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原子和分子水平上的电催化

四碳醇电氧化与铂表面结构及氧化态的研究

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有机小分子的电氧化是电化学催化的基础课题。有机小分子醇在铂电极上的吸附和氧化过程,既具有基础理论研究价值又有潜在的电化学能源转换(如直接燃料电池)和电化学合成方面的应用前景。这方面的研究通常是从反应物的分子结构效应和电极表面结构效应入手。多种异构体的存在使得含有四个碳原子的醇对分子结构效应的研究具有特殊意义。

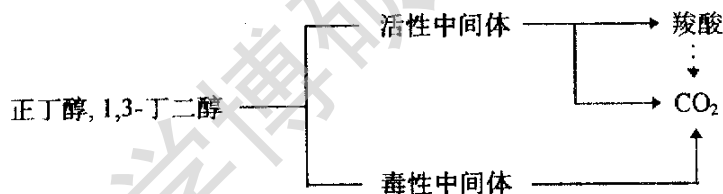
为了研究电极表面结构及表面状态与催化活性的关系、在分子和原子水平上认识和发展有机小分子电催化的理论,本论文工作中,采用原子排列结构明确的 Pt 单晶和多晶电极,联用电化学循环伏安法,电位阶跃暂态方法,电化学现场傅立叶变换红外反射光谱(FTIR)和电化学-光电子能谱(EC-XPS)研究方法,研究了铂表面氧化态对醇氧化的影响,以及正丁醇和 1,3-丁二醇在 Pt 电极上的电催化氧化过程及其机理。同时还探讨了 Pt 电极表面修饰了 Sb、Bi、S 等吸附原子后对 1,3-丁二醇氧化的影响。这些结果既发展了有机小分子的电氧化理论,同时又可对寻找合适的电催化剂起指导作用。

研究表明,不同的醇表现出不同的反应活性。根据正向电位扫描第一个氧化峰的峰值电流大小,四种醇的活性顺序依次为:甲醇($1.47\text{mA}\cdot\text{cm}^{-2}$)>乙醇($1.02\text{mA}\cdot\text{cm}^{-2}$)>丙醇($0.64\text{mA}\cdot\text{cm}^{-2}$)>丁醇($0.21\text{mA}\cdot\text{cm}^{-2}$)。同时发现小分子醇的电氧化具有共同的循环伏安特征,即在正向电位扫描中它们的氧化分别在 0.6 和 1.0 V 附近给出两个电流峰,而在负向扫描中给出一个小的还原电流峰和一个较大的氧化电流峰(0.4 V 左右),并且在 0.0 V 至 0.45 V 这段电位区间,正向和负向电位扫描中的电流值存在着很大的差异。通常认为这一差异是由于醇的自毒化相象引起,即醇在铂电极上解离吸附的产物在低电位下稳定地吸附于电极表面阻碍了醇的进一步氧化。现场红外反射光谱研究结果表明 CO 为主要解离吸附产物,它在高于 0.3 V 的电位下才会被氧化。正向电位扫描中醇的第一个氧化峰就是由醇的自毒化产物和醇本身的氧化引起。采用程序阶跃方法得到的结果指出,即使在没有毒化的电极上,醇的氧化在正向电位扫描中仍不会象负向扫描电位那样给出一个较大的电流峰。说明上述差异并不是通常认为的纯粹由毒物的作用引起。醇的氧化需要氧的参与,而从铂表面获得氧要比从

水溶液中获得容易。进一步的研究结果表明,在醇的电氧化过程中,铂的表面氧化态起着至关重要的作用。铂表面氧化物的形成与还原是不可逆的,铂氧化物的还原总是存在着滞后现象。在正向电位扫描中,低于 0.4 V 时铂表面氧化物缓慢形成,之后线性上升。在负向电位扫描中,在 1.20V 至 0.6V 的区间内,铂表面的残余电量几乎保持不变,随后以 $2300 \mu\text{C} \cdot \text{cm}^{-2} \cdot \text{V}^{-1}$ 的速率下降。同时发现,在高于 1.0 V 的电位下形成的氧化物是毒化物,随着这些氧化物在负向电位扫描中逐渐被还原,铂表面恢复活性,醇在 0.36 V 给出一个氧化峰。综上所述,铂表面的氧化物可分为活性和毒性氧化物。电化学光电子能谱的结果指出,在高于 1.0V 的电位下产生的铂的氧化物(如 $\text{Pt}(\text{OH})_3$)为毒性的,它阻碍了醇的氧化。活性氧化物是一些较低价态的物种,如 PtOH , PtO 和 $\text{Pt}(\text{OH})_2$ 等。

