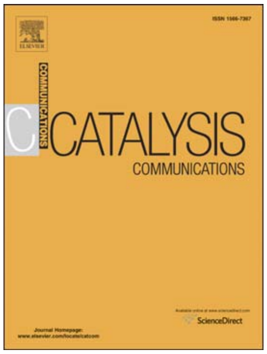

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Colloidal gold immobilized on mesoporous silica as a highly active and selective catalyst for styrene epoxidation with H_2O_2

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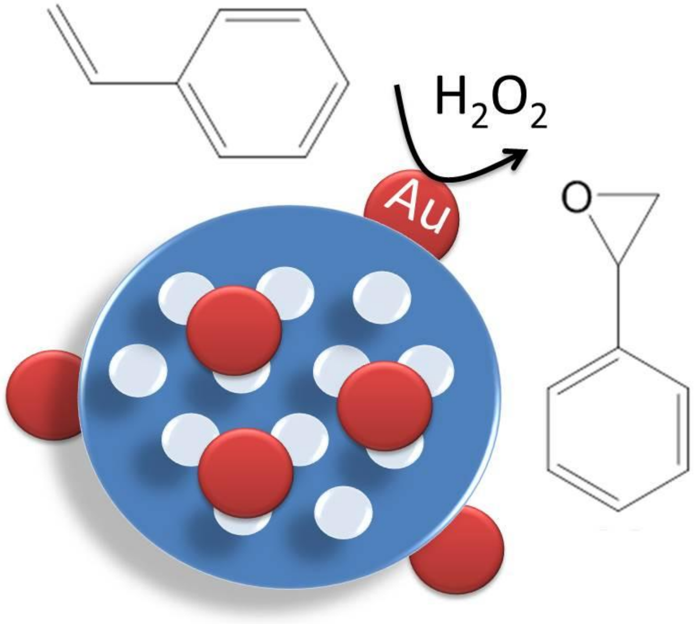
Abstract

Colloidal gold nanoparticles were synthesized by different procedures affording suspensions with two different mean sizes (2 and 5 nm). Au catalysts were prepared by sol immobilization onto several silica frameworks with different 2D and 3D mesoporosity. The catalysts were tested in styrene oxidation reactions showing excellent efficiency and selectivity. The effect of nanoparticle size and mesoporous framework on the physical and catalytic properties of the final materials was studied. The most selective catalyst was prepared from the 5 nm Au nanoparticles and the more interconnected silica framework (3D mesoporosity).

Keywords:

Gold nanoparticles; Colloids immobilization; Epoxidation; Mesostructured silica

Graphical abstract



1. Introduction

Gold was considered for a long time to be catalytically inactive [1]. However, in the late 1980's the low-temperature oxidation of CO [2] and the hydrochlorination of ethyne to vinyl chloride [3] over gold catalysts led to gold becoming a hot topic in catalysis research [4]. Nowadays, there is no debate about the myriad of possibilities that nano-gold can offer to activate molecules [5]. Supported gold nanoparticles (AuNPs) have been shown to be very active catalysts for a variety of transformations. Especially relevant are diverse selective oxidations in which AuNPs proved to be particularly efficient [6]. Furthermore, supported gold catalysts have been developed for a wide range of non-oxidative processes, such as additions to multiple C-C bonds, (benzannulations) [7] and the highly selective hydrogenation of N–O bonds [8].

Although there has been much controversy concerning the nature of the active sites of gold nanoparticles catalysts [4, 5], it has been accepted that the key parameters determining activity and selectivity are the size and dispersion level of the particles and the interaction between AuNPs and the support [9]. In this sense, the preparation method and type of support material used are crucial to obtain well dispersed nanoparticles [10]. Due to the peculiar characteristics of gold (low melting point, low affinity for oxides) the methods and supported matrices available for the preparation of supported AuNPs catalysts are limited. Usual methods such as impregnation or deposition-precipitation are intensely dependent on the isoelectric point (ISE) of the support. In the case of gold precursors, acidic oxides such as silica (ISE = 2) do not produce a good dispersion of AuNPs [11]. In this case, a better approach can be the sol immobilization technique, applicable regardless of the type of support. This technique also allows for the possibility to control the particle size/distribution, which normally produces highly dispersed metal catalysts. Notably, the immobilization of pre-formed colloidal AuNPs on carbon nanotubes has been shown to provide more active catalysts for the oxidation of glycerol in comparison to analogous catalysts made by conventional impregnation or deposition-precipitation methods [12].

