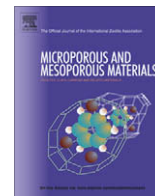




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Gold nanoparticles on silica monospheres modified by amino groups

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ABSTRACT

Silica monospheres with a diameter of 330 nm modified with aminosilane compounds of three different basicities have been prepared. Surface coverage of the silica with an organic compound leads to an increase of the point of zero charge (PZC) of the silica surface from 2.1 to 5.1, 6.5 and 7.2 values, depending on the amine used. From these silicas, gold-containing catalysts have been prepared by a deposition-precipitation method at the same pH as the PZC of the support. The best results have been obtained using 3-(Diethoxymethylsilyl) propylamine as a modifying agent, which has allowed obtaining a good dispersion of the gold particles with an average size of 3.8 nm.

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1. Introduction

In the last years the number of works related to the use of supported gold catalysts increased exponentially, due to the high activity of gold in a large number of catalytic processes, especially oxidation reactions [1–6]. The catalytic activity of these systems is determined by the state of oxidation, the size of the gold particles and the redox properties of the support, although the discussion still remains open for several determinant aspects of these factors, such as the nature of the active sites of gold and the reaction mechanisms. The majority of the investigated supports are reducible metal oxides (Fe₂O₃, TiO₂, CeO₂, etc.), which have been described as the more appropriate ones [5–7]. Non-reducible supports, such as Al₂O₃ and SiO₂, have been considered as less active systems in which the catalytic behaviour is a function essentially of the size of the gold particles: the higher activity is obtained for smaller particles. Nevertheless, the interest in these systems is based on the possibility to elucidate the role of the metal itself, since the weak interaction between the gold particles and the support surface minimizes the interaction effect. The catalytic behaviour also depends on other important factors such as the geometric and electronic structure of the gold particles [8]. The preparation of highly dispersed Au/Al₂O₃ catalysts has been described widely in the scientific literature and does not propose major difficulties, since methods commonly used for the synthesis of gold systems,

such as deposition-precipitation, co-precipitation and impregnation have been developed [2,6,9–11]. However, these methods have not been effective to obtain highly dispersed nanosize gold particles on SiO₂. The difficulty is related to the specific conditions of the deposition of gold. Due to the low value of the point of zero charge (PZC) of SiO₂ (close to 2), the surface of the silica is charged negatively at a pH higher than that value, making it very difficult for interaction and deposition of the gold anions (for instance [AuCl₄][−] that comes from the chloroauric acid (HAuCl₄) used as a gold precursor). To overcome the disadvantage of depositing negatively charged solution species on negatively charged silica surface, some authors propose the use of cationic species of gold, such as [Au(en)₂]³⁺ or [Au(PPh₃)₃]⁺ [12–14] or other methods of deposition, like sonochemical reduction [15], or other ones that do not include liquid solutions, e.g. chemical vapour deposition [16]. Recently other authors found it possible to prepare metal particles highly dispersed in mesoporous silica of SBA-15 type by functionalizing SBA-15 with a cationic organosilane [17]. This allowed generating a monolayer of positively charged groups on the pore surface of the material and, subsequently, incorporation of the [AuCl₄][−] species in the channels of the mesoporous structure by ion exchange.

The aim of the present work is to study the possibility of obtaining gold nanoparticles well dispersed on the surface of SiO₂ spheres by a standard deposition-precipitation method. The strategy of the synthesis is based on the surface modification of spherical silica particles by functionalization with organic aminosilane compounds with basic properties. This results in alteration of the point zero charge (PZC) of silica up to values higher than five. This allows formation of positive charged monolayer and reaching of pH values similar to PZC of the modified silica surface which deter-

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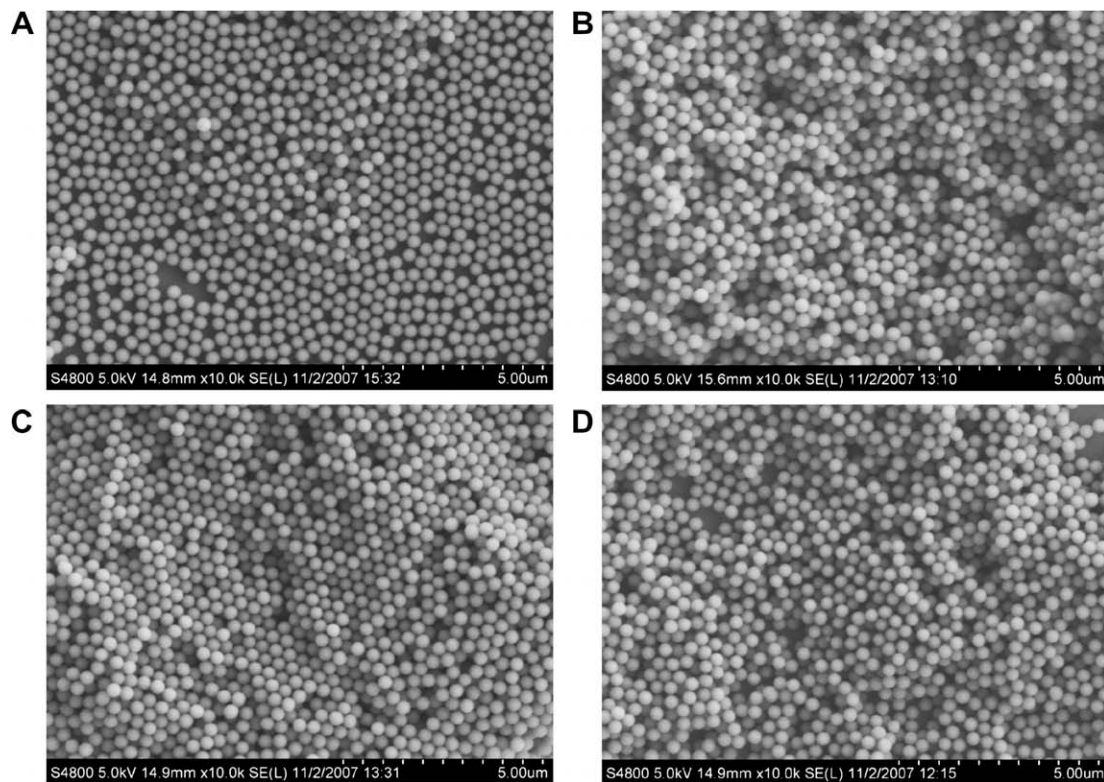