在四碳醇的电氧化研究中,首先研究了电极表面结构效应和反应分子结构效应。正丁醇和 1,3-丁二醇的氧化是表面结构敏感的过程。在三个基础晶面中,Pt(110)显示了最好的催化活性,它们的活性顺序对正丁醇的氧化依次为 $\text{Pt}(110)(0.39\text{mA} \cdot \text{cm}^{-2}) > \text{Pt}(100)(0.37\text{mA} \cdot \text{cm}^{-2}) > \text{Pt}(111)(0.30\text{mA} \cdot \text{cm}^{-2})$,而对 1,3-丁二醇的氧化为 $\text{Pt}(110)(0.19\text{mA} \cdot \text{cm}^{-2}) > \text{Pt}(111)(0.16\text{mA} \cdot \text{cm}^{-2}) > \text{Pt}(100)(0.13\text{mA} \cdot \text{cm}^{-2})$,Pt(111)是最不容易受毒化物影响的电极。正丁醇和 1,3-丁二醇虽都有四个碳原子且末端碳上都连有一个羟基,但由于分子大小不一且 1,3-丁二醇在 3 位碳上有一另外的羟基,二者的反应活性也就不一样。正丁醇的氧化活性要大于 1,3-丁二醇。

电化学现场 FTIR 反射光谱研究结果指出,正丁醇和 1,3-丁二醇的氧化都遵循如下双途径机理。



现场红外反射光谱的结果指认,正丁醇和 1,3-丁二醇在 Pt 电极上均可发生解离吸附反应,其产物 CO ($\sim 2045\text{cm}^{-1}$ 的峰)为主要的毒性中间体, CO_2 (对应于 2345cm^{-1} 的红外谱峰)为氧化的最终产物。比较 CO 的强度可知,正丁醇的解离吸附速率要大于 1,3-丁二醇。

不同的分子结构导致了活性中间体的不同。在正丁醇的氧化中,对应于水的消耗的 1650cm^{-1} 的正向峰,位于 2983cm^{-1} 和 2891cm^{-1} 附近对应于 CH_3 和 CH_2 的 C-H 振动峰和 CH_3 的不对称和对称弯曲振动峰(1459 和 1359cm^{-1})都可以检测到。另外, 1628cm^{-1} 附近的负向峰说明正丁醇在酸性介质中脱水形成含烯键的物种。同时可见羧酸的特征峰,羧酸的 OH 变

形振动峰和 C-O 振动峰分别位于 1273 和 1211 cm^{-1} , 1396 cm^{-1} 的峰为 O-H 变形振动峰, 1003 cm^{-1} 的峰为 OH...O 面外摇摆振动。最强的 1104 cm^{-1} 的负向峰是由于不同电位下薄层中 ClO_4^- 的量不同所引起的。以上结果说明正丁酸为正丁醇氧化的活性中间体,同时它也是氧化产物。