With the goal of further assessing methods for immobilization of colloidal AuNPs into porous solids, we describe herein the synthesis and catalytic properties of different catalysts prepared using various suspensions of AuNPs and mesoporous silicas as supports. The fine control in the dimension of the colloidal metal nanoparticles allowed us to study the nanoparticle size dependence of the catalytic reaction. All catalysts were tested in the epoxidation of styrene as the test reaction. Epoxides are very useful and versatile intermediates for the synthesis of many commodities and fine chemicals; therefore, studies on olefin epoxidation are a subject of great interest. Aqueous hydrogen peroxide (H_2O_2) was selected as environmentally friendly oxidant, since the only significant byproduct is water. All the supported AuNPs catalysts reported herein displayed very good catalytic performance, higher than similar catalysts previously reported.

2. Experimental section

2.1 Synthesis of the silica supports

Large-pore mesoporous silica with 3D wormhole framework structure (denoted MSU-J) was prepared through a supramolecular hydrogen-bonding assembly pathway from low-cost sodium silicate as the silica source and commercially available amine-terminated Jeffamine surfactant of the type $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_xNH_2$ as the structure-directing porogen. The synthetic procedure for MSU-J materials has been reported previously [13, 14]. For comparison purposes, SBA-15 hexagonal mesoporous silica with comparable textural parameters but a 2D pore structure was also synthesized. The synthesis of SBA-15 was carried out following a procedure reported previously [15].

2.2 Colloidal gold nanoparticles preparation and immobilization

Two different synthetic methods were used for the preparation of colloidal gold nanoparticles (AuNPs) to yield different mean sizes of the suspensions. First, Au nanoparticles (Au1), were obtained in toluene by reduction of $[AuCl_4]^-$ with $NaBH_4$ and subsequent stabilization using tetraoctylammonium bromide (TOAB) as a capping agent; see detailed method in [16]. The second procedure (Au2) used PPh_3 as a capping agent according to a method previously reported by Hutchison and co-workers [17]. Triphenyl phosphine was added to the toluene solution of $[AuCl_4]^-$/TOAB and the mixture vigorously stirred until the organic phase become white and cloudy. In both methods, the aqueous $NaBH_4$ reducing agent was added dropwise while maintaining the mixture under vigorous stirring. AuNPs formation was indicated when the mixtures turned a reddish color, after which, the suspensions were stirred for 3 more hours. The immobilization of the particles onto the mesoporous silica supports was carried out by dropping the nanoparticle suspensions into the previously dried support (150 ºC, 12 h). The volume of solution used was 95% of the silicas pore volume, as measured by N_2 adsorption. Strong vortex agitation was applied in order to homogenize the samples. Finally, the toluene was removed by drying under vacuum at 60 ºC for 24 h. Due to the different pore volumes of the supports, the procedure was repeated 2 times in the case of MSU supports and 3 times for SBA materials.

2.3 Styrene epoxidation

Catalytic reactions were carried out according to the following procedure: 1.04 g of styrene (10 mmol), 5.0 g of acetonitrile and 100 mg of catalyst were stirred for 5 min at room temperature. The mixture was then heated to 65 ºC under continuous stirring and a solution of 3.6 ml of H_2O_2 (30 wt.%) in methanol (7.69 g) was added dropwise during 1 h. The reaction time was started when the first drop of oxidant solution was added to the reaction mixture. During the whole process, aqueous NaOH (1 M) was added to maintain the pH value in the range of 9.0–9.5. This is a variation of the procedure proposed by Y. Jin *et al.* [18].

