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RESEARCH PAPER

Catalytic efficiency of macrocyclic-capped gold nanoparticles: cucurbit[n]urils versus cyclodextrins

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Abstract In this work, different macrocyclic systems, belonging to cucurbit[n]urils and cyclodextrins families, were employed as stabilizers of gold nanoparticles and their performance as catalysts in the reduction reaction of the toxic 4-nitrophenol to produce the valuable 4-aminophenol, was evaluated. To this goal, six nanosystems were prepared and compared under identical experimental conditions. The influence that (i) differences in shape, (ii) nature of chemical groups constituting the receptor entrances and (iii) differences in the portal sizes of those stabilizing agents have in the activity of these nanoparticles as catalysts in a nitro compound reduction reaction is evaluated and discussed. The TEM characterization of the nanocatalysts prepared is included. From these data, nanoparticles ranging from 3.7–10.7 nm in diameter, depending on the stabilizer employed, were obtained. The evaluation of kinetic rate constants normalized respect to gold concentration and catalyst surface for each system is included and discussed. In addition, the stability of the different nanocatalyst depending on the capping agent employed is also evaluated.

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Introduction

The scientific interest on gold nanoparticles (AuNPs) is ascribed to their unique physical and chemical properties. The applications of gold colloids extend in several areas as sensing, medicine or catalysis (Daniel and Astruc 2004). For example, AuNPs have shown a good performance as catalysts in methanol-based fuel cells for the production of electrical energy. In the design of new metallic nanocatalysts different factors, such as the nature of the active phase or the catalyst global cost, must be kept in mind because, usually, as the catalyst performance is improved, the catalyst cost is augmented. In this sense, as catalyzed chemical reactions normally occur on the surface, the most frequently strategy employed to diminish the overall cost, with no loss of the original catalytic activity, is to reduce the nanoparticle diameter. However, the issue of this strategy is the physical phenomenon of nanoparticle aggregation. As a result, the formation of nanoparticles clusters would lead to the situation of the beginning, the loss of active surface with the subsequent decrease of catalyst activity or the increase of costs. To avoid this issue, several supports or protecting agents have arisen but, again, the choice depends on the degree of catalytic efficiency required and how long the catalyst will be active. These above characteristics normally play in opposing directions so the best catalyst will be a trade balance (Ciganda et al. 2014; Wang et al. 2016). The state-of-the-art of highly efficient nanomaterials based on metals is the use of ligands with soft electron donors as nitrogen of 1,2,3-triazoles (Wang et al. 2016) or strong ligands such as thiolated ones that have to counterbalance time stability and bond strength to provide long-term durability but unfavorable catalytic effects (Ciganda et al. 2014). Nowadays, society demands greener technologies, so the procedures employed to synthesize catalyst should involve the use of environmentally friendly ligands and should avoid the use of harmful organic solvents in a trend to work in aqueous media (Ciganda et al. 2014; Wang et al. 2016; Hapiot et al. 2011; Huang et al. 2009).

A greatly extent strategy to evaluate new catalytic systems is to test their performance in the 4-nitrophenol (4-Np) reduction reaction. 4-Np is an anthropogenic substance that can cause several damages in the kidney and the nervous system. On the contrary, its reduced form, 4-aminophenol, has several uses as, for example, photographic developer, drying agent or in the synthesis of paracetamol (Zhao et al. 2015). From a green point of view, it would be desirable a reaction to transform the noxious 4-Np to the useful 4-aminophenol in an ecological media as aqueous medium employing sodium borohydride as reducing agent and at room temperature. However, in these conditions, the reaction does not progress. This issue was fortunately solved in 2002 by Pradhan et al. (2002) and Esumi et al. (2002) who studied that reaction in presence of AgNPs and AuNPs, respectively, as catalysts. From this date, the number of works which make use of this reaction is large. The reasons of this spread can be (i) the availability of the reductant, (ii) it is performed in water in ambient conditions, (iii) the reaction is easily monitored by simply photometry in the visible range, (iv) is a model reaction because there are no by-products and (v) the reaction mechanism is thoroughly understood (Zhao et al. 2015; Aditya et al. 2015; Herves et al. 2012).

Some examples of the use of gold, silver or nickel nanoparticles as catalyst for the 4-Np reduction reaction can be found in the literature (Aditya et al. 2015; Kastner and Thunemann 2016; Tarpani et al. 2016). Since these metal nanoparticles have demonstrated their activity for this reduction reaction, the study of the influence of the capping agent employed either on the stabilization of the nanoparticles or on their catalytic efficient and their final nanoparticles size is the focus of different researches. For instance, Daniel and Astruc (2004) reviewed the use of different AuNPs protected by citrate, thiols, phosphines or polyelectrolytes. Moreover, it has been reported that for the same Au(0) concentration, the increase in the diameter of AuNPs protected by α-CD or loaded in polystyrene beads gave slower reaction rate between 4-Np and $NaBH_4$ (Huang et al. 2009). Liu et al. (2007) found that the reaction rate depended on the functional groups of the polymers in which AuNPs were loaded and more recently, the comparison of AuNPs protected with 1,2,3-triazole, thiolate, citrate, polymers and dendrimers has been also reported (Ciganda et al. 2014; Wang et al. 2016). In addition, AgNPs with the same diameter, were covered either by poly(acrylic acid), bovine serum albumin or glutathione, in order to compare the influence that the covering thickness could have in the catalysis of 4-Np reduction reaction (Kastner and Thunemann 2016).