在 1,3-丁二醇的氧化中,位于 2993 和 2915 cm^{-1} 的双极峰可分别指认为 CH_3 和 CH_2 不对称振动, 1464 和 1365 cm^{-1} 的峰为 $-\text{CH}_3$ 的不对称和对称弯曲振动, CH_3 的平面内摇摆振动峰出现在 1018 cm^{-1} 附近。在酸性介质中,1,3-丁二醇脱水形成含烯键的物种, $>\text{C}=\text{C}<$ 振动峰出现在 1628 cm^{-1} 和 1600 cm^{-1} , 1303 cm^{-1} 的峰可指认为 $-\text{CH}=\text{CH}_2$ 基团中 CH 平面内变形振动峰。 1496 cm^{-1} 附近的峰对应于 CH_2 的剪式振动。提高分辨率到 8 cm^{-1} , 1720 cm^{-1} 的峰分裂为 1724 和 1712 cm^{-1} 两个峰,它们分别对应于酮和羧酸的羰基振动峰,故 $\text{CH}_3\text{COCH}_2\text{COOH}$ 为可能的中间体。归属于羧酸功能团的谱峰有 1396 cm^{-1} 附近的 C-OH 面内弯曲振动, 1281 cm^{-1} 的 C-OH 变形振动。此外, 1650 cm^{-1} 的对应于水消耗的正向峰和 1111 cm^{-1} 对应于 ClO_4^- 的谱峰都可以检测到。从这些谱峰我们可推测 1,3-丁二醇解离吸附产物可能为 CO (2045 cm^{-1}), $\text{CH}_3\text{CHOHCH}_3$, $\text{CH}_3\text{CH}=\text{CH}_2$ (前者的脱水产物), 而 $\text{CH}_2=\text{CHCH}_2\text{COOH}$, $\text{CH}_3\text{CH}=\text{CHCOOH}$, $\text{CH}_3\text{COCH}_2\text{COOH}$ 为氧化的中间体。从 CO_2 和 C=O 谱峰强度的比值来看,1,3-丁二醇比正丁醇更容易产生 CO_2 物种。这是由于 1,3-丁二醇氧化的活性中间体复杂,能氧化到 CO_2 的途径较多的原因。

电极的表面结构是影响电催化活性的最重要因素。我们在铂电极上修饰三种不同类型的吸附原子(Bi,Sb,S)来改变铂电极对 1,3-丁二醇氧化的催化活性。结果表明,Bi,Sb,S 这三种吸附原子都通过第三体效应影响醇的氧化。它们占据 Pt 表面的活性位,使剩余的连续的活性位小于醇氧化所需要的连续 Pt 表面位而部分阻碍了醇的氧化。例如,在修饰了 Sb 原子的铂电极上,1,3-丁二醇正向扫描的第一个氧化峰电流密度下降为 $0.17\text{ mA}\cdot\text{cm}^{-2}$,而在未修饰铂电极上为 $0.37\text{ mA}\cdot\text{cm}^{-2}$ 。我们第一次发现 Sb 和 S 吸附原子在较高的覆盖度下改变了 1,3-丁二醇氧化对反应途径的选择性。它们都有效地抑制了解离吸附产物 CO 的产生从而阻碍了 1,3-丁二醇通过毒性中间体的氧化途径。

但在 Pt/Sb_{ad} 电极上获得的红外光谱中 CO_2 谱峰强度与 CO 谱峰强度之比远大于在未修饰铂电极上所获得的数值(在未修饰铂电极上这一比值接近于 1 而在 Pt/Sb_{ad} 电极上最大值可达 5.12),说明 Sb 吸附原子的存在使氧化朝着更有利于生成 CO_2 的方向进行。这是由于 Sb 原子属于吸附氧的物种,它能在比铂形成表面氧化物更负的电位下吸附氧并将这些氧贡献给 1,3-丁二醇,使醇的氧化更彻底。Sb 吸附原子的另外一个催化性能还表现在它使 1,3-丁

二醇的氧化电位提前大约 0.14V(覆盖度大于 0.86 时,从 0.53 到 0.39 V)。

与 Sb 相反,S 吸附原子在高电位下自身被氧化成 HSO_4^- ,因此它首先获取电极附近的氧物种(这些氧物种也是 1,3-丁二醇氧化到 CO_2 所需的),从而抑制了 1,3-丁二醇断键物种及中间体羧酸进一步氧化生成 CO_2 的反应途径,使反应朝着更有利于生成羧酸的方向进行。因而只有在高电位(>1.0 伏)下吸附 S 被氧化后才开始观察到 CO_2 的谱峰(2045 cm^{-1})。

至于 Bi 吸附原子,由于在我们的实验方法中获得的最大覆盖度仅为 0.41,即相当于约 14%的 Pt 表面位被 Bi 原子占据(根据一个 Bi 吸附原子抑制三个 Pt 表面位),在此情况下它并未表现出明显的催化效应,反而部分抑制了 1,3-丁二醇的氧化,这可以从在 Pt/Bi_{ad} 电极上获得的 CO_2 和 C=O 谱峰的强度以及它们的比值接近于在干净铂电极上获得的结果看出。

