Supported Catalysts

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High-Temperature-Stable Catalysts by Hollow Sphere Encapsulation**

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Dedicated to Professor Klaus Unger on the occasion of his 70th birthday

Supported catalysts play a major role in many fields of chemical production and environmental protection, such as in automobile exhaust treatment.[1] In particular, noble metals are almost always dispersed on support materials of high surface area to expose a high fraction of atoms on the surface of the particles. However, particle growth at high temperatures, accompanied by a corresponding loss of catalytic activity, is a serious problem in many applications.[2–4] This is caused by the increased mobility of the particles on the support at higher temperatures. In spite of the great technological interest, general methods for the stabilization of particles against sintering are lacking, although stabilization of the dispersion has been achieved for special systems by optimizing the interaction with a support material.[5,6] We have now developed a general strategy to address this problem and demonstrate its applicability for the example of Au/ZrO_2 catalysts.

The novel sinter-stable catalyst needs to meet a number of requirements: 1) its components have to be thermally very stable to maintain the integrity of the system; 2) it should present no substantial mass transfer resistance; and 3) it should retain the catalytic activity after high-temperature treatment. The system was realized by combining two complementary technological components. It has been known for a number of years that metal nanoparticles (gold has been studied most often) can be covered by a silica layer.[7–9] In ideal cases, single nanoparticles can be produced in the center of silica shells that are identical in size by a method analogous to the well-known Stöber process. On the other hand, we have recently discovered that monodisperse, hollow, zirconia-based spheres with pores of only a few nanometers in the shells can be synthesized by coating silica with a zirconia shell and subsequent leaching of the silica core.[10] These two methods form the basis for the construction of the sinter-stable catalysts, that is, the production of hollow zirconia shells with exactly one gold nanoparticle in each shell. A related material with a carbon or silica shell was previously obtained by a different route, but no use of this material has been reported.[11] Gold was chosen as a model system, because it is presently one of the most frequently studied catalytic materials with remarkable properties, and several alternative methods for the coating of gold particles with a silica layer have been published.[12–15]

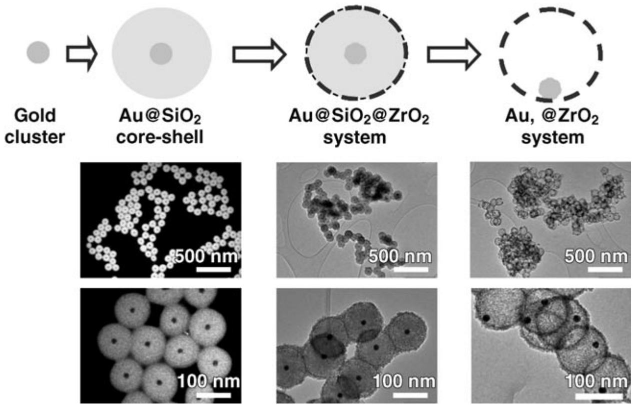

Figure 1. General scheme of the synthetic process and TEM images (left: dark field; middle and right: bright field) of the products obtained after each step. From left to right: in the first step, colloidal gold particles with sizes of approximately 15 nm are synthesized. These colloids are covered with a dense silica layer by a modified Stöber process to form monodisperse silica spheres with one gold particle in the center of each sphere. The spheres are then covered by a thin layer of zirconia particles with pores 3–4 nm in diameter between the individual zirconia particles. Finally, the silica is leached out and loose gold particles, now no longer in the center of the spheres, are obtained. (The formula "Au, @ZrO_2" indicates the presence of free space between the encapsulated gold particle and the mesoporous ZrO_2 shell.)

The pathway leading to the catalytic composites is shown schematically in Figure 1, in combination with TEM images of the product after each step. The gold colloid was prepared by following the route described by Enüstün and Turkevich,[16] which relies on reduction by sodium citrate and allows almost monodisperse gold particles to be obtained in the range 15–17 nm. The gold colloids were coated with silica by following essentially the route of Graf et al.[17] However, the amounts of reagents and their concentrations had to be modified to obtain reliable and reproducible results for our purpose. As the growth of the silica shell proceeds under well-controlled conditions that correspond to the Stöber process for the synthesis of monodisperse silica spheres, all particles reach an identical size after this process step, as can be seen in the TEM images in Figure 1. About 95% of the particles synthesized by this pathway contain exactly one gold nanoparticle in the center; occasionally, completely empty silica spheres or spheres containing two gold nanoparticles are observed. However, this small number of defective particles is not critical for the creation of stable catalysts.