Cyclodextrins (CDs) and cucurbit[n]urils (CB[n]s) are examples of macrocycles that have emerged as new stabilizers of metal nanoparticles (Montes-Garcia et al. 2014). CDs consist of different D-glucose units (6, 7 and 8 for α-CD, β-CD and γ-CD, respectively) linked by α-1,4-glucosidic bonds with a truncated cone shape and are biologically produced. Hydroxyl groups of C2 and C3 are located on the wider edge of the ring and the primary hydroxyl groups of C6 on the other edge (Del Valle 2004). Unlike CDs, CB[n]s are synthetically produced by the acid-catalyzed condensation of glycoluril and formaldehyde. CB[n]s present symmetrical shape that resemble an empty pumpkin in which glycoluril units are bound by methylene bridges and carbonyl oxygens delimit the entrance to the cavity. Depending on the number of glycoluril units ($n = 5$–8, 10) different CB[n] homologues are obtained with specific solubility in aqueous media (Lagona et al. 2005). In terms of size, α-CD is comparable with CB[6] and β-CD with CB[7].

Although some examples of the design of AuNPs stabilized with macrocyclic receptors can be found in the literature, their use as catalysts is less extended. In a previous work, we have demonstrated the operation of AuNPs capped with CB[7] as catalysts in the reduction of 4-Np and the antimicrobial nitrofurantoin with excellent results in terms of efficiency (Blanco et al. 2016). In this work, we present the comparison among different macrocyclic receptors as capping agents for AuNPs stabilization to evaluate the influence that (i) differences in shape, (ii) nature of chemical groups constituting the receptor entrances and (iii) differences in the portal sizes of those stabilizing agents, could have in the performance of these AuNPs as catalysts. To the best of our knowledge, this comparison about the steric and electronic effects of different macrocyclic receptors employed as AuNPs-stabilizing agents on the catalytic reduction of 4-Np is presented for the first time. To this goal, six nanocatalysts including strong stabilizers as thiol groups (AuNP-S-β-CD), stabilizers as CB[n]s and CDs (AuNP-CB[6], AuNP-CB[7], AuNP-α-CD, AuNP-β-CD) and AuNPs without any stabilizer (the so-called AuNPs-metastable) were prepared and compared under identical experimental conditions. From our knowledge, the use of CB[6] and β-CD protected AuNPs in the 4-Np reduction performance is evaluated for the first time.

Experimental

Materials

Cucurbit[n]uril ($n = 6, 7$), α-cyclodextrin, β-cyclodextrin, maltodextrin (4–7 dextrose equivalent) and 4-nitrophenol were purchased from Sigma Aldrich (St. Louis, MO, USA). Heptakis-(6-mercapto-6-deoxy)-beta-cyclodextrin (SH-β-CD) was obtained from Shandong Binzhou Zhiyuan Biotechnology Co. (Bunzhou, Sandong, China). Tetrachloroauric(III) acid trihydrate ($HAuCl_4 \cdot 3\ H_2O$) and sodium borohydride ($NaBH_4$) were obtained from Acros Organics (Geel, Belgium) and Riedel-de Haën (Seelze, Germany), respectively. Ethanol absolute and dimethyl sulfoxide (DMSO) were provided from Scharlau (Barcelona, Spain). Ultrapure water was used in this work and produced by a Milli-Q system (trademark) of Merck Millipore (Billerica, Massachusetts, United States).

A 10 mM 4-Np stock solution was prepared in water and stored at 4 °C until use. α-CD, β-CD, maltodextrin and CB[7] solutions were prepared in water at 1.0×10^{-3} M concentration level. CB[6] (1.0×10^{-3} M) was solubilized in NaCl solution.

Apparatus

A transmission electron microscope (JEOL JEM 2100F, Tokyo, Japan) was used to collect the TEM images of all gold nanoparticles under accelerating voltage of 100 kV. TEM samples were prepared by deposition of a carbon-coated copper TEM grid (Ted Pella, Inc., CA, USA) onto one gold nanoparticle colloid drop for 20 min. Then, the grid was dried at room temperature.

The UV-Vis measurements were recorded by a UV-Vis spectrophotometer (UV-1800) of Shimadzu Corporation (Kyoto, Japan) employing a 1.0 cm quartz cuvette. In order to control de temperature of the catalysis experiments, a refrigerated bath at 25 °C (JP Selecta S.A., Barcelona, Spain) was employed.

