

Rational synthesis of heterostructured active centers for Au nanocatalysts

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Introduction

Since Haruta's pioneering work in 1987 on the extraordinary catalytic activity of nanoscale gold particles for CO oxidation at low temperature,¹ synthetic methodologies for the preparation of gold nanoparticle catalysts have been extensively investigated. These include precipitation deposition,^{2,3} co-precipitation, ligand-assisted deposition,⁴ ion exchange,⁵ and colloidal deposition.^{6,7} Among these synthetic methods, the colloidal deposition (CD) is relatively new and has recently gained an increased popularity due to the advancement in solution-phase syntheses of monodispersed Au nanoparticles and deposition of these nanoparticles on various supports without the constraint of support surface properties (e.g., isoelectric point). In this CD methodology, gold nanoparticles are pre-synthesized and subsequently deposited on supports via wet impregnation or incipient wetness.^{6,7} The key drawback associated with the CD technique is that the pre-synthesized gold nanoparticles are only physically dispersed on oxide supports and the resultant gold catalysts lack direct metal-support interactions. Furthermore, these catalytic systems have limited thermal stabilities and often sinter under high-temperature catalytic reaction conditions.^{3,6} To overcome this intrinsic deficiency, we herein report a new CD methodology for the synthesis of sintering-resistant nanocomposite Au catalysts based on dumbbell-structured Au-Fe₃O₄ nanoparticles (Figure 1) and other Au-oxide heterostructured nanoparticles. Highly active gold catalysts for CO oxidation were prepared on carbon, silica, and titania.

Materials and Methods

Au-Fe₃O₄ dumbbell nanoparticles were prepared according to a literature method via in-situ decomposition of HAuCl₄ and Fe(CO)₅.⁸ By adjusting the Au/Fe molar ratio to 1:10, we have obtained the nanoparticles with Au particle size of 2.5-3.5 nm and Fe₃O₄ particle size of 15-16 nm (both in diameter), as analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. The dumbbell nanoparticles were then washed with

hexane/ethyl alcohol to remove extra surfactants and their hexane dispersion was deposited on amorphous silica, carbon, or titania supports. Solvent evaporation gave powders that appeared black for Au-Fe₃O₄/SiO₂ and Au-Fe₃O₄/C, and purple for Au-Fe₃O₄/TiO₂.

Results and Discussion

The essence of our new CD methodology is based on the self-assembly of dumbbell-like Au-Fe₃O₄ nanoparticles on various supports.⁸ The key structural feature of these nanoparticles is that each dumbbell consists of a gold nanoparticle at one end and an iron-oxide nanoparticle at another end. Due to the epitaxial growth of Fe₃O₄ on Au,⁸ a strong metal-oxide interaction exists at the interface of the dumbbell heterostructure. The dumbbell nanoparticles intrinsically entail a highly stable metal-oxide interface and therefore there is no need for these heterostructured nanoparticles to develop metal-support interactions. Our catalysis experiments indicated that the supported dumbbell-like Au-Fe₃O₄ nanoparticles showed significant activities for CO oxidation. Interestingly, different supports give rise to different catalytic light-off curves for CO oxidation. The CO oxidation mechanism on the surface of the Au-support catalyst proposed by Bond and Thompson suggests that the active sites are within 4 layers at the Au-support interfaces and the long-distance influence of solid supports on the catalytic activities of Au nanoparticles is negligible.⁹ If this holds true, then the pure dumbbell Au-Fe₃O₄ nanoparticles should have similar light-off curves compared with the supported catalysts. The observed differences among the pure dumbbell particles and three supported catalysts indicate that supports are involved in the formation of active sites by support-Au-Fe₃O₄ interfaces.

Significance

We developed a new bottom-up methodology to introduce Au catalysts on supports via heterostructured nanoparticles. Highly active Au catalysts for CO oxidation were prepared by using TiO₂, SiO₂, or even C as supports.

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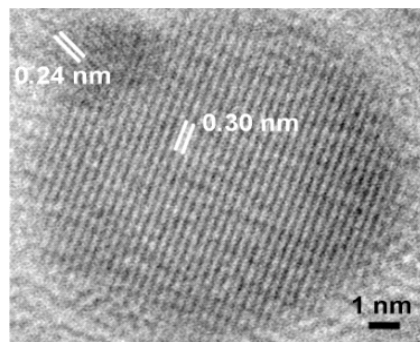


Figure 1. High-resolution TEM image of a single dumbbell-structured Au-Fe₃O₄ nanoparticle.