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In the next step, the Au@SiO_2 spheres are coated with zirconia by following the procedure described by us earlier for pure zirconia spheres.[10] Briefly, after covering the surface with a surfactant (Lutensol AO5), the system is reacted with zirconium butoxide, aged in water, and calcined at 1173 K. As the gold nanoparticles are embedded in the silica, no growth of the gold particles takes place during this step. Next, a shell of tetragonal zirconia, which consists of particles with sizes below 10 nm (and silicon compounds, the exact nature of which is not known at this time), is formed. The pores between the zirconia particles that form the shell are approximately 3–4 nm in size.

Finally, the silica is removed from the composite by treatment with NaOH solution (1 N). Some silica remains in the shells, probably in the form of a zirconium silicate which is X-ray amorphous.[10] The TEM images (Figure 1, right) show that after this step, the gold particles are no longer in the center of the spheres because the silica scaffold that fixed the particles has been dissolved. The particles are now deposited somewhere on the inside of the hollow zirconia sphere.

The gold particles are now effectively separated but are highly accessible to gas molecules, which is crucial for application in heterogeneous catalysis, because otherwise mass-transfer limitations will restrict the rates in narrow-pore systems. For mass transfer, the thin, porous zirconia shell with a thickness of only about 20 nm (this can be adjusted to some extent by the parameters of the synthesis) does not provide much resistance, and the rest of the pore system consists of the large voids within the hollow shells. Good performance can therefore be expected in heterogeneous catalytic reactions.

One of the standard reactions investigated over gold catalysts is the oxidation of CO.[12,18,19] Normally, catalysts are highly active only if the particle sizes are smaller than 5 nm. For 15-nm particles, as studied here, only very low activity would be expected. However, as Figure 2 shows, the temperature for half conversion is about 200 °C, which is quite remarkable for this particle size. The high activity may be related to the high-temperature treatment during the synthesis, which leads to faceting of the gold particles.

In particular, during the first calcination step (necessary to achieve the crystallization of zirconia) the presence of silica could modify the gold surface energy, and this may result in the expression of surfaces with different structure than during calcination in air. Furthermore, it has been demonstrated in a previous study that, after calcination at 800 °C, just a small fraction (< 15 %) of the {111} surface area is converted to the less "active" {100} surface, so that the higher-activity surfaces may be retained even after calcination without the silica being present.[20] The development of specific facets and the corresponding presence of special corner and edge sites has been correlated to the surprising activity of gold catalysts before.[21–24]

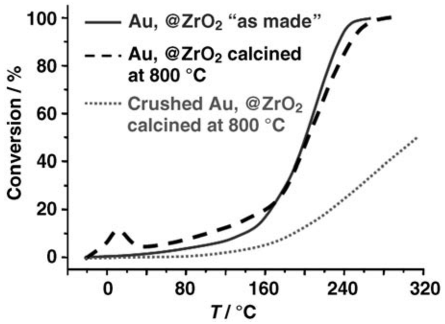

Figure 2. Catalytic performance of the different samples. The activities of the catalysts for the oxidation of CO were measured in a plug-flow reactor using 50 mg of catalyst in a gas mixture of 1 % CO in air (from Air Liquide, 99.997 % purity) at a flow rate of 67 $cm^3 min^{-1}$, which corresponds to a space velocity of 80000 $cm^3 h^{-1} g_{cat}^{-1}$.

