



Understanding the role of Ti-rich domains in the stabilization of gold nanoparticles on mesoporous silica-based catalysts



Alaina Moragues^a, Begoña Puértolas^b, Álvaro Mayoral^{c,d}, Raúl Arenal^{c,d}, Ana B. Hungría^e, Sonia Murcia-Mascarós^a, Stuart H. Taylor^f, Benjamín Solsona^{g,*}, Tomás García^{b,*}, Pedro Amorós^{a,*}

^a Institut de Ciència dels Materials, Universitat de València, P.O. Box 22085, 46071 Valencia, Spain

^b Instituto de Carboquímica (ICB-CSIC), C/ Miguel Luesma Castán 4, 50018 Zaragoza, Spain

^c Laboratorio de Microscopías Avanzadas (LMA), Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, Mariano Esquillor, 50018 Zaragoza, Spain

^d Fundación Agencia Aragonesa para la Investigación y el Desarrollo (ARAID), María de Luna 11, 50018 Zaragoza, Spain

^e Departamento de Ciencia de Materiales, Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Campus Río San Pedro, 11510 Puerto Real, Spain

^f Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, CF10 3AT Cardiff, United Kingdom

^g Departamento de Ingeniería Química, Universitat de València, Avenida de la Universitat, 46100 Burjassot, Valencia, Spain

ARTICLE INFO

Article history:

Received 9 January 2018

Revised 2 February 2018

Accepted 4 February 2018

Keywords:

CO oxidation

Gold

Nanoparticles

Mesoporous silica

Anatase

ABSTRACT

The preparation and stabilization of gold nanoparticles with a precise control of size and dispersion is highly attractive for a variety of applications, and a key aspect is thermal stability of the nanoparticles. This paper focuses on understanding the effect of TiO₂-based nanodomains, dispersed on mesoporous silicas, and how they control gold nanoparticle stability. The anatase domains have been incorporated through two different strategies: co-hydrolysis of Si and Ti reagents that directly form the mesoporous material through self-assembling with surfactant micelles, or the post-impregnation of the mesoporous silica with Ti(acac)₂. Both strategies lead to different incorporation of the anatase domains: partially embedded inside the silica walls, or occupying the mesopores. We have observed that the inclusion in the pores favors the stability of the final material due to a more favorable gold-support interaction and also due to a stabilizing effect associated with a scaffold effect of the anatase crystals, which hinders the collapse of the mesostructure.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

More than thirty years ago the inactivity of gold as a catalyst was refuted by the independent work of Haruta and Hutchings, who described the importance of supported gold nanoparticles as very active heterogeneous catalysts for low-temperature CO oxidation and ethyne hydrochlorination, respectively [1,2]. Subsequently, the nature and properties of catalysts based on gold nanoparticles have received increased attention due to their superior activity in many industrially and environmentally-friendly important reactions, including selective hydrogenation, epoxidation of alkenes, oxidation of alcohols and Volatile Organic Compounds, coupling reactions and direct H₂O₂ synthesis, amongst others [3–11]. Regardless of the reaction mechanism for each particular process, there is a reasonable consensus on the need for gold particles with a size of less than 10 nm, together with a high

particle dispersion [12]. Although gold can coexist as isolated centers, small clusters and nanoparticles, a recent study has shown that, for the oxidation of CO, the conversion rate of nanoparticles is about two orders of magnitude greater than that of isolated atoms [13]. To achieve the desired dispersion of gold a common strategy is the use of supports to control agglomeration and coalescence [2,7,8,11,14].

Generally, the catalytic activity of supported gold nanoparticles is governed by the intimate relationship between the size of the nanoparticle ensemble, the features of the support and the nature of the interface. The decrease of the particle size leads to an increasing proportion of low-coordinated surface atoms [15], together with changes in the electronic properties resulting from the quantum size effect [16,17]. In contrast to non-reducible oxides such as SiO₂, γ-Al₂O₃ or MgO, supports with redox properties, for example Fe₂O₃, Co₃O₄, Mn₂O₃, CeO₂ or TiO₂, seem to be beneficial for the catalytic activity [18–21]. They can impact the electronic properties of the gold particles and vice versa, by modifying the mechanism of oxygen vacancy formation and replenishment, which enhances the catalyst reactivity.

