



Gold nanostructured materials for the selective liquid phase catalytic oxidation

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Au(0) sols were obtained in aqueous solutions by reduction of NaAuCl₄ with NaBH₄ in the presence of protective agents [the long chain compound poly(oxyethylene(23)lauryl ether (C12E23), the polymer poly{bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea} (PEG), the poly quaternary salt obtained by reaction of a polyethyleneglycole with the bisphenol A diglycidyl ether (PEU), and a polysaccharide (dextrin)]. The sols, characterized by TEM microscopy and UV-Vis spectroscopy, consisted of nanoparticles of different size (2.6–6.9 nm) depending on the used stabilizing agent. The colloidal solutions were immobilized on activated carbon. The carbon-supported gold catalysts were used in a model reaction for the selective liquid phase oxidation of ethylene glycol to glycolate ($pO_2 = 300$ kPa, $T = 343$ K, r.t. = 1 h, [EG] = 0.5 M, EG/Au = 1000, EG/NaOH = 1, EG = ethylene glycol). A comparison of the catalytic activity underlines the importance of the stabilizing agent in both the steps of sol formation and support impregnation.

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1. Introduction

The immobilization of gold sols on a support is an established technique for the preparation of heterogeneous catalysts [1–7]. In this field we have recently reported the preparation of Au(0) colloids immobilized on activated carbon and titania [8]. In particular the Au/TiO₂ materials were found very active in the selective liquid phase oxidation of the ethylene glycol to glycolate. At that time we underlined the importance of using the correct sol with respect to the support for improving the catalytic activity.

In this paper, we report gold colloids stabilized by polymers or surfactants ([2–4] and [9–11]) chosen for the immobilization on activated carbon. The oxidation reaction of a model substrate was assessed and the conditions in which the stabilizer played an effect in determining the catalytic activity were highlighted.

The stabilization of the particles in the sols was carried out using the protective agents listed below, following the three methodologies: (a) steric stabilization, by interdigit of alkoxyalkyl chains (C12E23 and PEG) [C12E23 = C₁₂H₂₅(OCH₂CH₂)_nOH, $n = 23$; PEG = (CH₃)₂C{C₆H₄-4-[OCH₂CH(OH)CH₂(OCH₂CH₂)_nOH]}₂, Fig. 1]; (b) decrease of van der Waals forces by adsorption of a relatively rigid hydrophilic macromolecule as dextrin; (c) increase of surface potential and/or charge density by absorption

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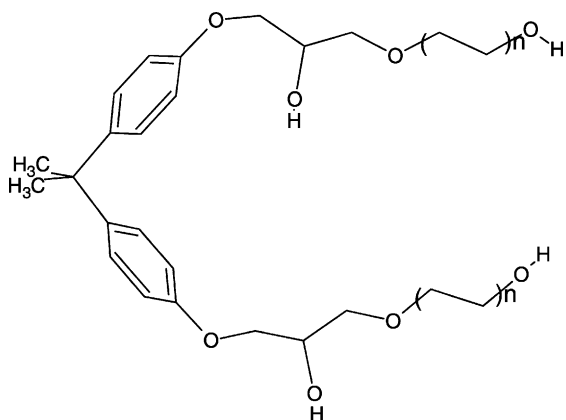


Fig. 1. PEG = polyethylene glycol reacted with bisphenol A diglycidyl ether, $[(\text{CH}_3)_2\text{C}\{\text{C}_6\text{H}_4-4-[\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}]\}_2]$.

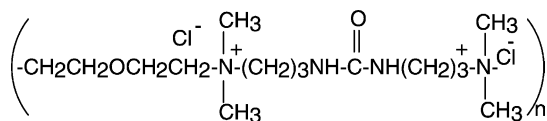


Fig. 2. PEU = poly{bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea}, $[(\text{CH}_3)_2\text{C}\{\text{C}_6\text{H}_4-4-[\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}]\}_2]$.

of the long-chain polyion PEU [PEU = $[(\text{CH}_3)_2\text{C}\{\text{C}_6\text{H}_4-4-[\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}]\}_2]$, Fig. 2].

