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Innovative Route to Prepare of Au/C Catalysts by Replication of Gold-containing Mesoporous Silicas

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Abstract

Gold-catalyzed aerobic epoxidations in the liquid phase are generally performed in low-polarity solvents, in which conventional oxide-supported catalysts are poorly dispersed. To improve the wettability of the catalytic powder and, thus, the efficiency of the catalyst, gold nanoparticles (NPs) have been dispersed on meso-structured carbons. Gold is first introduced in functionalized mesostructured silica and particles are formed inside the porosity. Silica pores are then impregnated with a carbon precursor and the composite material is heated at 900°C under vacuum or nitrogen. Silica is then removed by acid leaching, leading to partially encapsulated gold particles in mesoporous carbon. Carbon prevents aggregation of gold particles at high temperature, both the mean size and distribution being similar to those observed in silica. However, while Au@SiO$_2$ exhibit significant catalytic activity in the aerobic oxidation of *trans*-stilbene in the liquid phase, its Au@C mesostructured replica is quite inactive.

Keywords: Mesostructured carbon, Gold nanoparticles, Catalysis, Aerobic Oxidation

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1. Introduction

Gold nanoparticles are efficient oxidation catalysts in both the gas and liquid phases [1-5]. It is however essential to stabilize particles with diameters below a few nanometers, and this requires sophisticated chemical methods, which are usually support-specific [6]. Another strategy consists in limiting particle aggregation via physical confinement. Gold particles synthesized within mesoporous titania-modified silicates exhibit significant activity for structure-sensitive CO oxidation [7]and vapor phase epoxidation of propylene with oxygen and hydrogen [8]. However, aerobic epoxidations in the liquid phase require the use of low-polarity solvents [9], in which these

conventional oxide-supported catalysts are poorly dispersed. The use of high surface area carbons as supports, which enhances mass-transfer, could be beneficial to the efficiency of the overall catalytic system. However, conventional methods of preparation typically lead to large distributions of gold particle sizes on activated carbons [10]. Only colloidal deposition, which consists in the physical adsorption of a preformed gold sol on a preformed support, has proven successful so far in obtaining 3 nm gold catalysts on activated carbons [11-13].

We have developed a new strategy, based on the nanocasting concept, to prepare thermally stable gold nanoparticles highly dispersed and partly occluded in meso-structured carbons.

