

Nanoscale Heterogeneous Catalysis at the Center for Nanophase Materials Sciences
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Scientific Thrust Area

Functionality of “real world” nanomaterials is determined not only by their individual interfacial interactions, but also by the 3-D architectures that result from their assembly.. The goal of CNMS Catalytic Nanomaterials research is to explore these interactions and how they relate to catalytic functionality in nano-structured materials. Our approach integrates new methods of synthesis of nanostructured materials with techniques to probe the resulting catalytic performance and structure of these materials. We have focused on three types of materials, namely, bimetallic nanoparticles, synthetic carbon with tailored morphology, and isolated and interacting catalytic sites on mesoporous silica.

Research Achievement

We have explored the synthesis of isolatable NiAu alloy nanoparticles with tunable and relatively uniform sizes *via* a co-reduction method employing butyllithium as the reducing agent and trioctylphosphine as the protecting agent. NiAu alloy nanoparticles are obtained by these routes and these were then used as the precursor to prepare SiO₂ supported catalyst that can be highly active in low-temperature CO oxidation.[1,2] Pretreatment plays an important role in determining the final structure and activity for catalyzing CO oxidation, due to competing processes of removal of organics, oxidation of Ni, and growth of Au particles. XRD provides evidence that the initially synthesized NPs exist as a mixed reduced alloy. High temperature reductive treatments leads to a core-shell structure enriched in Ni on the outer surface. The combination of EXAFS, XANES and XRD indicates the formation of Au/NiO hetero-aggregate is generated through the oxidative phase separation of the Au@Ni core-shell intermediate. Pretreating the catalyst under optimal conditions, i.e., in H₂ at 600 or 720 °C followed by treating in O₂ at 300 °C, results in an Au-NiO/SiO₂ catalyst that is highly active in CO oxidation.

For comparison, solely pre-treating the bimetallic NiAu/SiO₂ sample in H₂ does not lead to a reasonably active catalyst. The Ni/Au ratio in the precursor NPs is also important for determining the final structure and catalytic activity. The most active Au-NiO/SiO₂ catalyst was obtained by keeping the Ni/Au ratio at 1:1.

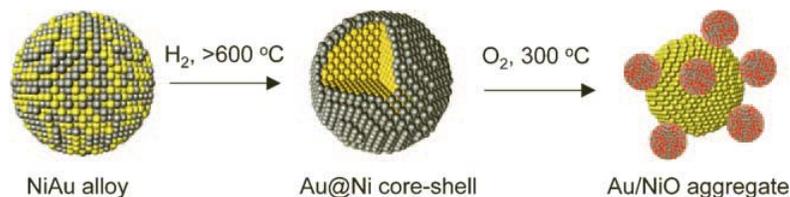


Figure 1. Schematic representation of the phase transformation from NiAu alloy to Au/NiO hetero-aggregate.

The effect of mesopores structure and surface functionalization has also been explored in synthetic carbon catalysts.[3] Carbon is catalytically active for oxidative dehydrogenation reactions, but little is known about the role of nanostructuring and surface functionalization upon the catalytic activity. High-temperature treatments on mesoporous amorphous carbon can convert it to a graphitized mesoporous carbon (GMC) with structure typical of glassy carbon, although the graphitic pore walls are only a few nanometers thick. Closed fullerene-like cavities were observed in this GMC. These cavities can be uniformly opened through air oxidation at 500 °C without affecting the graphitic structure of the glassy carbon. A secondary porosity of 2.5-nm size with complementary oxygenated functionalities was made accessible after oxidation. The oxygenated functionalities can be thermally removed by heating the carbon materials in helium at 1600 °C without affecting the openness of the cavities. Reheating of the oxidized GMC to 2600 °C caused the open fullerene-like cavities to close. Therefore, the fullerene-like cavities can be opened and closed reversibly through air oxidation and heat treatment. The GMCs showed obvious catalytic activities in the ODH reaction when the fullerene-like cavities were open, regardless of the existence of the surface-oxygenated functionalities. The GMC catalysts were deactivated after the fullerene-like cavities were closed by thermal treatment. Therefore, the catalytic activity is related to the openness of the fullerene-like cavities, and these open edges were most likely the active sites of the carbon catalysts in the ODH reactions. We anticipate that this synthesis approach could unravel an avenue for pursuing fundamental understanding of the unique catalytic properties of graphitic carbon nanostructures

Supported transition metal oxide represents an important class of heterogeneous catalyst and has been widely employed in a variety of redox reactions. The determination of the structure of surface metal oxide species is key in understanding the structure-catalysis relationship. Silica-supported vanadium oxide (VO_x/SiO_2) is selected as a model catalytic system and its molecular and electronic structures have been probed with *in situ* multi-wavelength (244, 325, 442, 532, and 633 nm) Raman spectroscopy and UV-visible diffuse reflectance spectroscopy (DRS). An evident resonance Raman effect is observed when the sample is excited with UV wavelengths, as evidenced by (1) detection of overtones up to 5th order of V=O band and combination bands of V-O and V=O, (2) clear detection of new bands related to V-O-Si mode; (3) extremely low detection limit of VO_x species at surface density at least 2 orders of magnitude lower than visible Raman. The observation of the interface modes (V-O-Si) is of catalytic significance since the interface bond is generally considered as the active site for redox reactions. Two different V=O bands are observed indicating at least two different types of isolated VO_x species are present. The new information obtained in this study clearly demonstrates the advantages of using multi-wavelength excitations in Raman characterization of supported metal oxide catalysts.

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Publications

- [1] Zhou, S. H.; Yin, H. F.; Schwartz, V.; Wu, Z. L.; Mullins, D.; Eichhorn, B.; Overbury, S. H.; Dai, S. *Chemphyschem* 9, 2475 (2008).
- [2] Zhou, S.; Ma, Z.; Yin, H.; Wu, Z.; Eichhorn, B.; Overbury, S. H.; Dai, S. *Journal of Physical Chemistry C* 113, 5758 (2009).
- [3] Liang, C.; Xie, H.; Schwartz, V.; Howe, J.; Dai, S.; Overbury, S. H. *J. Am. Chem. Soc.* in press, (2009).