

Synthesis of Metal-Silica Core-Shell and Yolk-Shell Nanocatalysts with Exceptional Dimensional Control

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Introduction

Nanomaterials hold great potential in catalytic applications, due to their inherently large surface area and to novel catalytic properties. However, the poor stability of nanoparticles constitutes a major hurdle in utilization of these materials in a technical environment. We have previously shown the successful stabilization of metal nanoparticles towards very high temperatures (~900°C) via embedding in a nanostructured oxide matrix. Here, we report on an alternate, related approach in which the metal nanoparticles are directly coated with a (nanoporous) oxide shell, resulting in accessible yet stable nanoparticles. While a number of previous reports have already demonstrated the fundamental feasibility of such an approach, significant challenges remain in establishing control over key material dimensions and maximizing accessibility to the nanoparticle via porosity of the shell without compromising the particle stability. We are demonstrating an exceptional degree of control over virtually all dimensions of the core-shell materials with relevance for catalysis using a rather straightforward one-pot synthesis route.

Materials and Methods

Ni nanoparticles with controllable diameter are synthesized in a reverse microemulsion-templated approach. In a typical synthesis, an aqueous nickel nitrate solution was added to 0.5M Brij-58/cyclohexane system and reduced by addition of hydrazine hydrate. Then, tetraethyl orthosilicate (TEOS) was added, followed by ammonia addition, and the mixture was hydrolyzed at 323K for an hour. The resulting precipitates were centrifuged and washed with iso-propanol, dried at 373K for 8 hrs, and then calcined at 773K for 2hrs. Material structure and morphology was tailored via careful adjustment of a number of critical synthesis parameters, such as relative amounts of TEOS, surfactant, ammonia, and metal salt, aging times, etc. The materials were characterized by a wide range of methods, including TEM, BET, XRD and CO-chemisorption, TPD, TPO and TPR.

Results and Discussion

TEM demonstrates the fine control over dimensions that was attained in the synthesis, with particles sizes of 20 nm–50 nm for nickel nanoparticles of 1-5 nm and silica wall thickness of 3-20 nm, and pore diameters of 3-4 nm (see figure 1 for select examples). careful control of essential synthesis parameters, we have been able to establish control over virtually all critical dimensions of the core-shell materials: For example, controlling the amount of TEOS and the pH of the solution allows control of the thickness of the silica coating, while step-wise addition of TEOS results in multiple silica coatings with “hierarchical: layering (see fig. 1d), without loss of porosity, i.e. maintaining full accessibility of the metal

nanoparticle. Adjusting the amount of surfactant in the microemulsion, the structure of the core-shell materials can be changed from solid (but porous) core-shell structures to “yolk-shell” structure (i.e. porous core-shell structures with a pronounced cavity), to yolk-shell structures with decoration of the inner walls by small Ni clusters, to strongly elongated rod-shaped structures with high aspect ratios, and finally to branched rod-shaped structures (see fig. 1a-c for select examples). First results with other metal cores (Ag, Cu) indicate that the synthesis route should be broadly applicable.

The porosity of the shells is demonstrated via complete oxidation and reduction of the Ni nanoparticle in TPO/TPR (with air and 5% H₂/He streams, respectively). No change in the structure of the material is observed other than complete oxidation and reduction of the metal core. Testing the thermal stability during calcination in air, we find no change in the porosity of the silica shells up to ~800°C, where onset of a softening/collapse of the cavity is observable (see figure 2). TEM demonstrates that the metal core is unchanged over the entire T-range.

Finally, the high activity of these materials, i.e. the excellent accessibility of the Ni cores is been demonstrated in low-temperature CO oxidation, where fast oxidation was observed at temperatures well below room temperature.

The pronounced cavity in the silica shell leaves the surface of the Ni nanoparticle much more accessible than in typical core-shell structures and the thin and highly porous silica walls facilitate gas diffusion. The materials hence combine excellent accessibility with high thermal stability, and we anticipate great potential in catalysis and related applications.

Figure 1. TEM images of Ni@SiO₂: transition from solid core-shell (a) to “yolk-shell” (b), to rod-shaped (c) structures with increasing surfactant concentration. A 2-layered coating is shown in (d). (Image size ~ 50x50nm)

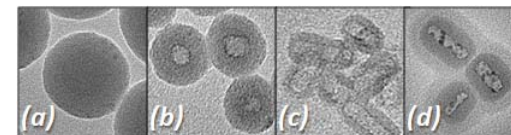
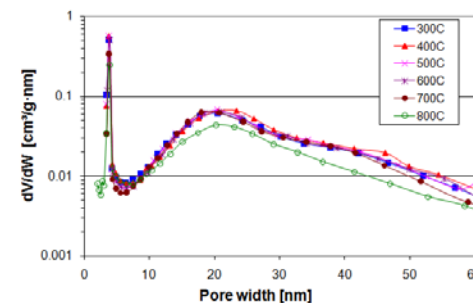


Figure 2. Pore size distributions for Ni@SiO₂ yolk-shell materials with increasing temperature. One can clearly distinguish the porosity of the shell (d~4 nm) and the cavity (d~10-50nm). The porosity is unchanged up to T~800°C.



Significance

The results demonstrate an exceptional degree of control over the key dimensions of core-shell nanocatalysts, opening up possibilities of catalyst design without compromising stability.