

## Ce-Zr 复合氧化物负载 Au 纳米粒子催化甲醇氧化反应中的载体效应

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**摘要** 采用沉积-沉淀法制备了不同 Ce/Zr 比的 Au/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> (x = 0, 0.2, 0.4, 0.6, 0.8) 催化剂, 研究了其催化甲醇完全氧化反应和选择氧化反应中的载体效应. 通过 X 射线衍射、拉曼光谱、X 射线光电子能谱、高分辨透射电镜、CO<sub>2</sub> 和 NH<sub>3</sub> 程序升温脱附以及 CO 吸附红外光谱等手段表征了催化剂的结构、组成和酸碱性. 结果表明, 这些催化剂具有相似的载体粒径和晶相结构、Au 担载量、Au 粒径和价态以及相似的表面酸碱性等. 在甲醇完全氧化和甲醇选择氧化反应中, Au/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> 催化剂活性均随载体中 Ce/Zr 比的减小而降低. 与催化剂储氧量, 即表面活性氧浓度下降一致. 对于甲醇选择氧化反应, 甲酸甲酯选择性则随 Ce/Zr 比减小而升高. 这不是由于催化剂表面酸碱性质差异所致, 而是与催化剂载体中 Ce 含量降低导致的表面活性氧浓度减小和催化剂的氧化能力减弱密切相关. Au 催化剂载体效应本质的认识将有助于为目标氧化反应设计具有更高活性或选择性的催化剂体系.

**关键词:** 氧化铈 氧化锆 复合氧化物 纳米金 甲醇氧化 载体效应 储氧量 甲酸甲酯

**Abstract:** Ce-Zr oxide-supported nano-sized Au catalysts Au/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> (x = 0, 0.2, 0.4, 0.6, 0.8) were prepared by a deposition-precipitation method. Their catalytic properties were examined in both the combustion of methanol and the selective oxidation of methanol to methyl formate. The composition and structure of the catalysts were characterized by complementary methods including nitrogen physisorption, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and high resolution transmission electron microscopy. Their acidity and basicity were probed by CO<sub>2</sub> and NH<sub>3</sub> temperature-programmed desorption and also Fourier transform infrared spectroscopy for CO adsorption. The characterization results showed that the catalysts possessed similar particle size and phase of the Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> supports, and their Au nanoparticles were of around 3.0 nm mainly in the state of Au<sup>0</sup>. In the CH<sub>3</sub>OH combustion reaction (1% CH<sub>3</sub>OH + 14% O<sub>2</sub>), the activity of the Au/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> catalysts decreased with decreasing the Ce contents in the Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> supports. Similar change was also found in the methanol selective oxidation (6% CH<sub>3</sub>OH + 3% O<sub>2</sub>), while the selectivity to methyl formate increased with decreasing the Ce contents. Such changes in the catalytic activity of the Au/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> catalysts were in positive parallel with their oxygen storage capacity values, which reflect the number of the lattice oxygen atoms active for the methanol oxidation. The support effects on the selectivity for methyl formate were clear not due to effects of the supports on the acid-base properties of the catalysts but to the effects on the active lattice oxygen atoms on catalyst surfaces and consequently their reducibility. Such understanding on the support effects provides useful information for design of oxide-supported Au catalysts with improved activity or selectivity for the targeted oxidation reactions.

**Keywords:** ceria, zirconia, mixed oxide, nano-gold, methanol oxidation, support effect, oxygen storage capacity, methyl formate

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