醇气相氧化催化剂 Au/Ni-fiber 活性位 Ni_2O_3-Au^+协同作用的光谱解释

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醇选择性催化氧化制备相应的醛酮是化工过程中非常重要的反应，到目前为止，许多催化剂被开发应用于该反应[1]。我们所开发的苯甲醇气相氧化制备苯甲醛催化剂Au/Ni-fiber，具有有趣的活性结构NiO@Au（即较大的Au颗粒被较小的NiO碎片部分覆盖），并且在Au颗粒和NiO界面处存在Ni_2O_3-Au^+协同作用[2]。为了进一步研究该协同作用，我们制备了以下三个样品：在苯甲醇气流中通O_2反应0.5 h制得工作状态下的样品1；断O_2后在苯甲醇气流中继续反应0.5 h制得样品2；再次通O_2反应0.5 h制得样品3。并采用XPS和XAFS对样品进行了谱学表征。结果表明(Fig. 1)：在O_2通-断-通的过程中，苯甲醇转化率和Au^+含量都出现了高-低-高的剧烈变化，伴随着这种剧烈变化，Ni_2O_3含量体现出轻微的高-低-高的变化，但是NiO的变化规律恰好相反。由上可知：Au^+和Ni_2O_3之间存在重要的协同关系，Au^+是醇氧化的活性中心，而Ni_2O_3即可以促使并稳定Au^+的存在，又可以起到活化O_2的作用，活性氧然后转移到Au^+上实现对醇的氧化。

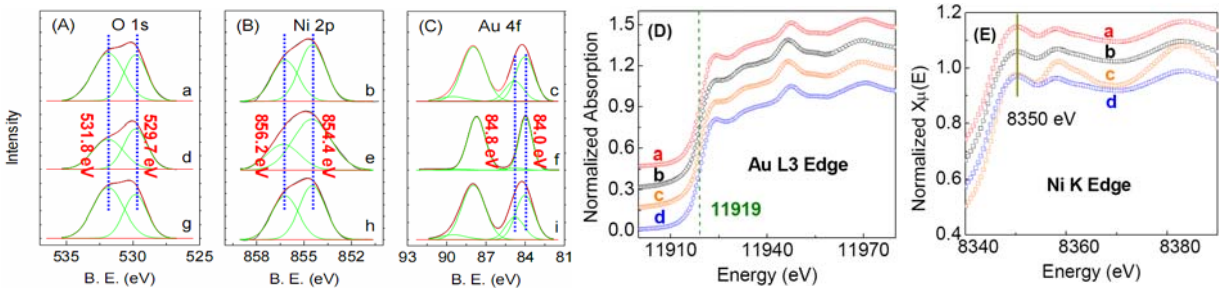

Fig. 1 XPS (A-C) and XANES (D-E) analysis of the catalyst Au/Ni-fiber over several samples. (A-C) a-c: sample 1; d-f: sample 2; g-i: sample 3; (D) a: sample 1; b: sample 2; c: Au foil; d: sample 3; (E) a: sample 1; b: sample 2; c: Ni foil; d: sample 3.

关键词： 金催化；镍；活性位；有氧氧化；醇

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The Spectroscopic Evidences for the Ni_2O_3-Au^+ Active Sites in Catalyst Au/Ni-fiber for the Low-temperature Gas-phase Oxidation of Alcohols

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An interesting date-cake-like ensembles of NiO@Au (*i.e.* 20-30 nm gold particle, like a cake, partially covered with very small NiO segments, like dates) are definitely identified to be highly active for low-temperature gas-phase oxidation of alcohols. On such NiO@Au ensembles, unique hybrid active-sites of Ni_2O_3-Au^+ are defined, bringing a step closer to the truth of the excellent low-temperature activity. By nature, the Ni_2O_3 specimens not only promote the formation of Au^+ ions and stabilize them, but act as also an oxygen supplier that is proposed to transfer oxygen species onto the Au^+ sites to react with alcohol there.