2. Experimental

Calibrated gold nanoparticles were formed inside the porosity of mesostructured silicas (SBA-15) using two different routes. In both routes, silica was preliminarily functionalized before contacting with an aqueous $HAuCl_4.3H_2O$ solution. The two routes essentially differed by the nature of the graft: N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (TPTAC) in Route 1 and 3-mercaptopropyltrilmethoxysilane (MPTMS) in Route 2. Gold was then introduced in functionalized mesoporous silicas and particles were formed upon reduction of Au^{3+} cations with sodium citrate and/or $NaBH_4$. The gold content was limited to 1-1.5 wt. % to favor a high metal dispersion inside the pores and to prevent the formation of large particles upon heating. In the case of MPTMS, gold nanoparticles were not formed at room temperature after chemical reduction and it was necessary to heat the sample in air at temperatures above 300°C. The silica pores were then impregnated with a carbon precursor (sucrose in H_2SO_4,) following the recipe of Ryoo et al. [14] and the composite material was heated at 900°C under vacuum. Silica was then removed by HF leaching, leading to partially encapsulated gold nanoparticles in mesoporous carbon (Scheme 1).
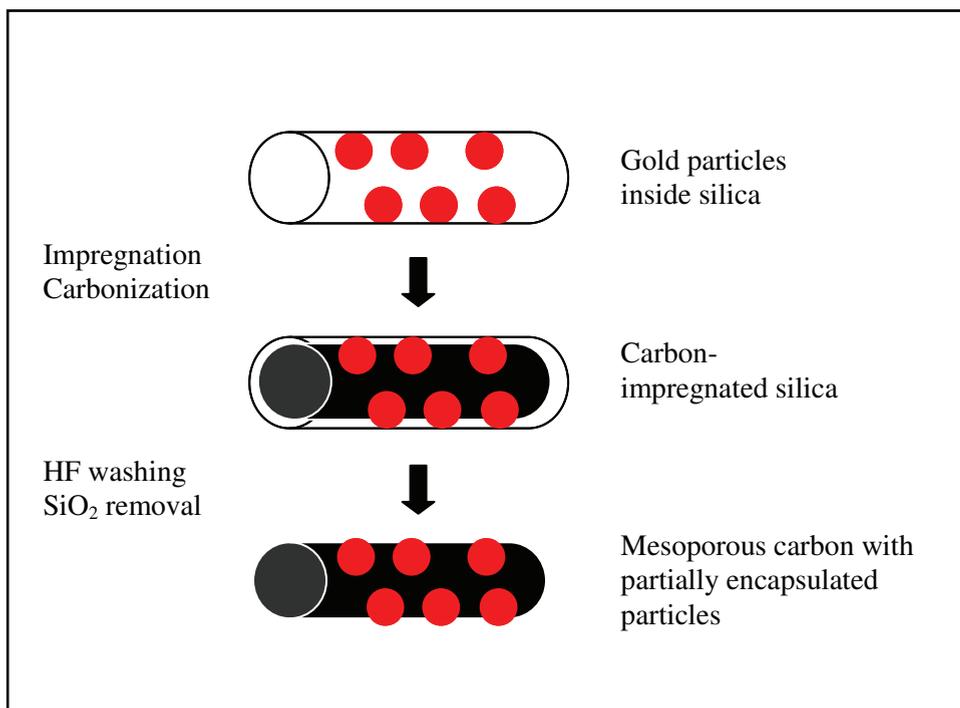
Scheme 1 The various steps in the synthesis of gold-containing mesostructured carbons.

All modified silicas and gold-containing mesoporous carbons were characterized by X-ray diffraction (XRD), N_2 adsorption and transmission electron microscopy (TEM).
After determination of the metal contents by inductively-coupled plasma optical emission spectroscopy (HORIBA Jobin Yvon Activa ICP-OES of IRCELYON-CNRS analytical core facilities), Au/silicas and the corresponding

Au/C replicas were tested in the aerobic oxidation of *trans*-stilbene in the liquid phase under optimized conditions previously described [15].

3. Results

All silicas were synthesized following literature procedures. Their structural and textural characteristics are reported in Table 1. Moreover, carbon replicas were also prepared on pristine silicas to evaluate their characteristics in the absence of gold particles.

Support/replica	S_{BET} (m^2/g)	Pore diameter (nm)
SBA-15	624	7.3
CMK-3	1218	4

Table 1 Textural properties of the various silicas and the corresponding carbon replicas.

As shown in the Table, all silica and carbon supports possess a high BET surface area, in excellent agreement with data reported in the literature for similar materials.

Moreover, the regularity and ordering of the porous network was evidenced by intense and well-defined reflections in the corresponding X-ray diffraction patterns (Figure 1).
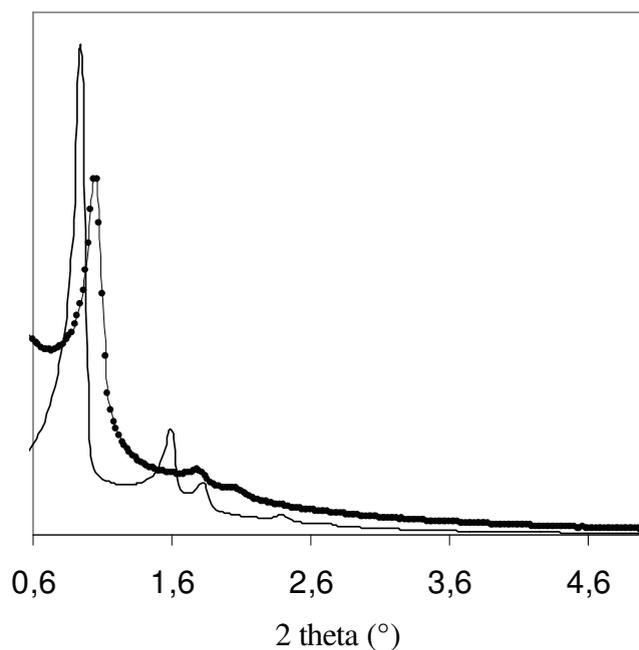