2. Experimental

2.1. Materials

$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ (99%), NaBH_4 (99%), $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, $n = 23$, poly(oxyethylene (23) lauryl ether (C12E23), $(\text{CH}_3)_2\text{C}\{\text{C}_6\text{H}_4-4-[\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}]\}_2$, poly{bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea} (62% (w/w) aqueous solution) (PEU, average $M_W \sim 10,000$ Da), and dextrin (average $M_W \sim 9000$ Da) were purchased from Aldrich.

Glycolic acid (99%), propionic acid (99.5%), ethylenglycole (99.5%) and the polyethylene glycol reacted with bisphenol A diglycidyl ether $[(\text{CH}_3)_2\text{C}\{\text{C}_6\text{H}_4-4-[\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}]\}_2]$

(PEG, average $M_W \sim 15,000$ – $20,000$ Da), were supplied by Fluka.

Activated carbon was supplied by Carbosorb (MK, SA = 900 – 1100 m^2/g , PV = 1.5 ml/g , pH 9–10) and gaseous oxygen (99.99%) was from Siad. Milli-Q water was used in all the preparations.

2.2. Stock solutions

The 4×10^{-4} M aqueous solution of NaAuCl_4 was prepared in Milli-Q water and stored for a maximum of 2 weeks. The aqueous solutions of PEG (2% (w/w)), PEU (1% (w/w)), dextrin (1% (w/w)), and NaBH_4 (0.1 M) were freshly prepared. All solutions were filtered off through a cellulose nitrate membrane ($0.2 \mu\text{m}$). Solid C12E23 (or a 0.05% (w/w) aqueous solution) was used.

2.3. Preparation of the solution of NaAuCl_4 and PEG (or PEU or dextrin)

Thirty milliliters of Milli-Q water, 2.0 ml of an aqueous solution of NaAuCl_4 (0.25% (w/w)) and the desired volume of an aqueous solution of the stabilizing agent were mixed under magnetic stirring obtaining a clear yellow solution ($[\text{AuCl}_4^-] = 4.0 \times 10^{-4}$ M, $[\text{PEG}] = 0.03$ – 0.14 mg/ml ; $[\text{dextrin}] = 0.02$ – 0.14 mg/ml ; $[\text{PEU}] = 0.014$ – 0.086 mg/ml).

2.4. Preparation of the solution of NaAuCl_4 and C12E23

The desired amount of C12E23 was dissolved in 60.0 ml of Milli-Q water ($[\text{C12E23}] = 1.8 \times 10^{-5}$ to 1.2×10^{-4} M) and stirred for 3–5 min, obtaining a colorless foamy solution. The addition of NaAuCl_4 produced a clear yellow solution (NaAuCl_4 (9.6 mg), $[\text{AuCl}_4^-] = 4.0 \times 10^{-4}$ M).

2.5. Preparation of the sols

The desired amount of the 0.1 M aqueous solution of NaBH_4 was quickly added, under vigorous magnetic stirring, to the solution containing the stabilizing agent and NaAuCl_4 ($[\text{BH}_4^-] = 1$ – 4×10^{-3} M). In few minutes the colored sols were obtained. The colors varied from red–violet (C12E23, PEG) to orange–pink (dextrin) and orange–red (PEU).

2.6. Gold sol immobilization

The sols were immobilized by dipping the support in the colloidal solution. The support amount was calculated so that the final gold loading was 1 wt.%. The slurry was magnetically stirred for 2 h, filtered off, and the absorption checked by ICP analyses of the filtrate. The supported catalysts were rinsed with large amounts of distilled water (ca. 20 ml), and their water content was determined by drying the samples for 4 h at 150 °C in air.

2.7. Oxidation procedures

The catalytic liquid phase oxidation of ethylene glycol (5 mmol) was carried out for a standard time of 1 h, in basic aqueous medium (NaOH, 5.1 mmol, total volume 10 ml) with a substrate/Au molar ratio equal to 1000, at an O₂ pressure of 300 kPa, and 373 K. Experimental procedures and quantitative analyses were performed as reported in [2].