Fig. 1. Scanning electron micrographs (SEM) of the silica and silica modified spheres: (A) SiO₂; (B) SiO₂-PAN; (C) SiO₂-DEM; (D) SiO₂-MAP.

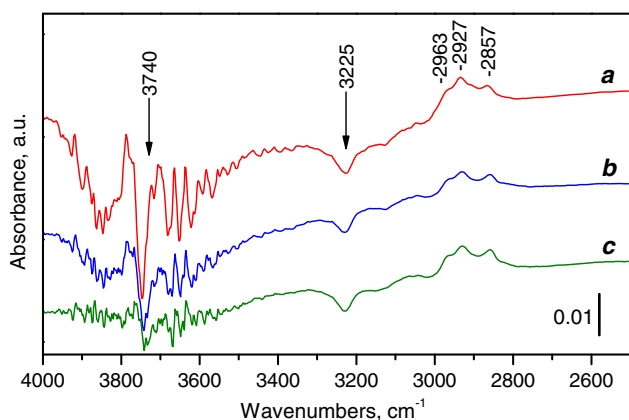


Fig. 2. Difference DRIFTS spectra obtained by rationing to the DRIFTS spectrum of the parent silica spheres collected “in situ” at 100 °C under a nitrogen flow. The DRIFTS spectrum of the corresponding modified silica is obtained under the same conditions: (a) Au/SiO₂-DEM; (b) Au/SiO₂-MAP and (c) Au/SiO₂-PAN.

mines the success of the deposition–precipitation process. The choice of the monodispersed SiO₂ spheres as a supporting material is based on their ability to facilitate the deposition of the gold particles, their potential applications in optics and biotechnology

Table 1

Textural properties and of the parent and modified silica

Silica	Aminosilane	S_{BET} (m ² /g)	PZC
SiO ₂	–	12.7	2.1
SiO ₂ -PAN	PANTMS	10.6	5.1
SiO ₂ -DEM	DEMSPA	8.9	6.5
SiO ₂ -MAP	MAPTMS	8.5	7.2

[18,19], as well as the growing interest in these materials as model systems in several fields [20,21].

2. Experimental

2.1. Syntheses

2.1.1. Silica support

A batch of 20 g of monodispersed spherical silica particles were prepared following the method proposed at first by Stöber et al. [20] and then modified by Giesche [21]. Tetraethylorthosilicate (TEOS, 99% pure, Alfa), absolute ethanol (Prolabo), ammonia (25%, Panreac) and deionised water were used as reagents. The synthesis proceeded as follows. Mixture A (154.66 ml H₂O, 48.02 ml NH₃, 197.32 ml C₂H₅OH) and Mixture B (72.1 ml TEOS, 327.48 ml C₂H₅OH) were heated separately under continuous stirring for 30 min at 40 °C. Then mixture B was added to mixture A quickly and kept under vigorous stirring for 1 h. After that, the solution became milky due to the precipitation of the silica. The solid was separated by centrifugation at 8000 rpm and washed four times with deionised water and ethanol. The obtained solid was dried overnight at 60 °C and finally calcined for 2 h at 200 °C.

2.1.2. Modified silica supports

[3-(Methylamino)propyl] trimethoxysilane (MAPTMS, Fluka 97% purum grade), [3-(Phenylamino)propyl] trimethoxysilane (PANTMS, Fluka 95% technical grade) and 3-(Diethoxymethylsilyl) propylamine (DEMSPA, Aldrich 97% pure) were used as a source of amino groups for functionalizing the silica support. The method used for the incorporation of the aminopropyl groups was based on that reported by Cauvel et al. [22]. Silica was freshly activated by heating for 2 h at 110–120 °C under continuous stirring. After that, 50 ml of a 0.1 M solution of the corresponding amino source in toluene was added, and kept for 24 h under refluxing. Then,

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