To check whether the encapsulation of the particles within the hollow, porous zirconia spheres is indeed advantageous for the thermal stabilization of the catalysts, a reference sample with nonencapsulated gold particles was prepared. To exclude any other factors that might affect the results, the reference sample was prepared by crushing one of the original samples in a press under a static pressure of 1 GPa. (Previous attempts to destroy the spheres by high-energy ball-milling had proven to be less successful, which demonstrates the excellent mechanical stability of the shells.) Then, both the original and the crushed samples were exposed to a thermal treatment in air. In particular, the samples were heated to 800 °C from room temperature with a heating rate of 2 K min^{-1} and then left in the oven during the cooling step (the total time of treatment was about 12 hours). Figure 3 shows TEM images from before and after this treatment. The Au,@ZrO_2 sample is completely unaffected and no growth of the gold particles has taken place, whereas the crushed sample has clearly suffered substantial growth of the gold particles after thermal treatment through a sintering process. This complete absence of sintering for the encapsulated particles can be attributed to the stability of the overall system: the shells stay intact and the pores in the shell are too small to allow the gold particles to pass, so that even if the gold particles are mobile in the shell, they never come into contact with each other to sinter as there is only one particle per shell.

Notably, the zirconia particles in the shells grow somewhat during the heat treatment, as the surface area decreases from about 270 to about 140 $m^2 g^{-1}$, consistent with our previous reports on the pure, hollow zirconia shells.[10] The pore size distribution of the mesoporous shell is only slightly affected by the calcination (shifted to larger sizes). The decrease in surface area is predominantly a result of loss of porosity of the system.

This difference in particle size should also influence the catalytic performance, and, as seen from Figure 2, the conversion over the Au,@ZrO_2 sample is unaffected even after treatment at 800 °C, with the exception of a reproducible low-temperature activity in the transient catalytic experiment, the reason for which is presently unclear. The nonencapsulated catalyst, in contrast, suffers a substantial loss in activity, with half conversion reached only at temperatures more than 100 °C higher.

These results clearly show that isolation of metal catalyst particles by hollow sphere encapsulation does indeed allow stabilization of the catalyst against sintering. This method is at present rather expensive and time-consuming, but for technical applications well-controlled properties, such as monodispersity of the spheres, are probably not necessary as long as

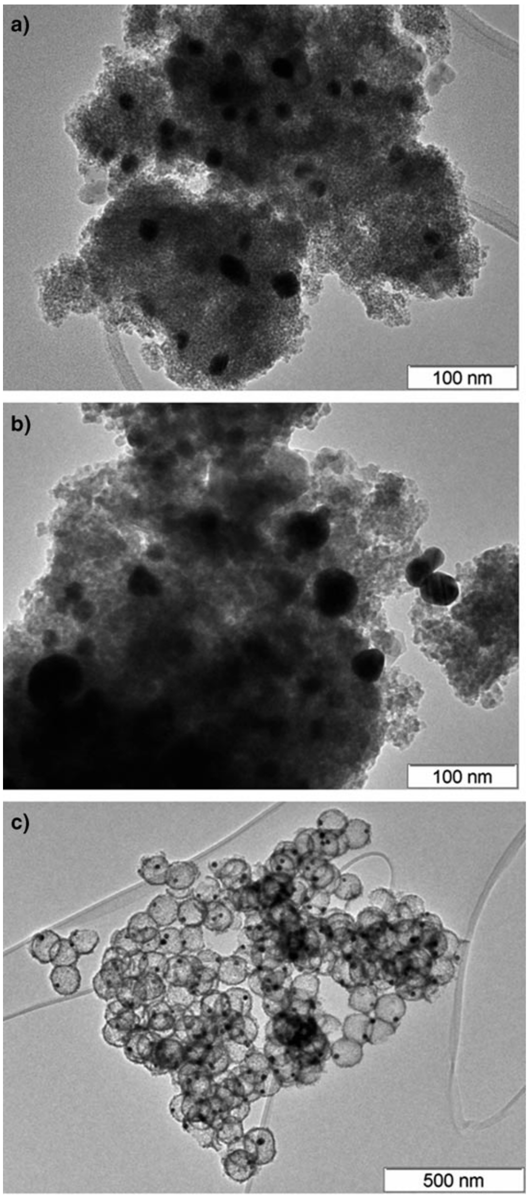

Figure 3. TEM images of encapsulated samples after crushing at a static pressure of 100 MPa (before and after calcination) and comparison with the core–shell system. a) The gold particle size is essentially unchanged compared to that of the core–shell sample before crushing. b) The crushed sample after heat treatment at 800 °C. The gold particle size has appreciably increased. c) The encapsulated sample after heat treatment at 800 °C. All gold particles are still the original size and the hollow shells are still intact. A larger scale was chosen to provide a better overview and prove that no particles had sintered.