2.8. Measurements and analyses

UV spectra were measured on an HP 8453 spectrophotometer using 150 µl of the sol (0.1 cm quartz cuvette). Samples of sols were deposited onto Cu grids (coated with a 2% Formvar film); TEM analyses were carried out on a JEOL 1200 EX electronic microscope. X-ray diffraction experiments were carried out with a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu K α radiation, equipped with a graphite monochromator in the diffracted beam. The gold crystallite sizes were estimated from the peak half-widths using Scherrer's equation with corrections for instrumental line broadening. The quantitative determinations of gold present in the filtrate of the supported catalysts were carried out by ICP-OES measurements on a Jobin Yvon (model 24) instrument. The content of Au(0) supported on C carbon was assayed by a Perkin-Elmer 3100 Atomic Absorption Instrument. The Au/C samples were heated with a 5:1 (v/v) mixture of concentrated HNO₃ and H₂SO₄ till carbon was burn off. Then a 3:1 (v/v) mixture of concentrated HCl and HNO₃ was added for the transformation of Au(0) into AuCl₄⁻; the yellow solution was then concentrated and diluted with Milli-Q water. This procedure was also carried

out on the used catalysts: no leaching of gold was detected.

3. Result and discussion

3.1. Au/C12E23 and Au/PEG systems

The long-chain compound C12E23 [C12E23 = poly(oxyethylene)lauryl ether] and the polymer PEG [PEG = poly(ethyleneglycole) reacted with bisphenol A diglycidyl ether], used with an aqueous solution of NaAuCl₄, proved to be good stabilizers in colloidal Au(0) synthesis, giving sols composed of particles with a narrow size distribution. Actually, the interaction of the hydrophilic hydroxy heads of C12E23 and PEG with the negative charged gold surface allows the interdigit of the lipophilic tails and avoids the coagulation [12,13].

The basic parameters in the preparation of a metal sol by the salt precursor method are: (i) the nature of the reducing agent; (ii) the pH of the medium; and (iii) the stabilizer/metal ratio [12]. Thus, the reduction of the chloroauric salt was set up varying the molar NaBH₄/Au ratio between 3 and 10 and the (w/w) stabilizer/Au ratio from 0.3 to 1.8 in C12E23 and dextrin based systems (Tables 1 and 2), from 0.3 to 1.0 with PEG (Table 3), while the ratio was maintained equal to 0.3 with PEU (Table 4) [2–4,8].

Plasmon resonance peaks indicative of nanosized Au(0) particles were detected from UV-Vis spectra of the red sols and the wavelengths (λ_{\max} = 526–509 nm) were found in agreement with TEM micrographs (mean diameters = 4.3–6.9 nm) ([12,14,15] and references therein).

Table 1 shows the results of the Au(0)/C12E23 system. The colloids 1–3, prepared with low amounts of reducing agent (NaBH₄/Au = 3) consist of particles with mean diameters of 6.7–6.9 nm (TEM). These sols supported on C generated fairly good 1% Au catalysts for the liquid phase oxidation of ethylene glycol to glycolate, because TOF was about 900 h⁻¹. The activity was substantiated by gold particles with diameters of 9.5–11 nm (XRPD).

Sols 4–6 generated with larger amounts of NaBH₄ produced smaller particles (4.3–5.1 nm) than 1–3 systems. In these runs the amount of the stabilizer added in the sol appeared significant for the

Table 1
Au(0)/C12E23 system^a

	Run					
	1	2	3	4	5	6
NaBH ₄ /Au ^b	3	3	3	5	5	5
C12E23/Au ^c	0.3	1.0	1.8	0.3	1.0	1.8
UV-Vis (nm)	514	512	509	512	520	526
<i>d</i> (TEM) ^d	6.9	6.7	n.d.	5.3	5.1	4.3
<i>d</i> (XRPD) ^e	11.0	10.6	9.5	8.2	7.0	7.0
Conversion (%)	74	74	89	76	84	74
TOF ^f	924 ^g	927 ^g	889	950	1678 ^h	924 ^g

^a C12E23 = C₁₂H₂₅(OCH₂CH₂)_nOH, *n* = 23.

^b Molar ratio.

^c Ratio (w/w).

^d Mean diameter (in nm) of the sol particles, determined by TEM.

