
BES022. Multiscale Tailoring of Highly Active and Stable Nanocomposite Catalysts for the Production of Clean Hydrogen Streams

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Abstract

By utilizing a range of different synthesis methods, we were able to demonstrate that through careful tailoring of composition and structure of both the active metal component and the oxide support matrix in nanocomposite catalysts, it is possible to design catalysts that combine exceptional high-temperature stability with high catalytic activity. Activity and stability of these materials was demonstrated through application in catalytic hydrogen production via catalytic partial oxidation of methane and water-gas-shift. Finally, implementation of these nanocomposites into a “macroscopic” support structure was demonstrated.

Progress Report

Below, we will use select examples from the project results to highlight and illustrate major findings from the investigations based on systematic tailoring of composition and structure of the support and the active (metal) component in order to reconcile high thermal stability with high activity in nanocatalysts.

Tailoring for Stability via Embedding: Metal-BHA Nanocomposites

Based on a rather straightforward, single-pot synthesis, a wide range of high surface area metal/oxide nanocomposite materials was successfully synthesized (including Pt, Rh, Pd, Au, Ni, Cu, Fe, Co, and Zn as (active) metal components, and BHA (barium-hexaaluminate), silica, magnesia, ceria, and La_2O_3 as oxide matrices) and the thermal stability of these materials was demonstrated. In particular BHA-based materials showed excellent high-temperature stability, which could be traced back to a simple “caging” of metal nanoparticles in the highly interconnected pore network of the BHA matrix. This is illustrated in figure 1 (bottom) shows the close agreement between Pt particle size (bars) and BHA pore neck size (blue line) for a Pt-BHA catalyst after calcinations at 600°C. Through a simple dip-coating procedure, it was furthermore possible to anchor this nanocomposite material onto different support structures, resulting in a robust, easy-to-handle catalyst formulation without compromising the carefully controlled nanostructure of the catalyst (see figure 1, top). The resulting catalysts showed excellent activity in partial oxidation of methane (Pt-BHA) as well as in chemical looping combustion (Ni-BHA & Cu-BHA) and chemical looping steam reforming (Fe-BHA). Overall, these results indicate

Objectives

The design of catalysts at the nanoscale offers vast opportunities the development of novel materials that meet the technological needs of fuel processing applications. To enable this vision, however, the current understanding and control of mechanical, thermal and chemical properties of nanomaterials needs to be improved. In particular nanocomposites hold vast potential, since they allow the targeted combination of characteristics which can reconcile often contradictory demands such as high activity (i.e. small particles) and good stability (i.e. larger particles). It is the objective of the present project to demonstrate this potential via systematic investigation (i.e. synthesis, characterization, and catalytic test) of nanocomposite materials for fuel processing applications with particular emphasis on thermal stability of the resulting materials.

Technical Barriers

Emergent novel properties on the nanoscale make nanomaterials highly interesting for heterogeneous catalysis. However, their low thermal stability currently restricts their use to low-to-moderate temperature conditions ($T < 500\text{C}$) and thus imposes severe limitations for technical application, particularly in high-temperature processes such as catalytic fuel processing. The current project aims to overcome this hurdle by tailoring the composition and characteristic dimensions of nanocomposite catalysts to combine the catalytic activity of nanoparticles with the stability of high-temperature ceramics in a technically applicable catalyst formulation.