Figure 1: XRD patterns of SBA-15 (-) and the corresponding carbon replica CMK-3 (-●-).

The regularity and long-range ordering of the pore system was not affected by the different post-synthesis treatments: gold-containing silicas still show well defined XRD patterns, even after reduction of Au^{3+} cations. Both routes lead to well dispersed Au particles in silica (Fig. 2). However, a systematic study performed with TPTAC showed that the number of functional groups attached onto the silica surface is critical for the size and location of Au particles. At low coverage, TPTAC molecules are preferentially located on the surface of silica particles, leading to large Au crystals upon reduction.
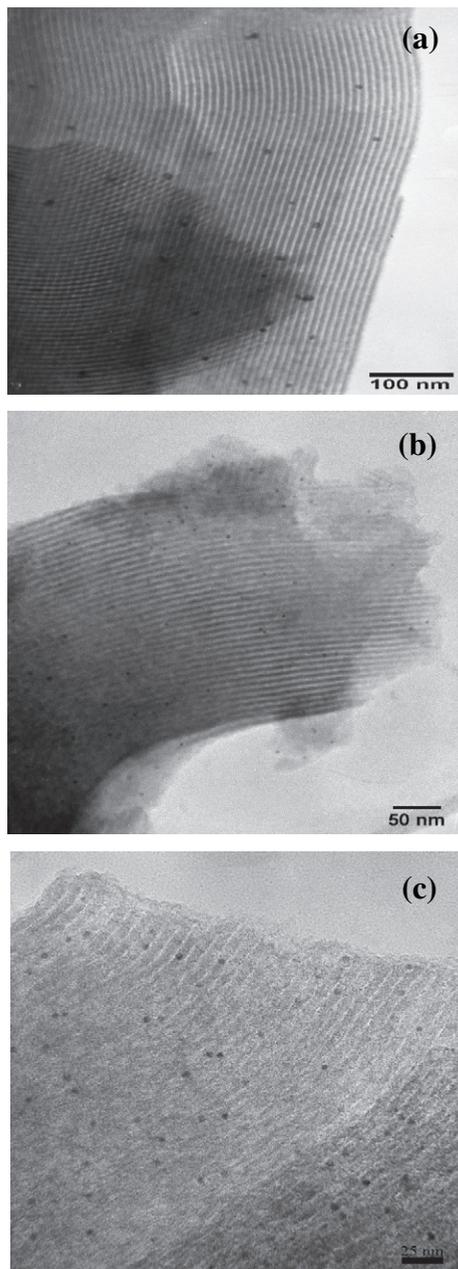

Figure 2: TEM pictures of Au/SBA-15 (0.3 wt. %) obtained with TPTAC (a) and MPTMS heated at 300°C (b) and Au/C obtained by replication of the sample prepared with MPTMS (c).

