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## V.D.23 Multiscale Tailoring of Highly Active and Stable Nanocomposite Catalysts for the Production of Clean Hydrogen Streams

Götz Vesper (Primary Contact), Tom Sanders  
Department of Chemical Engineering  
University of Pittsburgh  
1249 Benedum Hall  
Pittsburgh, PA 15261  
Phone: (412) 624-1042; Fax: (412) 624-9639  
E-mail: gveser@engr.pitt.edu

DOE Program Officer: Richard Kelley  
E-mail: Richard.Kelley@science.doe.gov

### Objectives

The design of catalysts at the nanoscale offers novel opportunities for developing materials that meet the technological needs for sustainable and economical hydrogen production. To enable this vision, however, the current understanding and control of mechanical, thermal and chemical properties of nanomaterials needs to be improved. In this context, nanocomposite materials 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 novel nanocomposite materials for fuel processing.

### Technical Barriers

While the large surface area as well as novel chemical properties of particles with nanometer dimensions makes these materials highly interesting for heterogeneous catalysis, their low thermal stability currently restricts their use to low-to-moderate temperature conditions ( $T < 500^{\circ}\text{C}$ ). This imposes severe limitations for the technical application of nanoscale materials, particularly as catalysts for high-temperature chemical processes such as the production of hydrogen from hydrocarbon feeds. The current project aims to overcome this hurdle by tailoring of the characteristic dimensions of a nanocomposite catalyst across many length scales to combine the catalytic activity of nanoparticles with the stability of high-temperature ceramics in a technically applicable catalyst formulation.

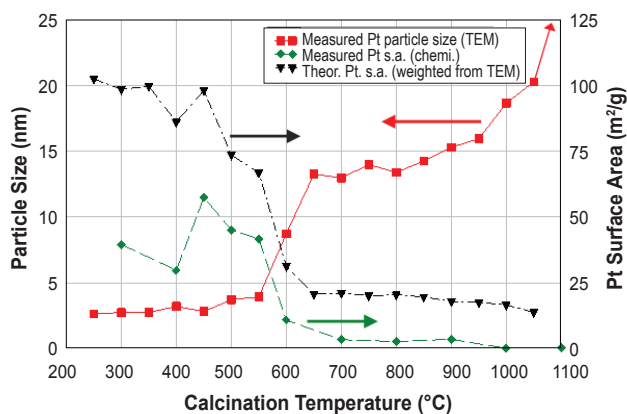
### Abstract

After successfully demonstrating the anchoring of the high-temperature stable nanocomposite catalysts onto a range of different conventional and novel support structures in the first 9 months of the project, the activities during the past 10 project months focused on a detailed investigation of nanostructure and thermal stability of these materials. Most significantly, we were able to demonstrate that the exceptional stability is caused by the embedding of metal nanoparticles in the pore cages of the irregular and highly interconnected pore network inside the ceramic matrix ('nanosponges'). The development of pore structure and particle size with temperature, as well as the effect of residual surfactant was investigated in detail. Furthermore, the flexibility of the synthesis path was demonstrated by changing the metal as well as the ceramic component. These results form the fundamental basis for a broad testing of the nanocomposites in catalytic fuel processing in the upcoming project period and for the development of structure-activity correlations from these tests.

### Progress Report

After successfully demonstrating the anchoring of the high-temperature stable nanocomposite catalysts onto a range of different conventional and novel support structures in the first 9 months of the project, the main focus of the activities during the past 10 project months was on a detailed investigation of the exceptional thermal stability of these materials. Towards this end, a thorough study of particle size and nanocomposite structure as a function of calcination conditions and temperature was conducted.

The main results of this study are summarized in Figure 1, where Pt particle size (determined from TEM; squares) is shown as a function of calcination temperature for a typical Pt-BHA nanocomposite (BHA = barium hexaaluminate). At low temperatures, the Pt nanoparticles inside the nanocomposite materials are ~3-4 nm in diameter. This size is unaffected by the calcination temperature up to  $T \sim 550^{\circ}\text{C}$ . Above this temperature, a large jump in particle size occurs. This point coincides with the complete removal of the residual surfactant inside the nanocomposite (as identified by MS, TGA, XPS, and FTIR; not shown in the figure), indicating that the surfactant plays a key



**FIGURE 1.** Platinum nanoparticle size (red squares), specific Pt surface area (green diamonds), and calculated Pt surface area (black triangles) versus calcination temperature.

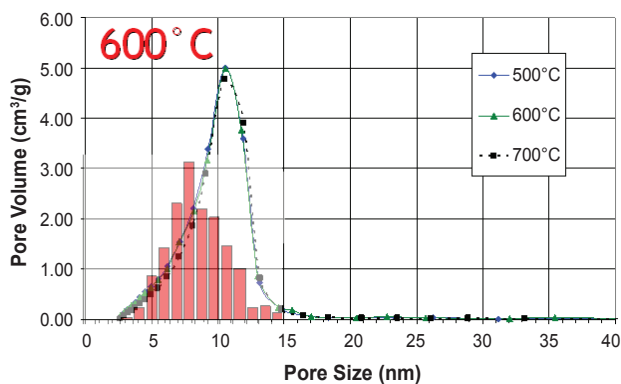
role in the stabilization of the metal nanoparticles at low temperatures.

Once the metal nanoparticles have become mobile, one would expect rapid sintering to occur, resulting in metal particles with sizes in the range of ~100 nm and above. Instead, the nanoparticle size stabilizes around 15 nm diameter and remains stable up to 950°C. Finally, once the temperature increases above 1000°C, rapid further particle growth occurs.