^e Particle diameter (in nm) of the supported Au/C, determined by XRPD.

^f 1 wt.% Au/C catalyst.

^g Reaction time: 0.80 h.

^h Reaction time: 0.5 h.

subsequent catalytic activity. A small quantity (run 4, C12E23/Au = 0.3, *d* (Au-sol) = 5.3 nm) produced immobilized particles of 8.2 nm, which exhibited a TOF of 950 h⁻¹. A C12E23/Au = 1.0 (run 5) gave a similar sol (*d* (Au-sol) = 5.1 nm), but during the deposition, the particle growth was moderate (mean diameters of Au/C particle = 7.0 nm, by XRPD) and TOF reached 1678 h⁻¹ (reaction time = 0.5 h). A large amount of stabilizer (run 6, C12E23/Au = 1.8) gave the smallest colloidal particles (*d* (Au-sol) =

4.3 nm) that grew on the support like those of run 5 (*d* (Au/C) = 7 nm); however in this case the activity was only 924 h⁻¹. Thus the catalysts 5 and 6, characterized by the same sized particles, exhibited different activities. This behavior can be explained considering that Au/C particles of run 6 are covered by a large amount of C12E23 (see also the dextrin/Au system) and insufficiently accessible to the substrate. Actually, the moderate decreasing in size of the supported particles (see the sixth line of Table 1 and Fig. 4) cannot be the only reason for the enhanced catalytic activity of run 5.

Table 2 shows the results obtained with the Au/PEG system. It was limited to NaBH₄/Au = 3, as the sols resulted unstable at high amounts of reducing agent and polymer. The colloids protected by PEG (average *M_w* ~ 15,000–20,000 Da) had smaller particles (close to 5 nm, by TEM) than those produced with C12E23, with the same NaBH₄/Au ratio, but the nanostructured Au/C material showed low conversions (TOF 650–750 h⁻¹). Large particle sizes were detected by XRPD (*d* (Au/C) = 12–14 nm) and we ascribed the low activity to the growth of the gold crystallites on carbon.

3.2. Au(0)/dextrin system

The stabilization by dextrin was carried out for evaluating the coordination effect of a rigid hydrophilic

Table 2
Au(0)/PEG system^a

	Run	
	1	2
NaBH ₄ /Au ^b	3	3
PEG/Au ^c	0.3	1.0
UV-Vis (nm)	516	518
<i>d</i> (TEM) ^d	5.3	5.2
<i>d</i> (XRPD) ^e	14	12
TOF ^f	670	746

^a PEG = (CH₃)₂C{C₆H₄-4-[OCH₂CH(OH)CH₂(OCH₂CH₂)_nOH]}₂.

^b Molar ratio.

^c Ratio (w/w).

^d Mean diameter (in nm) of the sol particles, determined by TEM.

^e Particle diameter (in nm) of the supported Au/C, determined by XRPD.

^f 1 wt.% Au/C catalyst. Reaction time: 1 h.

Table 3
Au(0)/dextrin system

	Run					
	1	2	3	4	5	6
NaBH ₄ /Au ^a	3	3	3	5	5	10
Dextrin/Au ^b	0.3	1.0	1.8	0.3	1.0	1.0
UV-Vis (nm)	504	512	488	512	516	n.d.
<i>d</i> (TEM) ^c	3.5	3.6	n.d.	3.6	3.1	2.8
<i>d</i> (XRPD) ^d	12	8.4	9.5	10.1	7.0	11.9
Conversion (%)	82	76	87	89	93	65
TOF ^e	818	948 ^f	871	890	1865 ^g	651

^a Molar ratio.

^b Ratio (w/w).

^c Mean diameter (in nm) of the sol particles, determined by TEM.

^d Particle diameter (in nm) of the supported Au/C, determined by XRPD.

^e 1 wt.% Au/C catalyst.

^f Reaction time: 0.8 h.

^g Reaction time: 0.5 h.

macromolecule on gold surface. In this case, some of the hydroxyl groups will be coordinated to gold surface and some of them will protrude from the particle forming an external shell.