Au particles are significantly bigger with TPTAC (6.1 nm) than with MPTMS (3.8 nm). Moreover, for MPTMS-modified supports, the particle size is not strongly affected by temperature (3.8 and 4.2 nm at 300 and 560°C, respectively). As shown in Figure 3, the distribution of gold NPs sizes is retained after carbon pyrolysis and dissolution of silica. Moreover, XRD and transmission electron microscopy confirm that the presence of grafts in silica pores has no influence on the formation and structure of the carbon replica. However, while Au/SBA-15 (MPTMS-300°C) exhibit significant catalytic properties for the aerobic oxidation of *trans*-stilbene (Figure 4), the corresponding Au/C replica is essentially inactive. This is attributed to the lower accessibility to the gold nanoparticles partially embedded within the carbon walls, which, besides, confer the particles their enhanced thermal stability up to temperatures close to the melting point of bulk gold (1064°C). Ways to tune this nanocasting-based strategy towards active mesostructured Au/C catalysts are under investigation.
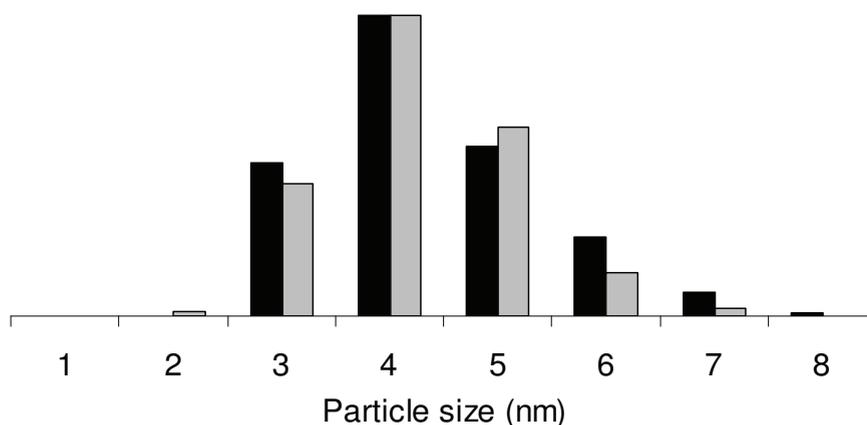

Figure 3: Distribution of gold particle sizes in SBA-15 (MPTMS-300°C, black) and the corresponding CMK-3 (grey).

Despite mass-transfer limitations, Au/SBA-15 (MPTMS-300°C) remains an interesting catalyst for this liquid phase reaction. Its selectivity is indeed quite different from that displayed by readily accessible (unconfined) gold nanoparticles supported on passivated high surface area silica [15]: in the confined mesostructure of MPTMS-functionnalized SBA-15, deoxybenzoin (1,2-diphenyl-ethanone) becomes a major product of the epoxidation reaction, with a yield of 45% at full conversion (78 h).
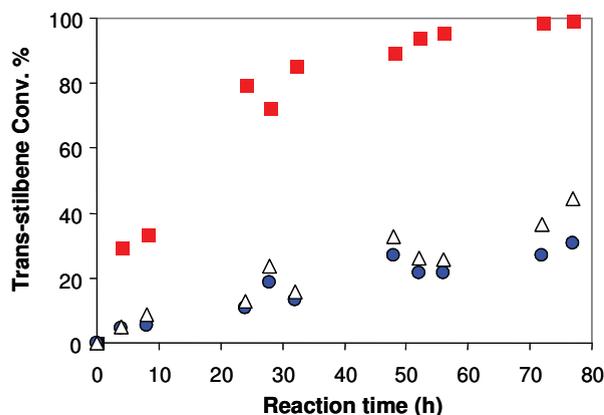
trans-stilbene conversion (■), epoxide (●) and deoxybenzoin (Δ) yields. Reaction conditions: *trans*-stilbene (1 mmol), methyl-cyclohexane (solvent, 20 mL), *tert*-butyl hydroperoxide (0.05 mmol / 7 □L of a 70% TBHP in water Aldrich solution), catalyst (91.7 mg / 2 μmol Au), 900 rpm, 80°C, air (atmospheric pressure).

Figure 4: Catalytic properties of 0.3%Au/SBA-15 (MPTMS-300°C) in the aerobic oxidation of *trans*-stilbene

4. Conclusion

New Au@C materials have been obtained using a nanocasting method, starting from preliminary functionalized silicas. Excellent dispersions of ultra-stable Au particles were obtained, with partial encapsulation in carbon walls. This route very could offer an alternative to colloidal deposition for the preparation of carbon-supported catalysts for the aerobic oxidation of olefins in the liquid phase.

5. References

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