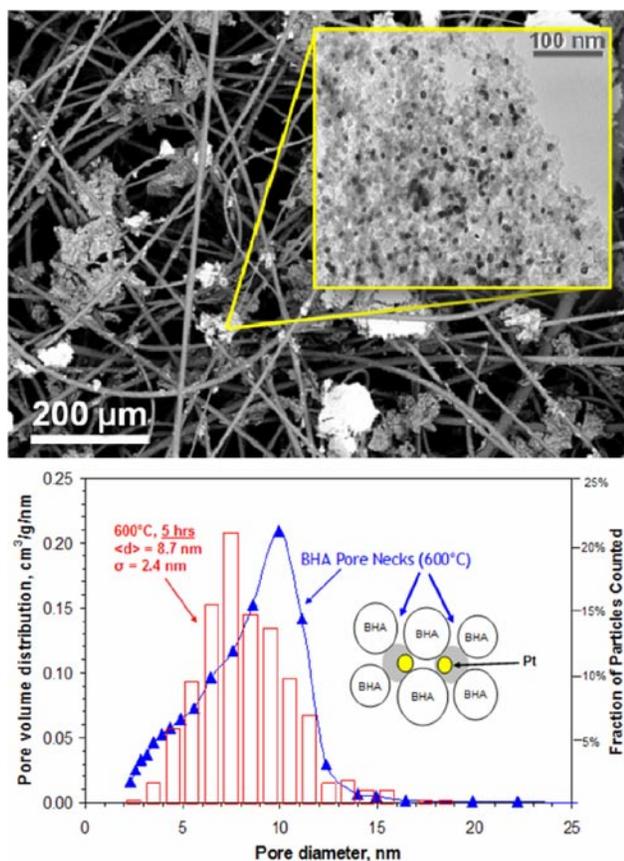


FIGURE 1. SEM image of a hierarchically structured catalyst in which a Pt-BHA nanocomposite (inset: TEM) is deposited onto a silica felt. Bottom: Thermal stability of the Pt-BHA nanocomposites results from the caging of Pt nanoparticles in the porous network of a high-temperature stable aluminate matrix. Shown is a comparison between BHA pore neck size (triangles; from a BJH analysis of the N_2 desorption isotherm) and Pt particle size (bars; from TEM) after calcination for 5 hours at 600°C .

that it is possible to reconcile activity and stability of nanomaterials via simple nanostructuring.

Tailoring for Stability via Encapsulation: Metal@Silica Core-Shell Materials

As alternate approach for the stabilization of metal nanoparticles, direct encapsulation with porous oxide shells was pursued. This was motivated by the fact that the above described approach is limited with regard to the minimum metal nanoparticle size which can be stabilized: Since the particles are stabilized via a simple mechanical ‘caging’, smaller stable particle diameters require increasingly smaller pores and hence ultimately result in mass transfer limitations. In contrast to that, direct coatings of nanoparticles can be kept sufficiently thin that mass transfer limitations (MTL) should be avoidable.

We were able to demonstrate fine control over key dimensions of silica-encapsulated metal nanoparticles ($M = \text{Ni}, \text{Cu}, \text{Co}, \text{Fe}, \text{Pd}$), including size of the metal nanoparticles (from sub-nm clusters up to $\sim 20\text{nm}$), size of the $M@SiO_2$ particle, thickness of the silica shell (see fig.2, top), and presence or absence of a cavity inside the silica shell (see insets in fig. 2). Again, excellent high-temperature stability was demonstrated along with high activity & selectivity in catalytic methane partial oxidation (CPOM, see fig. 2, bottom), and a critical shell thickness for avoidance of MTL was demonstrated.

Tailoring for Stability via Alloying: Bimetallic Nanocomposites

As third alternative for achieving high-temperature stable metal nanoparticles, the alloying of the metal nanoparticles with a second metal was investigated. This was motivated by the aim to increase the stability limits of metal NPs without the use of a stabilizing matrix (as in the two approaches above), i.e. by transitioning from stabilization via structural tailoring to stabilization via compositional tailoring.

One can expect that the addition of a second, higher-melting point metal will result in increased thermal stability, since sintering is known to be strongly correlated with the melting point of a metal. Using Pt-BHA as starting material and carefully adjusting the composition of the metal nanoparticle via step-wise increase in the second metal (for PtRh, PtSn, and PtPd), we found that such stabilization is indeed possible. Unexpectedly, however, it was observed that this stabilization extends to much higher temperatures than predicted by the (initial) composition of the alloy. This was traced back to a sacrificial self-stabilization of the nanoparticles, which bleeds out the lower melting point component (M_1) in a continuous, distillation-like process. This results in the formation of larger nanoparticles which are composed of pure M_1 , while retaining the entire original population of small metal nanoparticles, which get increasingly enriched in M_2 . Overall, this brings about a remarkable self-stabilization of the catalyst, as demonstrated using methane combustion as test reaction. While this stabilization mechanism has limitations due to the fact that the alloying with the second metal must not negatively affect the reactivity of the catalyst, it is remarkable in its simplicity and the fact that it is not dependent on a specific support.

