

Structure and stability of core-shell AuTiOx nanoparticles for CO oxidation

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Background

A catalyst's stability and longevity under operating conditions is key for their long-term application in industrial processes. This calls for an understanding of deactivation mechanisms to advance catalyst design strategies that can counteract such mechanisms. Here we focus on gold (Au) nanoparticles (NPs) as a catalyst for the CO oxidation reaction (1). Specifically, we demonstrate that NPs formed by titanium (Ti) and Au alloying enables the development of an anchoring shell over the Au NPs, that suppresses sintering during operation. This new design strategy could be generally applicable and offers a higher degree of flexibility in preparing sinter-resistant catalyst nanoparticles. Here we report the synthesis, structural characterization and stability testing of colloidal core-shell AuTiOx nanoparticles, displaying improved stability under thermal CO oxidation conditions on silicon nitride and TiOx supports (2).

Method

An Au_{0.5}Ti_{0.5} alloy target was used to synthesize mass-selected nanoparticles of 160k amu under high vacuum conditions onto material supports that were used for the present characterization. Ion Scattering Spectroscopy (ISS), X-ray Photoelectron Spectroscopy (XPS) and High-Resolution Transmission Electron Microscopy (HRTEM) were used to elucidate the structure and chemical composition of the synthesized NPs. The catalytic characteristics of the AuTiOx NPs were then studied by performing comparative studies of the NPs and reference Au NPs under CO oxidation conditions. The NPs deposited on silicon nitride were studied by HRTEM under reactive conditions, by introducing a few mbar CO and O₂ at various sample temperatures in a FEI Titan ETEM operated at 300 kV. Precautions were taken to acquire images of areas that were previously unexposed to the electron beam to differentiate beam-induced and environment-induced phenomena. The CO oxidation activity of the NPs deposited on TiOx were studied by running flow reactor experiments with the samples and reactive gasses at various temperatures and measuring gas conversion via a quadrupole mass spectrometer.

Results

ISS of the as-synthesized NPs, produced from the Au_{0.5}Ti_{0.5} alloy, showed that only a small portion of the outermost layer contained Au atoms. HRTEM imaging of the nanoparticles after air exposure demonstrated that the NPs were composed of a 2.1±2 nm metallic Au core phase surrounded by a lighter ~0.8 nm shell. By XPS measurement the shell layer was identified as primarily consisting of TiOx. Imaging of the NPs in the reactive environment showed that a filament growth mechanism was present in the interface between the Au NPs and silicon nitride support at temperatures ≥200 °C, mobilizing the Au NPs. The AuTiOx NPs maintained their core-shell shape and size up to at least a temperature of 400 °C and did not demonstrate any growth mechanisms. This finding suggests that the TiOx shell acts as a protective layer for the Au NPs in this instance. Comparative activity measurements of the AuTiOx and Au NPs deposited on a TiOx support showed an improved stability of the NP activity for the AuTiOx NPs in comparison to the Au NPs. Furthermore, the AuTiOx NPs showed a characteristic in which their activity increased over time after the sample

temperature was increased. In certain cases, the activity would increase by >2 fold over the span of hours while maintaining a certain temperature. This phenomenon was observed to be reversible when lowering the sample temperature. Nonetheless, the average NP site turnover frequency (TOF) was lower for the AuTiOx NPs than the Au NPs, likely due to a blocking of active sites on the core-shell structure.

Conclusion

Characterization of the AuTiOx alloy nanoparticles revealed an Au core and TiOx dominant shell containing small traces of Au atoms. Supported on silicon nitride, the Au NPs were observed to facilitate a filament growth under CO oxidation conditions while the phenomenon was not observed for the AuTiOx NPs, suggesting that the TiOx shell can act as a protective layer. Activity measurements of the NPs supported on TiOx, showed a time dependent deactivation was observable for the Au NPs and not for the AuTiOx NPs. The average TOF of the core-shell NPs was observed to be lower than the Au NPs, which could be explained by a blocking of NP active sites by the shell layer. Treatment methods to enhance the shell layer porosity could likely improve the activity of the core-shell nanoparticles while maintaining their stability characteristics. Development of such colloidal alloy NPs could lead to significant advances in producing highly stable catalysts for industrial use.

Keywords:

Stability, alloy nanoparticles, electron microscopy

Reference:

1. Haruta M. Chance and necessity: my encounter with gold catalysts. *Angew Chem Int Ed Engl.* 2014 Jan 3;53(1):52-6. doi: 10.1002/anie.201305987. Epub 2013 Nov 27. PMID: 24285610.
2. Tankard RE, Romeggio F, Akazawa SK, Krabbe A, Sloth OF, Secher NM, Colding-Fagerholt S, Helveg S, Palmer R, Damsgaard CD, Kibsgaard J, Chorkendorff I. Stable mass-selected AuTiOx nanoparticles for CO oxidation. *Phys Chem Chem Phys.* 2024 Mar 20;26(12):9253-9263. doi: 10.1039/d4cp00211c. PMID: 38445363.
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