

Ligand and support effect on supported Au nanoclusters in selective hydrogenation of alkynes

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The application of metal nanoparticles for heterogeneous catalysis has significantly increased due to the advancement of nanoscience and the adaptable chemistry of these materials. Among these materials, thiole protected gold nanoclusters (Au_n(SR)_m) have emerged as catalysts of notable catalytic activity. These novel nanomaterials possess intriguing molecular-like characteristics, precise molecular structures, and atomic-scale production capabilities. Their small particle sizes enable activity across diverse catalytic processes. However, their efficacy is contingent upon multiple parameters, including the nature of ligands, doping, pretreatment conditions, and support materials. One of the most promising doped nanoclusters is the Ag_xAu_{25-x} cluster. Here, the Ag atom does not occupy the central position but sits on a surface site. The change in electronic structure can lead to enhanced structural flexibility and increased catalytic activity.

Catalytic hydrogenation is a crucial process technology in various industries, making up around 25% of all chemical reactions. Usually, these events are caused by the homolytic dissociation of H₂ on the surface of noble metals like Pt, Pd, and Rh. Due to its importance in producing fine chemicals and polymers, the semi-hydrogenation of alkynes has drawn attention to several catalytic hydrogenation reactions. However, these commercially used catalysts often lead to an over-hydrogenation and offer no selectivity. Therefore, new catalysts are required to achieve more sustainable processes.

Our research investigates the selective semi hydrogenation of phenylacetylene to styrene, revealing the role of support materials, pretreatments, and doping in catalytic performance. Through systematic experimentation of diverse supports such as MgO, Al₂O₃, Zeolite CBV 720, and Mg/Al hydrotalcite, it was observed that the interaction between Au clusters and the support profoundly influence catalytic activity and selectivity. Here, acidity and basicity have the biggest influence. Higher activity is obtained for gold supported on basic materials, with the best results obtained by hydrotalcite for Au₂₅. This was explained by the intermediate basicity of the support that favors the heterolytic cleavage of H₂ while avoiding overreduction. However, the same cannot be said for the Ag doped cluster, which shows the highest activity for Zeolite. The higher activity of the Ag_xAu_{25-x} cluster can be attributed to the different metallic species formed during catalysis. Similarly, Au₁₁ has the highest conversion when supported on Zeolite, possibly due to porosity and cluster size interplay.

Experimental investigations conducted under reductive atmospheres at elevated temperatures involved the thermal activation of catalysts to facilitate ligand removal and enhance accessibility to active sites. These experiments were performed in the gas phase and monitored using a mass spectrometer. Additional characterization methods and in situ synchrotron measurements were performed, where EXAFS, XANES, and XRDS were measured. This provided valuable insight into active sites' reaction dynamics and structural changes.

In conclusion, this research underscores the significance of support materials in designing efficient heterogeneous catalysts for selective organic transformations, offering valuable insights for future research and industrial applications.