本论文获得的结果不仅对于发展表面电化学和电化学催化基础理论有重要价值,而且具有潜在的应用前景,如直接燃料电池中高性能电催化剂表面的制备和电有机合成中产物选择性的提高,等等。

论文分五章,各章主要内容提要如下:

第一章 引论。在参考了 72 篇文献的基础上,简介了有机分子电催化氧化研究的意义和研究方法进展,并阐述了本论文的研究目的和预期结果。

第二章 实验部分。主要介绍了两种电化学方法(循环伏安和微机控制电化学暂态方法)和两种谱学技术(电化学现场傅立叶变换红外反射光谱法和电化学光电子能谱方法)。同时,介绍了铂电极上修饰吸附原子(Sb, Bi, S)方法。

第三章 报道了铂表面氧化态对有机分子醇电氧化的影响。

第四章 在分子水平上阐述了正丁醇和 1,3-丁二醇的电氧化反应机理,并考察了电极表面的结构效应和反应物的分子结构效应。

第五章 研究了铂电极表面修饰不同的吸附原子(S, Sb, Bi)后对 1,3-丁二醇氧化的催化活性的影响。

第六章 总结了论文工作所获得的主要研究结果。

关键词

表面电化学 红外光谱 电化学催化

**ELECTROCATALYSIS AT ATOMIC AND
MOLECULAR LEVEL**

STUDIES OF THE ELECTROOXIDATION OF C₄ ALCOHOL
AND THE ROLE OF STRUCTURE AND OXIDATION
STATES OF PLATINUM SURFACE

BY

NANHAI LI

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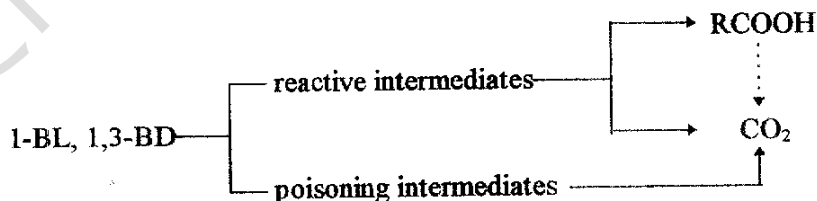
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Abstract

The research on electrooxidation of small organic molecules is a subject of both fundamental and application for electrocatalysis. The alcohol containing four carbon atoms has great interest in studies of the effect of molecule structure due to the existence of various isomers. In the studies of this thesis, cyclic voltammetry, programmed potential step technique, in situ FTIR spectroscopy and X-ray photoelectron spectroscopy were combined to investigate the electrooxidation of C_4 alcohol on Pt electrode, and the influence of adatoms (Sb, Bi, S) on the electrocatalytic activity of Pt electrode towards the oxidation of 1,3-BD. Also, the role of different oxidation states of Pt surface in alcohol oxidation was investigated. All these results have great significance in divers applications, especially in electrocatalysis of fuel cells and electrosynthesis.

Different oxidation states of Pt surface oxide play a key role in the oxidation of alcohol. The Pt oxides are distinguished as active and poison species. The active oxide is in lower oxidation states. The oxide formed at potential higher than 1.0V (e.g., $Pt(OH)_2$) is a poison while other lower states of Pt oxides such as PtO, $Pt(OH)_2$, PtOH are the possible active oxide for alcohol oxidation. These results provided further understanding on the reaction mechanism of electrooxidation of small alcohol.

The oxidation of 1-BL and 1,3-BD is a surface structure sensitive reaction. Among the three basal planes of Pt single crystal, Pt(110) displays the highest electrocatalytic activity while Pt(111) is the most stable surface. The reactivity of 1-BL is higher than that of 1,3-BD. The electrooxidation of both 1-BL and 1,3-BD obeys the dual-path reaction mechanism, i.e.,



As determined by in situ FTIRS, CO species was the main poisoning intermediate involved in 1-BL and 1,3-BD oxidation, and CO₂ was the final oxidation product. The reactive intermediates varied with 1-BL and 1,3-BD. Butyric acid and acetoacetic acid may be the main reactive intermediates for 1-BL and 1,3-BD oxidation, respectively. These species were also served as the reaction product compounds. The oxidation of 1,3-BD can produce CO₂ more easily than that of 1-BL does. The oxidation mechanisms of 1-butanol and 1,3-butanediol were proposed for the 1st time, which is quite meaningful in understanding the anodic processes of direct fuel cells of small organic molecules.