3. Results and discussion

Colloidal suspensions of AuNPs were synthesized using a variation of the well-known two phases method and two different capping agents, TOAB or PPh_3. This approach to AuNP preparation yields highly monodispersed Au nanoparticles (see Fig. 1) and ensures two important features: (i) AuNPs prepared in toluene show low agglomeration ratio, narrow particle size distribution and small average size and (ii) in the case of Au1, the non-covalent interaction between the metal nanoparticles and TOAB enables an easily replacement of the capping agent. Whereas the Au1 suspension using TOAB as the capping agent consists of metal nanoparticles around 5 nm of average size, Au2 suspension with PPh_3 as the capping agent produces smaller nanoparticles around 2 nm average size. This difference in size is confirmed by UV-Vis measurements. As expected, the UV–Vis absorbance profile of the larger Au1 nanoparticle toluene suspensions clearly show the typical plasmon resonance band observed near 530 nm for particles in the 5-20 nm diameter range (see Fig. 1 (d), continuous line). On the other hand, a representative UV-Vis spectrum of Au2 (Fig. 1 (d), dotted line) shows a weaker band and almost no plasmon resonance, indicative of gold nanoparticles that are smaller than 2 nm in diameter [17], which is in good agreement with TEM observations. Thus, these observations are in agreement with previous results [19] that show the particle plasmon absorption band becoming sharp and more intense with increasing particle size.

Fig. 1. Characterization of colloidal Au NPs: (a) representative TEM image of Au1 suspension and (b) the corresponding size distribution, (c) representative TEM image of Au2 suspension and (d) UV-Vis spectra of both solutions.

The incorporation of AuNPs into the different mesoporous silica frameworks influences their textural properties in very different manners; as illustrated by the nitrogen adsorption isotherms and porosymmetry data in Fig. 2 and Table 1. Whereas the immobilization of metal nanoparticles onto the 2D mesoporous structure of SBA-15 substantially decreases the BET surface area and pore volume of the material, the surface area decrease for the 3D framework MSU-J is much less marked and the pore volume remains practically unchanged. This is probably due to the blocking of the pores by the nanoparticles in the SBA-15 which leads to a decrease in adsorption capacity and therefore, to a decrease in pore volume and surface area. For the MSU-J support matrix, pore blocking by the nanoparticles is less significant, probably because of its 3D mesoporous structure. In any case, immobilization of AuNPs onto the solids only slightly decreases the average pore size of both materials, as showed in the pore size distributions of Fig. 2 insets.

Fig. 2. Nitrogen isotherms at 77 K and its corresponding pore size distribution calculated by the BJH method (inset) of samples prepared by immobilization of AuNPs in (a) SBA-15 and (b) MSU-J silicas.

Table 1 Textural parameters and metal loading of the supported mesoporous catalysts.

Support	D_{nanoAu}.(nm)	Au Loading (wt%)[a]	S_{BET}[b] (m^2g^{-1})	V_{meso}[c] (cm^3g^{-1})	$Ø_{meso}$[c] (nm)
SBA-15	–	–	710	1.0	7.2
	2	0.2	490	0.8	7.1
	5	0.6	350	0.6	6.8
MSU-J	–	–	480	1.7	8.8
	2	0.2	430	1.7	8.6
	5	0.6	350	1.6	8.2

[a] Observed Au loading determined by ICP-MS analysis of the filtrate after treatment of the samples with *aqua regia.* [b] Surface area estimated by multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.30. [c] Mesopore volume and average pore diameter calculated from the adsorption branch according to the BJH method.

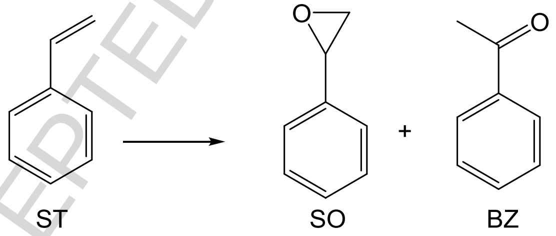
Representative TEM images of gold-containing mesoporous silicas are shown in Fig. 3 (a) and Fig. SI1 (a). From these images it can be clearly seen that the catalysts contain well-dispersed AuNPs and they maintain approximately the same size found for the previously synthesized suspensions. The use of the sol stabilizer and high surface area supports affords very good metal dispersions. SBA-15 catalysts made with Au1 suspensions features particle sizes with average diameters of 6 nm within the silica material (see Fig. 3 (b)), while MSU-J catalysts show slightly bigger sizes of around 7 nm (see Fig. SI1 (b)).

Fig. 3. (a) Representative TEM image of SBA-15 mesoporous silica with immobilized AuNPs prepared from suspension Au1 and (b) the corresponding particle size distribution.