* Corresponding authors.

E-mail addresses: benjamin.solsona@uv.es (B. Solsona), tomas@icb.csic.es (T. García), pedro.amoros@uv.es (P. Amorós).

Together with the intrinsic nature of the support composition, additional aspects related to its morphology and porosity seems to be the key to stabilizing gold nanoparticles. Although SiO₂ may not be the best choice of support specifically for gold nanoparticles, it does have many beneficial properties as a catalyst support. In order to take advantage of the high surface area of mesoporous silicas and their confinement effect inside the mesopores [22], silica can be modified with organic (including periodic mesoporous organosilicas, PMO) and inorganic species to favor the interaction with gold [23–26]. In fact, different metal oxides can be included into the mesoporous silicas. These metal oxides act as inorganic anchors, able to interact with gold precursor species favoring the gold-support interaction [27]. Depending on the chemical nature and crystallinity of the oxidic domains, different environments can be achieved, leading in some cases to strong interfacial interactions when crystalline oxides are present [22,28,29]. This last aspect is essential in many industrially and environmentally important reactions.

A challenging problem for the industrial implementation of gold-based catalysts relies on attaining thermally-stable materials under highly demanding operating conditions [30]. In fact, only a few examples exist of supported gold catalysts preserving activity at temperatures higher than 700 °C. Supported and unsupported metal nanoparticles show rapid particle aggregation, especially at elevated reaction temperatures [31,32], at which the hydrothermal stability of the catalysts becomes a crucial issue [33,34]. Strategies such as post modification of Au/TiO₂ by amorphous SiO₂ decoration [35], the production of core-shell nanostructures [36,37], FeO_x modified hydroxyapatite supported Au catalysts [38], the synthesis of thin porous alumina sheets [39], gold on cobalt oxide particles supported on a mixture of zirconia-based ceria [40], or the formation of complex Au₂Sr₅O₆ mixed oxides [41] have been proposed to address this problem. Additionally, the suitability of mesoporous materials, such as M41s or SBA, as matrices to immobilize catalytically active species and provide nano-size confinements inside the pore system has also been reported [42]. However, the lack of thermal stability of nanoparticles on silica supports under severe operating conditions remains a challenge [43]. In fact, even confined inside mesopores, migration of gold nanoparticles occurs both along the channels and in traverse directions through the silica walls when a SBA-15 silica support is used at temperatures above 550 °C, according to direct imaging observations [44]. In this regard, we recently proposed gold supported on a TiO₂ impregnated SiO₂ bimodal mesoporous UVM-7 support as a suitable structure to stabilize highly dispersed gold nanoparticles at temperatures as high as 800 °C [45]. The UVM-7 support belongs to the Nanoparticulated Bimodal porous Silicas, in which the decrease of the particle size leads to a shortening of the maximum length of mesopores, together with the generation of a supplementary textural-type inter-particle porosity [46–48]. The dual role of TiO₂ domains as a scaffold [45], preventing the collapse of the SiO₂ mesostructure, and as anchoring islands to avoid gold sintering, are the factors responsible for the stability of gold nanoparticles.

Enticed by the versatility of UVM-7 to be tuned by the incorporation of different metal species in the structure, herein, we synthesize gold-supported TiO₂-containing UVM-7 catalysts via the *one-pot* Atrane route and contrast their properties and performance for CO oxidation, selected as a model reaction, with those previously reported (in which the Ti was incorporated through a second preparative step) [45]. We investigate how the nature and location of Ti-rich domains included in mesoporous silicas impact on stability and activity as heterogeneous gold-containing catalysts. We compare here the influence of the synthesis method (*one-pot* or *two-pot*) and the calcination temperature on the structural organization and activity of the catalyst. Advanced

characterization methods including spherical aberration (Cs) corrected scanning transmission electron microscopy, X-ray photoelectron spectroscopy and ²⁹Si MAS NMR spectroscopy are able to rationalize the impact of the speciation of the TiO₂ domains, and the activation temperature of the catalysts on the stability of the support and gold nanoparticles.

