Ultimate Size Control of Encapsulated Gold Nanoparticles

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Electronic Supplementary Information

1.Synthesis of Au@silicalite-1

Silicalite-1 was synthesized from the crystallization of gels containing tetraethyl orthosilicate (TEOS, Aldrich, 98%), 1M TPAOH solutions (prepared from TPABr by exchange with Ag₂O) and water. In a typical synthesis, TEOS was first hydrolyzed in TPAOH at room temperature, then water was added and the mixture was heated at 75°C for 3 hours under stirring. The resulting gel, with the composition: SiO₂-0.4TPAOH-35H₂O, was transferred into a Teflon-lined autoclave and heated under static conditions at 170°C for 3 days. The autoclave was then cooled and the solid recovered by centrifugation and dried overnight at 110°C. It was finally calcined at 525°C in air for 12 hours.

Gold impregnation loading was performed using the so-called incipient wetness impregnation (IWI) method. The zeolite was first desorbed under vacuum at 200°C, purged with argon, and impregnated with an aqueous solution of HAuCl₄ with a volume of solution corresponding to the pore volume of the zeolite (0.23 ml for 1 g of zeolite). The mixture was stirred at 50°C overnight until complete evaporation of the liquid and then dried at 110°C. Au@silicalite-1 solids were then reduced under H₂ (20% in nitrogen) at 350°C for 2 hours. The dissolution/crystallisation process was achieved by treating gold loaded zeolite crystals (1g) in the presence of TPAOH (7.5 ml; 0.55M) in a Teflon-lined autoclave at 170°C for 24 hours. The gold loaded hollow zeolites were washed with water, dried and calcined in air at 525°C. Materials with gold contents between 0.08 and 1.2 wt. % were prepared by adjusting the concentration of the HAuCl₄ solution (see Table ES1). Samples are denoted w-Au@ Silicalite-1, where w is the experimental Au loading (wt%).

Sample Name	HAuCl ₄ concentration	Au loading (wt%)	Dispersion (%)
	(mol/L)		
0.08-Au@ silicalite-1	0.05M	0.08	38.2
0.28-Au@ silicalite-1	0.11M	0.28	28.3
0.52-Au@ silicalite-1	0.22 M	0.52	24.5
1.2-Au@ silicalite-1	0.44M	1.20	17.7
0.38-Au@ silicalite-1	0.22M	0.38	7.3
post-impregnated			

Table S1: Gold content and dispersion of x-Au@silicalite-1 samples.

The volume mean diameter, $d_{30} = (\sum n_i d_i^3 / \sum n_i)^{1/3}$ is the diameter of a hypothetical particle having volume (or mass if all the particles have the same density) equal to the average volume of the true distribution. This is also the diameter of a monodisperse distribution which have the same number of particle and the same total volume (or mass) than the true distribution.

 $w = m_{Au}/(m_{zeolite} + m_{Au})$ where w is the Au loading (wt%)

When considering a zeolite mass $(m_{zeolite}) = 1g$ and the $m_{zeolite} >> m_{Au}$, the gold mass for a sample of 1 gram be simplified as:

$$m_{Au} = w/(1-w) \sim w$$

On the other hand the mass of a population of nanodisperse gold sphere can be expressed as:

$$m_{Au} = n.\rho.f.d^3$$

where n is the number of particles in the sample, ρ the density of gold and f a shape factor ($\pi/6$ for spherical particles); the term ρ f.d³ represents the mass of a single metal particle.

The relationship between the volume mean diameter and the metal loading (w) is for one mass unit of support:

$$w/(1-w) = n\rho f.d^3$$

If one assumes that the metal loading (w) is small the relationship becomes:

 $w = n\rho f.d^3$.

As ρ and f are constant, if n (the d number of gold particles per gram of support) is constant, one have a linear relationship between the volume mean diameter cubed (d³) and the gold content (w) of the various samples.

2. Powder X-Ray Diffraction

X-ray powder patterns were recorded on a Bruker (Siemens) D 5005 diffractometer, from 4 to 80° (2-theta) with 0.02° steps and 1s per step.



Figure S1: XRD patterns of (a) hollow silicalite-1 crystals, (b) 0.52-Au@ silicalite-1 and (c) 0.38-Au@ silicalite-1 post-impregnated materials.

3. Transmission Electronic Microscopy

HRTEM pictures were obtained on a Jeol 2010 LaB6 microscope operating at 200 kV. A dispersion of the catalyst crushed in ethanol was deposited on standard holey carboncovered copper TEM grids.



Figure S2 : TEM pictures of 0.08-Au@silicalite-1 (a), 0.28-Au@silicalite-1 (b), 0.52-Au@silicalite-1 (c) and 1.2-Au @silicalite-1 materials (d).



Figure S3 : TEM picture and corresponding particle size distribution of sample 0.38-Au@ silicalite-1 post-impregnated.

4. N₂ adsorption isotherms

 N_2 adsorption isotherms of starting silicalite-1 and resulting samples were measured on an ASAP 2020 (Micromeritics) sorption apparatus. Approx. 100 mg of zeolite was degassed in a cell at 350°C for 3 hours prior to adsorption. Apparent surface area (BET method) and microporous volume were estimated from the t-plot curve and are displayed in table S2.



Figure S4 : N2 adsorption/desorption isotherms of Silicalite-1 (■), 0.52-Au@ Silicalite-1 (●) and 0.38-Au@ Silicalite-1 post-impregnated (▲)

Table S2 : Porous structure results

Sample	$S_{BET} (m^2 g^{-1})$	$V_{\text{micro}} (\text{cm}^3 \text{g}^{-1})$
Silicalite-1	449	0.23
0.52-Au@ Silicalite-1	385	0.11
0.38-Au@ Silicalite-1 post-	368	0.11
impregnated		

5. Modified synthesis protocol for the synthesis of multiple gold nanoparticles encapsulated in silicalite-1

Large zeolite crystals were obtained using a mixture of tetrabutylphosphonium and tetraethylphosphonium cations (TBP+/TEP+ = 3) following a literature procedure*. Mixtures of phosphonium templates lead to large crystals, typically 20-30 μ m. The Si:/template, Si/H₂O and crystallization conditions (T, time) were similar to those used for the nanocrystals. The calcined zeolite was impregnated with a gold solution and reduced in hydrogen. It was then treated with TPAOH for 24 hours. In contrast to the nanocrystals, the treatment did not form a single large hole but many smaller holes, all with regular shapes and faces parallel to those of the original crystal. TEM images show that each small cavity contains one Au particle. *A. Tuel, Y. Ben Taârit, *Zeolites* **14** (1994) 272)



Figure S5 : TEM pictures of Au@ silicalite-1 obtained from large silicalite-1 crystals