The performance of each catalyst for the peroxide oxidation of styrene to styrene oxide is summarized in Table 2. The catalytic tests were carried out using acetonitrile as solvent under basic conditions, which is a prerequisite for epoxidations involving the Payne reaction [18]. Under these reaction conditions all catalysts gave quantitative conversions after 6 h of reaction, the two main products being styrene oxide and benzaldehyde (> 90%). In the table, we focus for simplicity on the conversion of styrene to these two products. As expected, smaller nanoparticles sizes resulted in more active catalysts which can obtain the same conversion of the larger particles, but with a third of gold loading. On the other hand, catalysts prepared from the larger nanoparticles showed better selectivity to styrene oxide, regardless of the mesoporous silica used to support the particles. This improved selectivity can be related to the lower reactivity of the catalysts with bigger nanoparticle sizes. The decrease in the selectivity upon complete conversion of styrene maybe due to the subsequent decomposition of styrene oxide [20]. The selectivity is also dependent on the silica framework used for the stabilization of the AuNPs, with the 3D framework of the MSU-J support providing higher selectivity.

Table 2 also compares the reactivity of our silica supported catalysts with catalysts previously reported in the literature. To the best of our knowledge, the catalysts developed in the present work are more active than the best catalysts previously reported, including Au_{25} clusters supported on hydroxyapatite (HAP) [20], Au supported on a periodic mesoporous silica (denoted PMO-SBA-15) [21] and on silica formed in a one-pot synthesis method [22]. Also, the selectivity toward styrene oxide for our mesoporous catalyst systems are among the highest reported. Only the previously reported Au-2S-1L-4.5 catalyst system [18] wherein Au is immobilized on a hybrid mesoporous organic-inorganic support shows substantially higher selectivity to the epoxide. In this latter system sulfur centers on the organic moiety is used to capture and stabilize the gold particles. But the higher selectivity in this case may more likely be due to the incomplete styrene conversion and slower subsequent decomposition of the epoxide to the aldehyde. Thus, the results reported here indicated that nanogold particles supported on surfactant-templated mesoporous silica supports by sol immobilization are very promising catalysts for the selective oxidation of olefins based on the Payne oxidation and the use of a green H_2O_2 oxidant.

Table 2. Catalytic activity of supported AuNPs on mesoporous silicas for the epoxidation of styrene in comparison with earlier reported catalysts.



Support	D_{nanoAu}. (nm)	Au Loading (wt%)	Rxn. Time (h)	Conversion (%)	Selectivity SO/BZ
SBA-15	2	0.2	6	99	9
	5	0.6	6	99	18
MSU-J	2	0.2	6	99	15
	5	0.6	6	98.5	23
Au-2S-1L-4.5 [18]	7.6	4.5	8	60	77
HAP [20]	1.4	0.5	12	>99[a]	> 12[b]
PMO-SBA-15 [21]	1.8	2.0	12	95[a]	4.5
Silica, one-pot [22]	6.4	4.0	14	99[a]	5.4

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[a] These reactions use TBHP as oxidant. [b] No selectivity for the rest of products is given.

4. Conclusions

Colloidal gold nanoparticles of two different mean sizes (2 and 5 nm) have been synthesized and immobilized into mesoporous silica frameworks (MSU-J and SBA-15 mesostructures) with retention of the average particle size of the nanoparticles formed in suspension. In comparison to the hexagonal 2D mesopore structure of SBA-15 the textural properties of the more interconnected framework of MSU-J silica with 3D mesoporosity are less affected by the immobilization of the nanoparticles and the blocking of the pores by the nanoparticles. The final catalysts are highly active for styrene oxidation, showing a good selectivity to the styrene oxide product, especially in the case of the larger nanoparticles.

