 的物相变化规律;“阶跃式”升温时,样品则遵循 AMT→WO₃→WO₂→WC 的物相变化规律.另外还发现,介孔结构空心球状形貌的形成可能与前驱体的性质、喷雾干燥微球化处理、反应过程中生成的气体和 WO₃ 的升华等密切相关.

在国内外首先提出了采用恒电流阳极充电法对 WC 催化剂在不同电解液中进行电氧化行为和稳定性的研究.结果表明,电极电位低于 800 mV 时,WC 在酸性溶液中对氢氧化反应具有良好的电催化活性和电化学稳定性;电极电位高于 800

mV 时, WC 中的 W 开始发生氧化, 电极表面的活性中心受到破坏, 电极处于不稳定状态. 在碱性溶液中 WC 主要发生自身的电氧化或析气反应, 因此 WC 不宜作碱性溶液中氢氧化反应的电极材料. 对 WC 自身电氧化过程的研究表明, 在 2.0 mol/L H_2SO_4 电解液中, 电极电位大于 800 mV 时, WC 将氧化成 W_2O_5 , 而在 3.5 mol/L HCl 中, WC 的氧化产物则为 W_8O_{23} , 在 2.5 mol/L KOH 电解液中, WC 将直接氧化成 WO_3 .

本工作首先以 WC 粉体为催化材料制成防水型 WC 气体扩散电极, 同时考察了在酸性电解液中氢阳极氧化的电化学性能. 研究表明, 这种气体扩散电极对氢阳极氧化反应具有较高的电催化活性, 在 3.5 mol/L HCl 溶液中进行反应时其表观活化能为 23.3 kJ/mol, 在 2.0 mol/L H_2SO_4 中为 14.5 kJ/mol, 在 85% H_3PO_4 中为 13.7 kJ/mol, 在同等条件下文献值一般为 33.4 kJ/mol, 最佳值为 16.7 kJ/mol. 此外, 研究还发现, 氢在 WC 和 W_2C 电极上的阳极氧化反应具有不同的反应机理. 以 WC 为主物相的碳化钨粉末对氢电氧化反应具有较高的催化活性, 在 30°C、22% HCl 溶液中进行氢阳极氧化时, 其交换电流密度为 8.58 mA/cm², 传递系数为 0.75. 与 WC 电极相比, W_2C 电极上氢阳极氧化反应的交换电流密度要低约 100 倍, 这表明 W_2C 电极对氢阳极氧化反应的催化活性较低. 经稳态极化法研究表明, 以 W_2C 为主相的碳化钨粉末在不同性质的电解液中对析氢反应均具有良好的电极活性.

研究还表明,WC 催化材料对有机电化学加氢反应具有良好的催化活性.在酸性介质中,硝基苯在 WC 电极上进行电化学还原时的表观活化能为 23.7 kJ/mol,同时发现电还原过程受扩散和电化学步骤混合控制.在碱性介质中,硝基苯在 WC-Ni 电极上的还原峰电流是 Ni 电极的 3 倍,具有较高的电极活性.另外还发现,WC 电极对硝基甲烷的还原反应也具有良好的电催化性能.

此外,本工作在国内外首先提出了采用粉末微电极技术考察介孔结构空心球状碳化钨粉体在对硝基苯酚(PNP)电还原反应中的催化性能.研究表明,WC 粉末微电极对 PNP 的电还原反应具有良好的催化活性.在相同测试条件下,WC 粉末微电极在 PNP 电还原过程中的峰电流比 Cu-Hg 微电极和 Pt 微电极高 3 倍以上.

关键词: 碳化钨, 制备, 电催化, 电化学性能, 气体扩散电极, 粉末微电极

Abstract

The preparation, property and application of the catalytic materials of tungsten carbides (WC) in the field of catalysis have been comprehensively reviewed in this dissertation, and the various factors affecting the catalytic activity of tungsten carbides and reaction mechanism for the preparation of tungsten carbides are also discussed. With this understanding, the preparation, characterization, forming mechanism, chemical and electrochemical stabilities and electrochemical activities of tungsten carbides are investigated from the point view of preparing electrocatalysis with high activities.

First of all, the preparation processes using yellow H_2WO_4 or $(\text{NH}_4)_6(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot 4\text{H}_2\text{O}$ as tungsten source and CO/CO_2 as carbon source at continuous mode or batch mode were investigated. The experimental results showed that three stages of pyrolysis, reduction and carbonization were occurred in turn during the preparation of tungsten carbides; and the phase composition, surface composition and specific surface area were greatly affected by the preparing conditions. The better conditions for preparing tungsten carbides at batch mode were as follows: flux of CO and CO_2 were $480 \text{ mL/h} \cdot \text{g H}_2\text{WO}_4$ and $48 \text{ mL/h} \cdot \text{g H}_2\text{WO}_4$,

respectively; the tungsten source materials were first heated at 500 °C for 1 h to get rid of crystalline water, then reacted at 750 °C for 12 h. The better conditions for preparing tungsten carbides at batch mode were as follows: flux of CO was 1.5~3 m³/h, the rest time of the solid materials in the reactor was 9~12 h, the temperatures at the inlet of solid materials, wall at the middle of the reactor and inlet of gas were 400 ~ 500 °C, (850 ± 20)°C and 400 ~ 600 °C, respectively.