In order to obtain a suitable electrocatalyst for 1,3-butanediol oxidation, Pt electrode was modified with different adatoms (Bi, Sb, S) to change its electrocatalytic activity. The results pointed out that all these three adatoms influence the electrocatalytic oxidation of 1,3-BD by a "third-body" effect. The modification of both Sb and S adatoms at high coverage can successfully raise the selectivity of reaction pathways but in different ways, according to their ability to adsorb oxygen. They both hinder the dissociation of 1,3-BD into CO thus preventing the oxidation via the poisoning intermediate. The principal oxidation pathway of 1,3-BD on Pt electrode modified with high coverage of Sb_{ad} is towards the production of CO₂ with the help of oxygen adsorbed on Sb_{ad}. While on Pt/S_{ad} electrode the oxidation of 1,3-BD is oriented to the production of carboxylic acid containing C=C bonds, because the oxidation of S_{ad} captured firstly the oxygen species which were required in the oxidation. Moreover, Sb adatoms make the oxidation potential of 1,3-butanediol shift to a negative value. These results threw a light on seeking the best electrocatalyst for fuel cells and controlling the product-selectivity in electrosynthesis.

This thesis consists of 6 chapters. It has been organized as follows:

Chapter 1 is the introduction. It reviewed, based on 72 reference papers, the significance and the development of research on electrocatalytic oxidation of small organic molecules. Also, The purpose of studies of this thesis was also outlined in this chapter.

Chapter 2 described the experimental details. Two electrochemical methods (cyclic voltammetry and programmed potential step) as well as two spectroscopic techniques (in situ FTIRS and EC-XPS) have been introduced. The technique of modifying Pt electrode surface with adatoms (Bi, Sb, S) was also be given.

Chapter 3 studied the role of oxidation states of Pt surface oxide in the electrocatalytic oxidation of small alcohol molecules.

Chapter 4 concentrated to investigate the reaction mechanism of electrooxidation of 1-butanol and 1,3-butanediol on Pt electrodes. The effect of molecular structure of reagents and the effects of surface structure of Pt electrode was demonstrated.

Chapter 5 investigated the influence of adatoms (S, Sb, Bi) on electrocatalytic activity of Pt surface upon the 1,3-butanediol oxidation.

The main conclusions obtained from studies throughout this thesis have been summarized in the last chapter, chapter 6.

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Chapter 1 Introduction

1.1 Overview

The electrocatalytic oxidation of small organic molecules has become a subject of growing interest since the beginning of 1960s, when the modern interest in fuel cells arose with concerns programs of human space navigation. Fuel cells using hydrogen as fuels, which have theoretically the ability of converting directly the chemical energy into electrical energy without the limitations due to Carnot's theorem (i.e., with a high energy efficiency), have been employed successively to power the Gemini and Apollo space crafts. Since then tremendous efforts have been undertaken to develop fuel cells which can use hydrocarbons as fuels and can be employed in terrestrial duties. At the present, fuel cells are particularly attractive for autonomous power source in the demand of our society development on clean and efficient energy^[1-2].

In such fuel cell applications, the rate of conversion of the organic compound by oxidation into carbon dioxide has to be as high as possible, in order to obtain the maximum energy available from the fuel and thus the maximum efficiency. However, the incomplete oxidation of organic molecules is also of great interest in organic electrosynthesis, rigorous control of the experimental conditions may allow such reactions to become highly selective, leading to the development of industrial processes for the production of chemicals based on electrochemical oxidation.