Light-red sols (Table 3, 1–3) were obtained reducing NaAuCl₄ with NaBH₄/Au = 3 and varying the (w/w) dextrin/Au between 0.3 and 1.8. The colloidal nanoparticles of mean diameter close to 3.5 nm (TEM), gave Au/C catalysts exhibiting fairly good conversions, with TOFs between 800 and 900 h⁻¹. The mean particle size, determined by XRPD, was

between 8.4 and 12 nm. Ruby-red sols (Table 3, 4–6) composed of smaller particles (2.8–3.6 nm, by TEM), were obtained with larger amounts of the reducing agent (NaBH₄/Au = 5 and 10; dextrin/Au = 0.3–1.0). The immobilization on C gave 1% Au catalysts with high activity (TOF = 1865 h⁻¹, reaction time = 0.5 h, dextrin/Au = 1.0). The dimension of the gold crystallites on carbon was from 7 to 11.9 nm.

The heterogeneous material, obtained by dipping the activated carbon in the dextrin-gold colloidal solution, was investigated by TEM microscopy, after the application of a uranyl acetate solution (as a contrasting agent) to the samples [12]. Fig. 3 shows the micrograph of the catalyst obtained immobilizing sol 5 on carbon (*d* (Au/C) = 7 nm, by XRPD). We can observe a residue of dextrin that contains gold particles located at the boundaries and in the bulk. Thus we have to consider the formation of a protecting shell over the gold in the catalytic reaction. A comparison of the results of Table 3 indicated that the growth of the particles on carbon could be related to the amount of dextrin. At low dextrin/Au ratio (0.3) the diameter of Au/C particles was around 10 nm; at a higher ratio (dextrin/Au = 1.0) it was close to 7.0 nm. Accordingly, TOFs varied from 890 to 1865 h⁻¹.

Fig. 4 shows the variation of TOF with size of the particles in the sol and on support. Although the maximum of the catalytic activity (triangles) corresponds to the smallest supported particles (circles), also in this case an increased surface area cannot explain the high

Table 4
Au(0)/PEU system^a

	Run		
	1	2	3
NaBH ₄ /Au ^b	3	5	10
PEU/Au ^c	0.3	0.3	0.3
UV-Vis (nm)	512	510	508
<i>d</i> (TEM) ^d	4.2	3.1	3.6
<i>d</i> (XRPD) ^e	14	4.7	6.5
TOF ^f	837	904	918

^a PEU = poly{bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea}.

^b Molar ratio.

^c Ratio (w/w).

^d Mean diameter (in nm) of the sol particles, determined by TEM.

^e Particle diameter (in nm) of the supported Au/C, determined by XRPD.

^f 1 wt.% Au/C catalyst. Reaction time: 1 h.

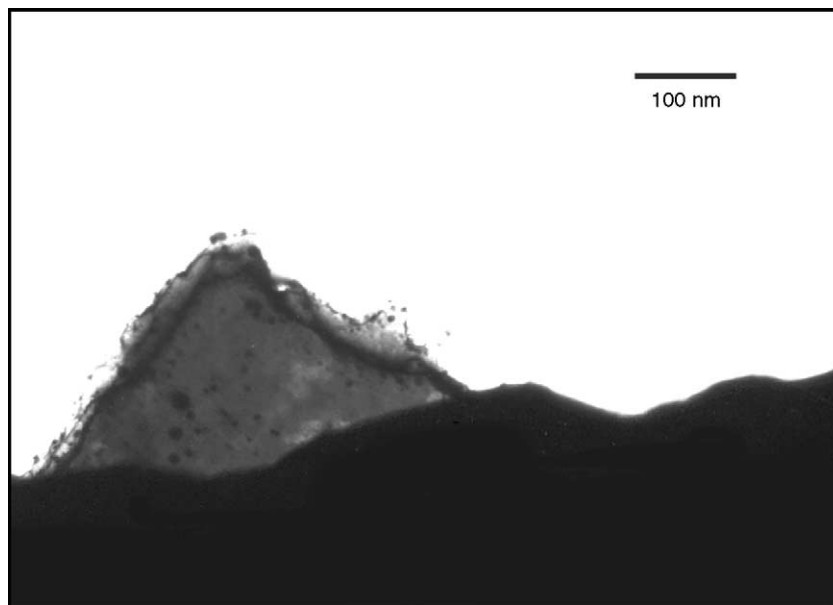


Fig. 3. TEM micrograph of the catalyst obtained immobilizing on carbon a dextrin-protected sol (sol 5 of Table 3; bar = 100 nm).