Based on the above results, an experimental setup for preparing nano-size tungsten carbides with the spray drying-fixed bed method was successfully constructed. And a kind of tungsten carbide powders with mesopores and hollow ball shapes were made for the first time. These powders were formed by pillar-like species with the length of 100~800 nm and width of 50~150 nm, and mesopores were constructed by these pillar-like species. The further studies indicated that the carbonization temperature and cooling rate of the products had remarkable influence on the surface profile and structure of tungsten carbides. The tungsten carbide prepared with rapid cooling rate had porous structure and was mainly composed by hexagon WC. W, C and O were contained in this sample with the atomic ratio of W to (C + O) of 0.977. WC with such composition exhibited good electrocatalytic activities.

In situ XRD technique combined with SEM was introduced to elucidate the phase transformation and profiles

of the samples during the process for preparing WC, and the forming mechanism of WC particles with mesopores and hollow ball shapes were also discussed. The results showed that the phase transformation was closely related to the temperature for reduction and carbonization and the rising rate of temperature for the preparing tungsten carbides from $(\text{NH}_4)_6(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot 4\text{H}_2\text{O}$ in the atmosphere of CO/CO_2 . For lower rising rate of temperature, the phase transformation was as follows: $\text{AMT} \rightarrow \text{WO}_3 \rightarrow \text{WO}_2 \rightarrow \text{W}_2\text{C} \rightarrow \text{WC}$; for stair case rising of temperature, the phase transformation was as follows: $\text{AMT} \rightarrow \text{WO}_3 \rightarrow \text{WO}_2 \rightarrow \text{WC}$. In addition, the dependence of the profiles of tungsten carbides on the nature of precursor, spray-drying process, gas released during the reaction and the sublimation of WO_3 were also observed.

The electro-oxidation behavior and stability of WC in different electrolytes were first investigated by galvanostatic anodic charging method. High electrocatalytic activity for hydrogen oxidation and better electrochemical stability of WC in acidic solutions were found for the potential below 800 mV; for the potential over than 800 mV, W contained in WC became to oxidized and the active sites at the surface of the electrode was destroyed. In basic solution the main reaction occurred at the WC anode was the oxidation of WC itself or the evolution of gas. This indicated that WC was not suitable as anode material for hydrogen oxidation in basic solution. It was found that the products of the oxidation of

WC were W_2O_5 in 2.0 mol/L H_2SO_4 above 800 mV, W_8O_{23} in 3.5 mol/L HCl, WO_3 in 2.5 mol/L KOH, respectively.

In addition, the performance of gas diffusion electrode catalyzed with WC on hydrogen oxidation in acidic solutions was also evaluated. High electrocatalytic activity was found for the anodic oxidation of hydrogen. The apparent activation energies were 23.3 kJ/mol in 3.5 mol/L HCl, 14.5 kJ/mol in 2.0 mol/L H_2SO_4 and 13.7 kJ/mol in 85% H_3PO_4 , respectively. Under the same conditions, 33.4 kJ/mol was commonly reported in the documents and 16.7 kJ/mol was the best one. Furthermore, different reaction mechanisms were observed for anodic oxidation of hydrogen at WC electrode and W_2C electrode. High catalytic activity for hydrogen oxidation was found on the tungsten carbides with WC as the main phase. The exchange current density and transfer coefficient were 8.58 mA/cm² and 0.75 respectively for hydrogen oxidation in 22% HCl solution at 30 °C. Compared to WC electrode, the exchange current density for hydrogen oxidation at W_2C electrode was about 100 fold lower. This indicated that lower catalytic activity of W_2C to hydrogen oxidation. The steady state polarization method testified that tungsten carbides with W_2C as the main phase had good electrocatalytic activity for the evolution of hydrogen in various aqueous solution with different pH value.

The studies also proved that WC had good electrocatalytic activity on organic electrochemical reactions. In acidic media, the apparent activity energy for the

electroreduction of nitrobenzene at WC electrode was 23.7 kJ/mol, and the electrode process was controlled by diffusion and electrochemical steps simultaneously. In basic media, the peak current for the reduction of nitrobenzene at WC - Ni was 3 times bigger than that at Ni electrode. In addition, good electrocatalytic activity of WC was also found for the reduction of nitromethane.

Furthermore, powder microelectrode technique was introduced to evaluate the catalytic activity of tungsten carbides with mesopores and hollow ball shapes for the electroreduction of *p*-nitrophenol (PNP). The results showed that the WC powder microelectrode had good catalytic activity for the reduction of PNP. At the same conditions, the peak current for the reduction of PNP at WC powder microelectrode was 3 times higher than those at Cu - Hg microelectrode and Pt microelectrode.

Key words Tungsten carbide, preparation, electrocatalysis, electrochemical performance, gas diffusion electrode, powder microelectrode

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