Excepting the application in energy conversion and electrosynthesis, the significance of studying the electrocatalytic oxidation of small organic molecules is evident in many fields of fundamental researches. The relatively simple structure of small organic molecules makes it possible to understand clearly the reaction mechanism of these molecules, which is very helpful in elucidating the reaction mechanism of complex molecules used in electrosynthesis or as additives in many

applications (electroplating, metal protecting etc.) Besides, the reaction of small organic molecules, especially the C_1 molecules ($CO^{[3]}$, $HCOOH^{[4]}$, $CH_3OH^{[5]}$, $HCHO^{[6]}$), can serve as probes to test the performances of electrocatalysts. This reaction is often used to investigate the effect of surface structure upon the catalytic properties of electrocatalyst.

The extensive studies reported recently in the literature on electrocatalytic oxidation of small organic molecules may consist mainly in two aspects: the effect of surface structure of electrode and the effect of molecular structure of reagents.

1.1.1 the effect of surface structure of electrode

Electrocatalysis plays a key role in the mechanism of electrochemical reactions at solid/liquid interfaces. The kinetics of electrocatalytic reactions depends strongly on the chemical nature, the electronic structure, and the atomic arrangement of electrode surface. Thus, the surface nature and the surface structure of an electrode are the most important factors determining its electrocatalytic properties^[7].

The electrocatalytic activity of an electrode can be altered to a large extent by changing simply the electrode material from transition metals to noble metals. A typical example was known that in acid solutions the platinum appears to be the best electrocatalyst sufficiently active and stable for practical application, while the gold displays high electrocatalytic activity in alkaline medium^[8].

The geometry and the electronic structure of electrode surface can be easily varied using different planes of single crystal. Studies of well-defined and well-controlled platinum single-crystal electrodes were firstly developed by Clavilier et al. in 1980^[9]. The electrode was annealed in a hydrogen + oxygen flame to recover the initial state of clean and well-defined surface and quenched with ultrapure water, it was then transferred to the electrochemical cell under the protection of a water droplet. The single crystal electrodes of Pt, Au and Ir, have been used extensively to study the electrooxidation of small organic molecules such as HCHO, HCOOH, CH_3OH and CO etc.^[10,11,12,13]. The results demonstrated that different single-crystal

planes of the same metal behave very differently in the electrooxidation of small organic molecules, yielding different reactivity for adsorption and oxidation of organic molecules. Of the three low-index planes of platinum single-crystal, the catalytic activity of (110) in 1,3-butanediol oxidation is close to that of (100) but is greater than the electrocatalytic activity of (111). However, the (111) plane is the most stable in considering the sensitivity of these single-crystal planes to poisoning effect^[14].

The electrocatalytic activity may be improved by using different materials containing more than one element as electrodes, such as binary alloys, intermetallic compounds^[15] and amorphous^[16]. These materials lead usually to enhance the rate of electrocatalytic oxidation of small organic molecule via a synergy effect. For example, the enhancement in electrocatalytic activity reported for oxidation of formic acid at Pt/Rh^[17], Pt/Pd^[18] and Pd/Au^[19] alloy electrodes, and for oxidation of methanol at Pt/Rh^[20] and Pt/Pd^[21] alloy electrodes, and also for the oxidation of ethylene glycol at Pt/Au/Pd^[22] electrodes.

Another convenient way to enhance the electrocatalytic activity of a given metallic electrode is to modify the surface with various foreign adatoms, such as Cu, Ag, Tl, Hg, Pb, As, Bi, Te and Se; Ge, Sn and Sb, either by irreversible adsorption^[23] or by underpotential deposition^[24-35].

The enhancement effect of adatoms has been interpreted by "third body" effect^[32] or by the effect of modification of the geometric structure of surface^[31]. It has been considered that the number of Pt sites occupied by an adatom is different for different adatom species, which gives different effect in oxidation of small organic molecules. It has been considered that a minimum number of contiguous surface sites may be required for taking place a particular reaction^[36,37].

It existed an alternative explanation which is based on the experimental fact that the Ru^[38], Ge^[39], Sn^[40], As^[41], Sb^[42] adatoms can adsorb oxygen at a potential more negative than the potential of oxygen adsorption on Pt surface. As the oxygen atoms adsorbed by these ad-atoms can be donated to a molecule or a reaction intermediate adsorbed on Pt sites adjacent to the ad-atoms, the oxidation process was

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