2. Experimental details

2.1. Chemicals

All the synthesis reagents were analytically pure, and were used as received from Aldrich [tetraethyl-orthosilicate ≥ 98.0% (TEOS), cetyl-trimethylammonium bromide ≥ 98% (CTMABr), triethanolamine ≥ 99.0% (TEA), tetrabutyl-orthotitanate ≥ 98.0% (TBOT), titanium(IV) oxyacetylacetonate 90% (TiO(acac)₂), potassium tetrachloroaurate(III) 98% (KAuCl₄), sodium hydroxide ≥ 98% (NaOH) and ethanol].

2.2. Catalyst preparation

Two families of gold containing catalysts, based on the deposition of Au on Ti-modified UVM-7-type mesoporous silicas, were synthesized: Ti-UVM-7 and TiO₂/UVM-7. While the Ti-UVM-7 derivatives were isolated through a *one-pot* method, the TiO₂-UVM-7 catalysts were synthesized through a post functionalization strategy from pure UVM-7 silicas.

Synthesis of UVM-7 pure silica: The synthesis of UVM-7 silica was achieved through the “Atrane route”, which combines the use of a cationic surfactant (CTMABr) as a structural directing agent, and consequently as a porogen after template removal, and a complexing polyalcohol (TEA) as hydrolysis retarding agent [49]. The molar ratio of the reagents was; 2 TEOS:7 TEA:0.52 CTMABr:180 H₂O [46,47]. In a typical synthesis, the corresponding amounts of TEOS (10.7 mL) and TEA (22.3 mL) were mixed under continuous stirring at 140 °C until a homogeneous dispersion was achieved. The temperature was then decreased to 120 °C and the CTMABr (4.23 g) added. The resulting gel was cooled to 80 °C and distilled water (80 mL) was added. This mixture was aged at room temperature for 16 h under continuous stirring. The resulting mesostructured powder was separated by filtration, washed extensively with deionized water and ethanol, and dried at 60 °C for 16 h. In order to prepare the final porous material, the template was removed by calcination at 550 °C for 6 h (heating ramp = 5 °C/min) under static air atmosphere. A sample of the pure silica UVM-7 was calcined at 800 °C for comparative purposes, and was labelled as UVM-7 800.

Synthesis of Ti-UVM-7: Titanium was included into the UVM-7 following a co-condensation method: the titanium precursor (TBOT) was included in the first step of the UVM-7 synthesis to obtain a mixture of atrane complexes (Si and Ti), and then the protocol was the same as for UVM-7 [50]. The Ti content can be modulated between Si/Ti = ∞ to Si/Ti = 1 starting from the 2-xTEOS:x TBOT:7 TEA:0.52 CTMABr:180 H₂O molar ratio. In this work we synthesized four supports with nominal Si/Ti values of 21, 5, 4 and 1 that have been denoted as Tix-UVM-7(1)RT (x = 22, 5, 4 and 1; (1) indicates *one-pot* synthesis).

Synthesis of TiO₂/UVM-7: The titanium incorporation was carried out through a wet-impregnation procedure, previously described by Narkhede et al. [51]. The corresponding weight of TiO(acac)₂ was dissolved in 100 mL of pure ethanol. Deionized water was slowly added while continuous vigorous stirring. Subsequently, the impregnation of the calcined UVM-7 silica support (0.6 g) was carried out by stirring the sample for 2 h with the Ti solution. The mixture was filtered and washed thoroughly. The

Download English Version:

<https://daneshyari.com/en/article/6526765>

Download Persian Version:

<https://daneshyari.com/article/6526765>

[Daneshyari.com](https://daneshyari.com)