the basic principle, full encapsulation of the metals in hollow, thermostable containers, is achieved. The results presented describe the elements of a synthetic platform that is highly flexible. By proper choice of the reaction conditions the size of the silica spheres can be adjusted, the thickness of the zirconia shell can be varied, and the pore sizes of the zirconia shells can be tuned. As has been shown in the literature, other metals can be encapsulated, and also the chemical nature of the shell can be varied.[25] We have already shown that hollow carbon shells can be created, and first results with titania are also promising.[26] It is therefore probable that the route described above provides access to a wide range of different materials systems.

Experimental Section

Catalyst preparation: Millipore water (212.5 mL, $18.2\ \mathrm{M\Omega\,cm^{-2}}$) was vigorously stirred under reflux and a $HAuCl_4$ solution (25 mL, $2.54\times10^{-3}\ \mathrm{M}$; Alfa-Aesar, 99.99 %) was added. The resultant solution was stirred until boiling point was reached again. Then, a sodium citrate solution (12.5 mL, $10\ \mathrm{mg\,mL^{-1}}$; citric acid trisodium salt dehydrate, 99 % purity from ACROS Organics) was added and the system was refluxed for 30 min. Finally, the resultant colloid was cooled to room temperature. Next, a solution of polyvinylpyrrolidone (0.325 mL, $12.8\ \mathrm{mg\,mL^{-1}}$), which was freshly prepared by dissolution in Millipore water with ultrasonication (30 min), was added to a previously prepared, cold, colloidal gold solution (240 mL). The resultant mixture was stirred for 24 h to allow complete adsorption of the polymer on the gold surface. After this time, the solution was centrifuged (10 000 rpm; 50 min) and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 6 mL by dilution with water. The colloid was vigorously stirred for 5 min, followed by addition of ethanol (18.90 mL) premixed with concentrated ammonia solution (0.84 mL, 28–30 % NH_3 in water). Immediately afterwards, a solution of tetraethylorthosilicate (1.19 mL) in ethanol (12.80 mL) was added. The reaction mixture was then stirred for an additional 12 h at room temperature. The resultant colloid was centrifuged (10 000 rpm; 30 min) and washed twice with water and twice with absolute ethanol. In between washing and following centrifugation the solid was redispersed by ultrasonication. After washing, the colloid was dispersed in pure ethanol (25 g) in a 100-mL flask, which was sealed with a septum and heated under stirring at 30 °C. Then an aqueous solution (0.125 mL) of Lutensol AO5 (from BASF; 0.43 g dissolved in 11 g MilliQ water) was added to the stirred solution. After 1 h, zirconium butoxide (0.45 mL, 80 % w/w in butanol, from Aldrich) was added and the reaction was allowed to proceed overnight. The liquid phase of the colloid was then exchanged for water by centrifugation and redispersion of the solid in water (25 mL) four times. The particles were aged at 20 °C for 3 days. Removal of the organics and crystallization of zirconia were achieved by calcination in air by heating the system from room temperature to 900 °C at a rate of $2\ \mathrm{K\,min^{-1}}$. Silica was removed from the composite by treatment with NaOH ($1\ \mathrm{N}$). Specifically, the sample was kept for 16 h in a NaOH solution under stirring and then the alkaline solution was exchanged with a fresh one and the process was continued for another 12 h at 50 °C. Finally, the core–shell particles were washed five times with water and once with ethyl *tert*-butyl ether.

Ball-milling: A ball-milling experiment was conducted using a Retsch MM2000 apparatus. The sample was milled for 120 min with stainless-steel balls ($\varnothing = 2$ mm) at a frequency of 20 Hz.

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