

Au(111) 表面上乙醇选择性氧化反应机理的密度泛函理论研究

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摘要 采用密度泛函理论研究了吸附有 O 原子的 Au(111) 表面上乙醇选择性氧化的反应机理. 反应结果表明, 除 O 原子和中间产物二齿醋酸根 (CH₃CHOO) 外, 其他中间产物在 Au(111) 表面扩散能垒均较低, 不会对反应速控步骤的确定造成影响. 乙醇羟基氧化脱氢为反应的第一步, 当氧化剂为吸附态的 O 原子或者为 OH 基时, 反应活化能分别为 0.20 和 0.17 eV. 氧化产物乙氧基 (CH₃CH₂O) 进一步氧化脱氢生成乙醛则需要表面吸附的 O 原子或另一表面吸附的 OH 基的参与, 所需活化能为 0.29 或 0.27 eV. 同时, 乙醛易与表面吸附的乙氧基反应生成乙氧基半缩醛 (CH₃CHOOC₂H₅), 其可进一步与 O 原子作用, 脱氢形成乙酸乙酯. 此外, 在乙醛深度氧化成酸的过程中需要克服较高的反应能垒, 因而在表面反应温度较低时无法进行, 这与实验结果相符.

关键词: 反应机理 选择性氧化 乙醇 金(111) 密度泛函理论

Abstract: The reaction mechanism of selective oxidation of ethanol on Au(111) covered with atomic oxygen was described employing density functional theory calculations. The first step, dissociation of the O-H bond in ethanol, has lower barrier for transfer of the H to adsorbed oxygen or surface hydroxyl than to gold with a barrier of 0.20 or 0.17 eV, respectively. The two lower activation energies for the β-H elimination of ethoxyl, 0.29 and 0.27 eV, come from transfer of H atom to surface O atom or another ethoxyl. Ethyl acetate is formed through the β-H elimination of ethoxy hemiacetal. The formation of acetic acid is not facile through the reaction between the surface hydroxyl and acetaldehyde or between the surface oxygen and acetaldehyde at low temperature due to a high activation barrier. Except for surface oxygen and bidentate acetate, all other surface species have low diffusion barriers, suggesting that rearrangement and movement of these species from the preferred adsorption sites to the ideal configurations for reactions are facile.

Keywords: mechanism, selective oxidation, ethanol, Au(111) surface, density functional theory

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