The reason for the surprising stabilization of the Pt size in the high-temperature range between 650°C and 950°C is revealed in Figure 2, where the size distribution of the pore necks (i.e. the channels connecting the pores in the network) for a pure BHA sample after calcination at 500, 600, and 700°C is shown (determined from BJH desorption curves; line graphs). The bar graph overlay shows, in comparison, the particle size distribution (determined from TEM studies) for a Pt-BHA sample after calcination at 600°C. The Pt particle size distribution is perfectly bracketed by the size distribution of the pore necks, indicating that particle mobility is restricted by the narrow pore necks at temperatures where particle migration is energetically possible. Interestingly, we found that even at temperatures as high as 1000°C (not shown in the figure) the particle size is still bracketed by the dimensions of the pore network. However, at these temperatures, the ceramic pore network starts to recrystallize, apparently opening up the pore necks sufficiently for the Pt particles to migrate through. Correspondingly, metal particle sizes are not determined solely by the pore necks any more, but are bracketed on the small end by the pore necks and on the large end by the size of the pore cages.

Further significant results from the investigations during the current report period:

- Demonstrated possibility to change noble metal loading without affecting metal particle size



**FIGURE 2.** Size distribution of platinum nanoparticles (red bar graph; from TEM; arbitrary vertical scale) and pore necks (line graph; from BJH) in Pt-BHA samples after calcination at 600°C.

(i.e. only by changing the number density of the particles). This is highly interesting for catalysis, since it allows to tailor the metal loading (and hence study the effect of metal loading) without affecting the chemical characteristics of the catalyst through changes in particle size or distribution.

- Identified importance of residual surfactant at low and moderate temperatures ( $T < 500^\circ\text{C}$ ). Up to 50 wt% residual surfactant is present at low temperatures, guiding the structural evolution of the materials and blocking active metal sites. Several washing methods for surfactant removal (washing with acetone,  $\text{CH}_2\text{Cl}_2$ , and water, including extensive refluxing) were tested, but showed very little effect.
- Tested the influence of calcination conditions on stability of metal particle (calcination in flowing air, stagnant air, hydrogen, and inert gas). Calcination in inert gas gives significantly smaller Pt particle size at elevated temperature, which can be traced back to inefficient surfactant removal in an inert gas atmosphere (i.e. surfactant removal proceeds via an oxidation reaction). Most interestingly, however, calcination in  $\text{H}_2$  allows complete removal of residual surfactant at temperatures below 250°C, i.e. more than 200°C lower than previously possible. This finally makes the full potential of these nanocomposites available for low-temperature catalytic reactions, in particular for PrOX.
- Extended synthesis onto other metal components (Ni, Fe, Cu, Co) and further ceramic phases (other hexaaluminates, magnesia, silica). This extension demonstrates the flexibility of the simple, one-pot synthesis, and opens the possibility to investigate whether any interactions between metal nanoparticles and the ceramic matrix exist beyond the purely physical stabilization.
- Silica was identified as an additional support of particular interest due to low molecular weight and very large specific surface areas ( $> 600 \text{ m}^2/\text{g}$ ). Since

the synthesis route had to be altered for silica-based materials, the influence of major synthesis parameters on nanocomposite silica materials were studied in detail.

Overall, the results from the past report period allowed us to develop a qualitatively improved understanding of the nanocomposite structure and, in particular, of the interactions between the ceramic structure and the metal nanoparticles, including identification of the origin of the exceptional high-temperature stability of the metal nanoparticles. This lays the groundwork for detailed investigations correlating catalytic kinetics with structural properties of the nanocomposite materials.

### Future Directions

The results from the investigations during the past 10 months (i.e. the current report period) form the basis for the upcoming broad testing of the nanocomposites in catalytic fuel processing. The main focus of our studies will hence shift from synthesis and (structural) characterization of the materials to extended reactive tests. While our studies to-date have focused on syngas/hydrogen production from methane via catalytic partial oxidation as 'standard test reaction', we will now start to investigate select nanocomposite materials in steam reforming of methane, water-gas shift, and

preferential oxidation of CO in hydrogen streams. Aim of these studies will be the development of correlations between catalytic activity and structural properties of nanocomposites over a wide range of temperatures and feed stream compositions.

### Publications

1. T. Liu, T. Simonyi, T. Sanders, R. Siriwardane, and G. Veser, "Novel Ni-Nanocomposites as Oxygen Carriers for Chemical Looping Combustion", *Green Chemistry*, submitted (2006).
2. N. A. Khan, S. Natesakhawat, C. Matranga, T. Sanders, and G. Veser, "The Role of Residual Surfactants on the Structure and Chemical Properties of Nanostructured Barium Hexaaluminate Type Catalysts", *J. Phys. Chem.*, submitted (2007).
3. T. Sanders and G. Veser, "Supported Nanocomposite Catalysts for High-Temperature Methane Conversion", *ACS Fuel Chemistry Preprints* 51 (1) (2006).
4. T. Liu, T. Simonyi, T. Sanders, R. Siriwardane, and G. Veser, "Nanocomposite Oxygen Carriers for Chemical Looping Combustion", *ACS Fuel Chemistry Preprints* 52 (1) (2006).
5. T. Sanders, P. Pappas, and G. Veser, "Supported Nanocomposite Catalysts for High-Temperature Applications", in preparation for *J. Catal.*