Acknowledgements

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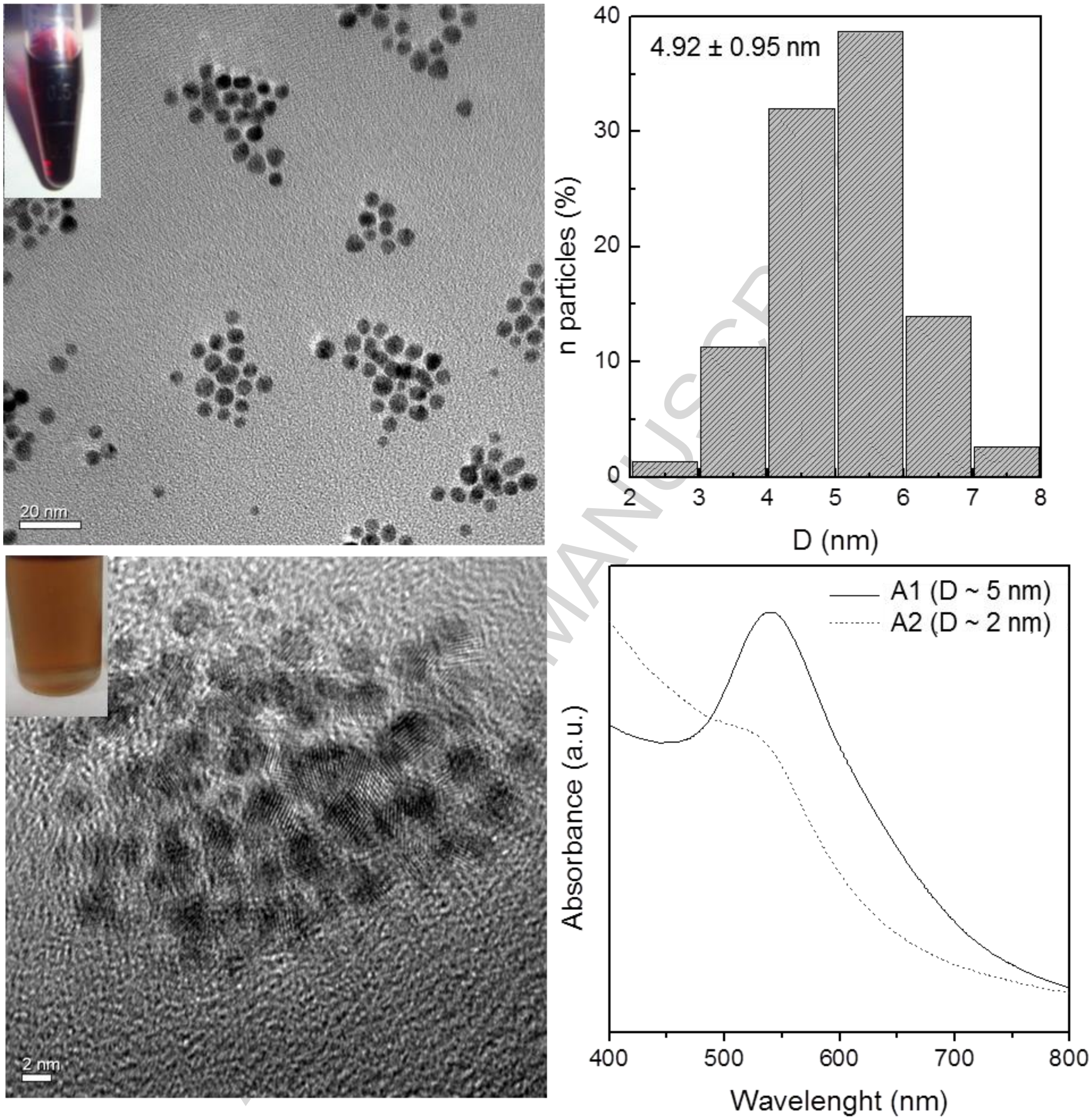
20 nm
2 nm
4.92 ± 0.95 nm
n particles (%)
0
10
20
30
40
2
3
4
5
6
7
8
D (nm)
A1 (D ~ 5 nm)
A2 (D ~ 2 nm)
Absorbance (a.u.)
400
500
600
700
800
Wavelenght (nm)