TOF value. Therefore we consider that the stabilizer residue may act as an effective catalyst modifier, controlling the activity of the heterogeneous catalyst. We could also suggest some molecular interactions of the protruding hydroxyl groups with the substrate, thus favoring the proximity between substrate and catalyst.

3.3. Au(0)/PEU system

Nanostructured gold colloids were obtained also by using the polycation ammonium salt PEU [PEU = poly{bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethyl-

amino)propyl]urea}, Fig. 2]. This stabilizer was chosen for increasing the ionic cloud in the electrical double layer, thus raising the electric repulsion between the gold particles in the sol.

Table 4 shows the results of PEU-based systems. In this case we noted an influence of the stabilizer on the loading on the carbon, being the immobilization not complete at high values of PEU/Au (>0.3). Small particles were obtained in these sols (mean diameters between 3.1 and 4.2 nm) and when supported on carbon gave fairly good conversions (TOF of sol 3 supported on C = 918 h⁻¹, Table 4) in agreement with Au/C particles of 6.5 nm.

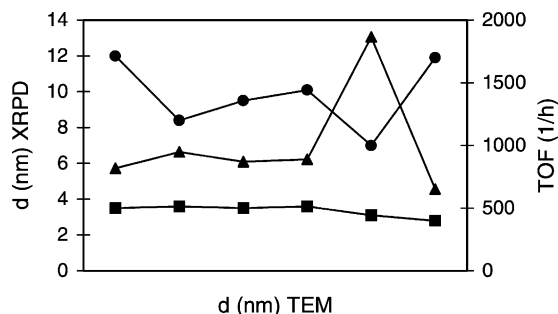


Fig. 4. Au/dextrin system: TOF–diameter relationship of the colloidal and supported gold particles. (■) TEM; (●) XRPD; (▲) TOF.

4. Conclusions

On the basis of our previous experience [2–4,8] we have prepared colloidal gold particles for the immobilization on activated carbon and studied the catalytic activity in the liquid phase oxidation of ethyleneglycol to glycolate by O₂.

In the sol, the gold nanoparticles are basically determined by the amount of NaBH₄, as we found a decrease in particle size with the increasing of NaBH₄/Au [with the same concentration of Au(III)]

(Tables 1–4) [8,12]. The nature of the protective agent plays a role in the stabilization as the hydroxyl compounds like C12E23, dextrin, and PEG were really efficient, as already reported for PVA [2–4]. The polyfunctional dextrin produced the smallest particles in the sol (mean diameters = 2.8–3.6 nm) compared to PEG (5.2–5.3 nm) and C12E23 (4.3–6.9 nm). The polyionic PEU stabilizes gold sol only in a narrow range of experimental conditions (PEU/Au = 0.3) giving very small particles (3–4 nm).

The immobilization of gold sols on carbon produced supported particles of various sizes depending on the employed colloid, but in all cases we observed agglomeration of the crystallites, as outlined by XRPD spectra (Tables 1–4). In particular, a lower agglomeration on carbon was achieved by adjusting the amount of the stabilizer in the sol (stabilizer/Au = 1, d (Au-sol) = 3–5 nm, d (Au/C) = 7 nm, Tables 1 and 3) [3,8]. Only in these cases we observed enhanced TOF values (1600–1800 h⁻¹).

TEM microscopy was used for analyzing the dextrin-protected sol immobilized on carbon and the images revealed dextrin residues on its surface. The gold particles are located at the boundaries and in the bulk of the residue (Fig. 3).

The catalytic activity was related to the size of supported gold nanoparticles and the stabilizer on carbon. Actually, we suppose that a too small amount of stabilizer lowers the catalytic activity favoring the agglomeration, while a too high quantity leads to a heavy covering of the gold, thus lowering the interaction between catalyst and substrate. A correct compromise between these two events produces the best results in term of catalytic activity.

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