Tailoring for Activity via Composition & Structure: Metal/Mixed-Oxide Catalysts

Finally, the concept of tailoring via composition and structure was applied to a more complex case in which the support takes on a key reactive role (beyond acting as a stabilizing matrix). Water-gas-shift (WGS) over

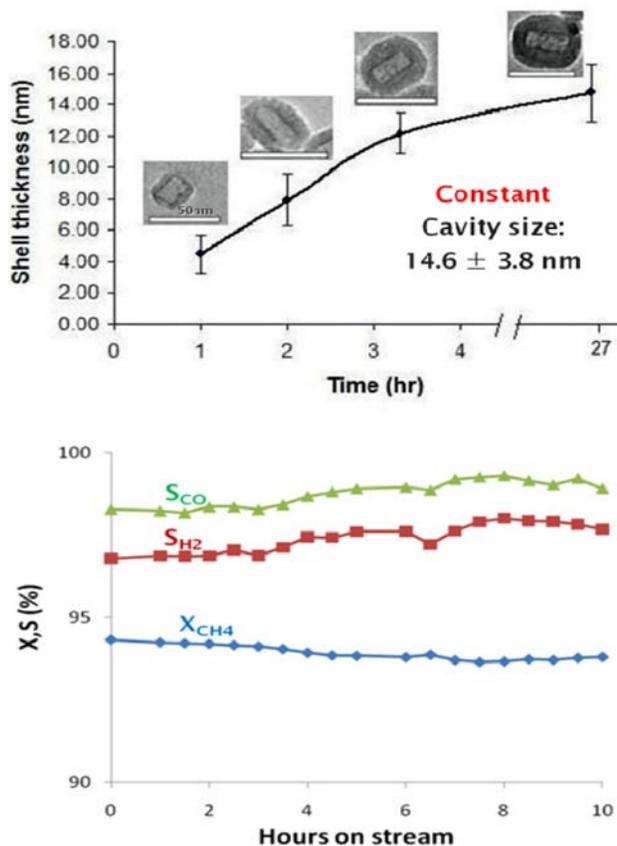


FIGURE 2. Silica shell thickness in Ni@SiO₂ as function of synthesis time, illustrating the fine control over characteristic dimensions in these materials (top; insets show representative TEM images); selectivities and conversion in CPOM over a Ni@SiO₂ catalyst at 800°C (bottom) demonstrate the high-temperature stability of these materials.

Au/ceria catalysts was chosen as test system. Based on a similar microemulsion-templated sol-gel synthesis as of the BHA-based materials above, high surface area ceria and ceria/lanthana mixed oxides were synthesized, characterized, and, after Au deposition, utilized in WGS. A strong correlation between composition, reducibility, and activity of the catalysts was observed, were addition of moderate amounts of La (up to ~25%) resulted in significant improvements in WGS activity (see fig. 4). Utilizing an alternate (hydrothermal) synthesis, ceria and mixed oxide nanorods were also synthesized and compared to the nanoparticulate catalysts. Structuring the catalyst into nanorods results in a strong increase in WGS activity which again can be traced back to the increased reducibility of the oxides (due to predominant exposure of low-stability surface orientations).

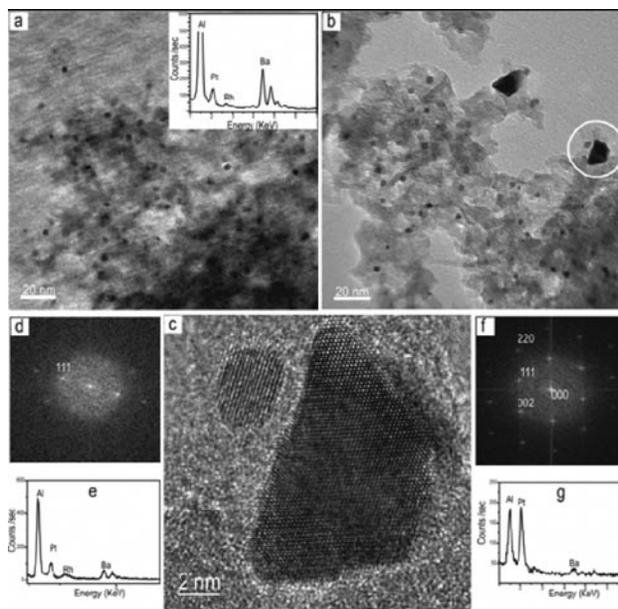


FIGURE 3. TEM and EDAX characterization of PtRh-BHA (3:1) calcined at (a) 600 °C, (inset is its EDAX pattern), and (b) 700°C. Two representative small and large particles are indicated by the white circle and shown enlarged in the HRTEM image in (c). (d) and (e) show the fast Fourier transformation pattern and EDAX spectrum for the smaller particle, and (f) and (g) the fast Fourier transformation pattern and EDAX spectrum for the larger particle.