Figure 1

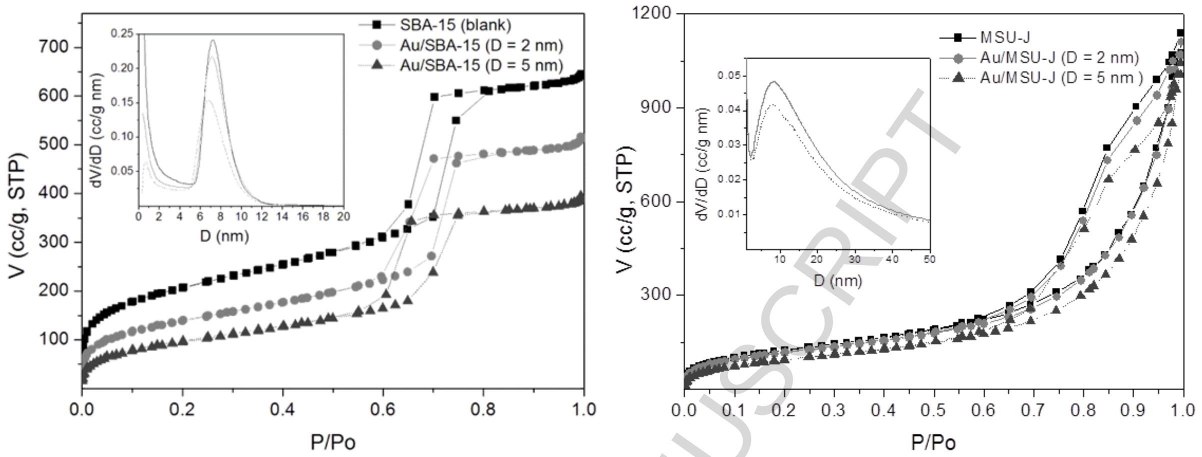
SBA-15 (blank)
Au/SBA-15 (D = 2 nm)
Au/SBA-15 (D = 5 nm)
V (cc/g, STP)
P/Po
dV/dD (cc/g nm)
D (nm)
0.25
0.20
0.15
0.10
0.05
0 2 4 6 8 10 12 14 16 18 20
100
200
300
400
500
600
700
0.0
0.2
0.4
0.6
0.8
1.0
MSU-J
Au/MSU-J (D = 2 nm)
Au/MSU-J (D = 5 nm)
1200
900
600
300
0.05
0.04
0.03
0.02
0.01
10 20 30 40 50
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

Figure 2

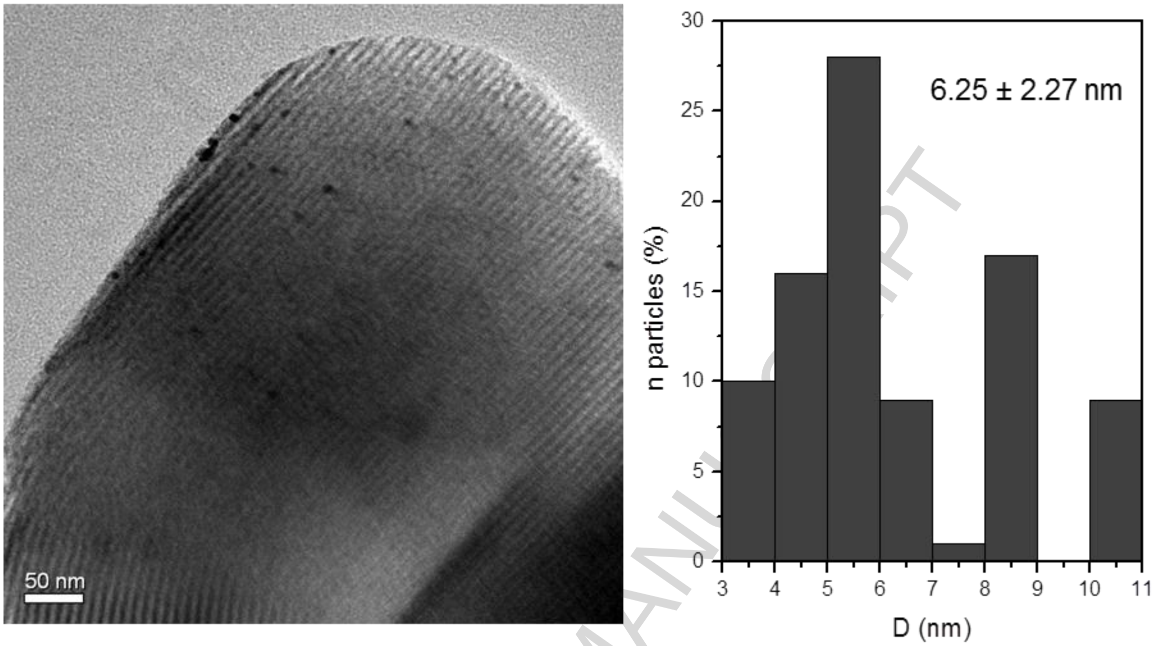

Figure 3

Highlights:

1. Synthesis of Au suspensions with different particles size by different methods.

2. Immobilization of Au nanoparticles in several silica frameworks.

3. Active materials in the oxidation of alkenes using H_2O_2 as green oxidant.

4. Highly active and selective catalysts under mild reaction conditions.