At 600°C the metal nanoparticles are uniformly small, while after exposure to 700°C larger (~20nm) Pt nanoparticles form in addition to the small (~3nm) PtRh nanoparticles via selective “bleeding” of Pt.

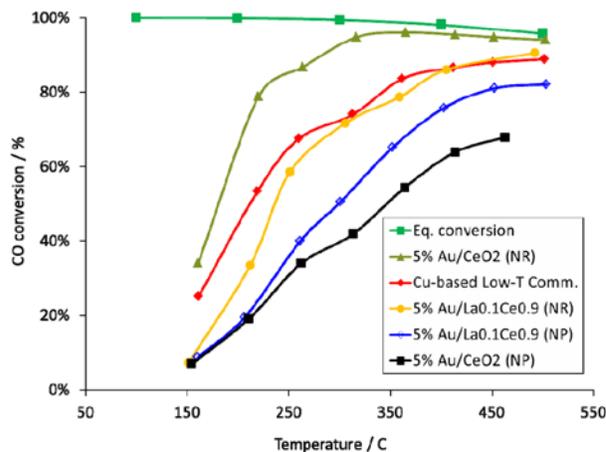


FIGURE 4. Effect of compositional and structural tailoring of Au/mixed Ceria/Lanthana catalysts on WGS activity. CO conversion vs temperature for (from bottom to top): Au/CeO₂ nanoparticles (NP; black squares), Au/La_{0.1}Ce_{0.9}O_{1.95} NP (blue diamonds), Au/La_{0.1}Ce_{0.9}O_{1.95} nanorods (NR; yellow diamonds), a commercial Cu-based low-T WGS catalyst (red diamonds), and Au/CeO₂ NR (golden triangles) along with the equilibrium conversion curve (green squares). All catalysts have a 5wt% Au loading (via deposition precipitation).

Future Directions

The project ended in August 2009, and no extension was applied for. However, the results demonstrate the potential of tailoring catalyst activity and stability via careful compositional and structural control at the “nano-level”, and we are currently extending this concept onto related catalytic reactions.

Publications (including patents) acknowledging the grant or contract

1. T. Sanders, Ph. Pappas, and G. Veser, “Supported nanocomposite catalysts for high-temperature partial oxidation of methane”, *Chem. Eng. J.*, 142 (2008), 122-132.
2. Cao and G. Veser, “Exceptional high-temperature stability through “distillative” self-stabilization in bimetallic nanoparticles”, *Nature Materials* 9 (2010), 75-81.
3. Y. Wang, S. Liang, A. Cao, R.L. Thompson, and G. Veser, “Au-mixed lanthanum/cerium oxide catalysts for water-gas-shift”, *Appl. Cat. B*, (2010) in revision.
4. G. Veser, “Multiscale Process Intensification for Catalytic Fuel Processing: From Nanostructured Catalysts to Integrated Reactor Concepts”, *Catal. Today*, (2010) in review.
5. S. Liang, Y. Wang, E. Broitman, A. Cao, and G. Veser, “Highly stable, mesoporous mixed lanthanum-cerium oxides with tailored structure and reducibility”, *Chem. Mat.*, (2010), submitted.
6. R. Solunke and G. Veser, “Hydrogen production via Chemical-looping in a fixed bed reactor”, *Ind. Eng. Chem. Res.* (2010) submitted.
7. T. Sanders, M. Kirchhoff, T. Liu, S. Bhavsar, and G. Veser, “Particle Size Focusing in Metal-Oxide Nanocomposites”, in preparation (2010).
8. L. Whaley, R. Lu, M. Najera, A. Cao, and G. Veser, “Metal@Silica Yolk-Shell Materials with Highly Accessible Subnanometer Metal Clusters”, in preparation (2010).