Procedures

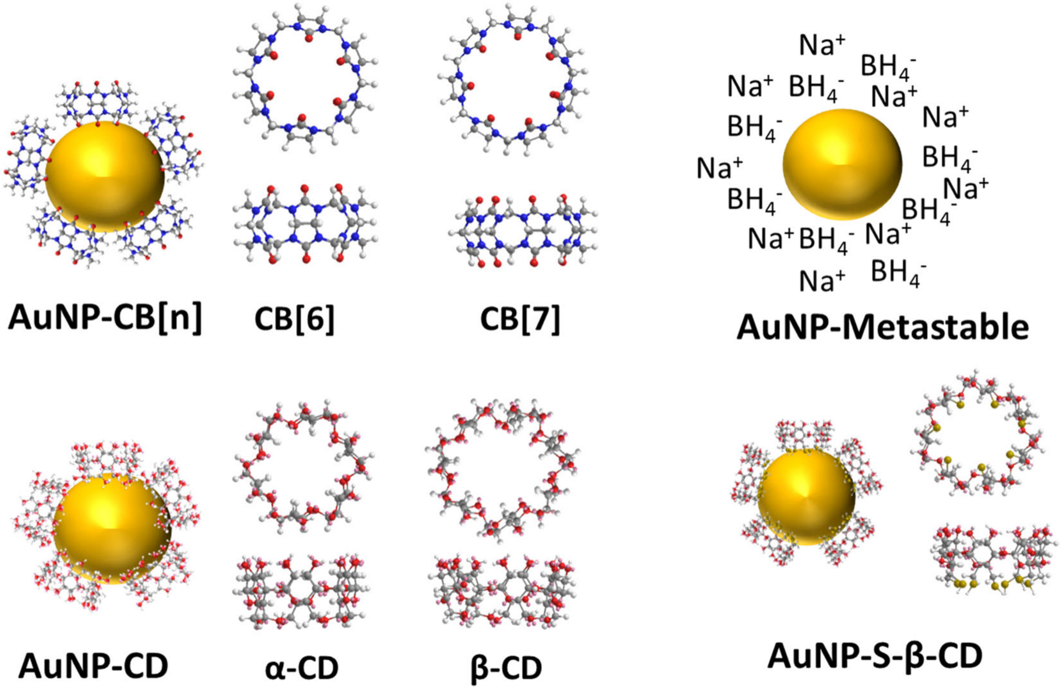
Synthesis of macrocyclic receptor-capped gold nanoparticles

AuNP-metastable, AuNP-CB[n], AuNP-α-CD and AuNP-β-CD were synthesized following the procedure previously reported by Lee and Scherman (2012) for CB[5–8]-capped AuNPs with some modifications (Blanco et al. 2016). Prior to the synthesis, a 100 mL round-bottom flask was cleaned with aqua regia (highly corrosive chemical), rinsed with water and dried in an oven. Next, $HAuCl_4$ aqueous solution (100 μL, 40 mM) was added to 40 mL of water:ethanol (1:1 *v*/*v*) and sonicated during few seconds obtaining a light yellow solution. Then, under vigorous hand-swirling, a recently prepared solution of reductant, $NaBH_4$ (100 μL, 0.1 M), was quickly added and the solution turned to red. In this point of the synthesis, the so-called AuNP-metastable was ready. To obtain the rest of gold nanoparticles (AuNP-CB[n], AuNP-α-CD and AuNP-β-CD), the solution was aged during 1 h before the addition of the corresponding macrocyclic receptor. Subsequently, a water solution of CB[n] or α-CD or β-CD was added to achieve a 0.1 mM final concentration under vigorous hand-swirling. Macrocyclic receptor capped-gold nanoparticles solutions were aged during 2 days before use.

AuNP-S-β-CD were synthesized as reported previously by Li et al. (2008). $HAuCl_4$ (50 mg) was dissolved in 20 mL of DMSO. Next, the solution was quickly mixed with 20 mL of a solution containing $NaBH_4$ (75.5 mg) and SH-β-CD (16.8 mg) in DMSO. The mixture was stirred during 24 h obtaining a dark violet solution. Two hundred microlitres of this suspension were diluted to 1 mL with DMSO before being used.

Catalytic reduction of 4-nitrophenol

In a quartz cuvette containing 2.0 mL of 4-Np (0.055 mM), 200 μL of a freshly $NaBH_4$ solution (56 mM) were added maintaining the temperature at 25 °C. Next, the cuvette was placed in the UV-Vis spectrophotometer and a volume of the corresponding



Scheme 1 Different gold nanoparticles synthesized

gold colloid suspension was added. Afterwards, the UV-Vis spectra were recorded, in a range of 500 to 240 nm, at regular intervals of 30 s monitoring the absorbance value at 400 nm. Different catalyst volumes were studied (5–40 μL) remaining constant the 4-Np and the reduction agent ones.

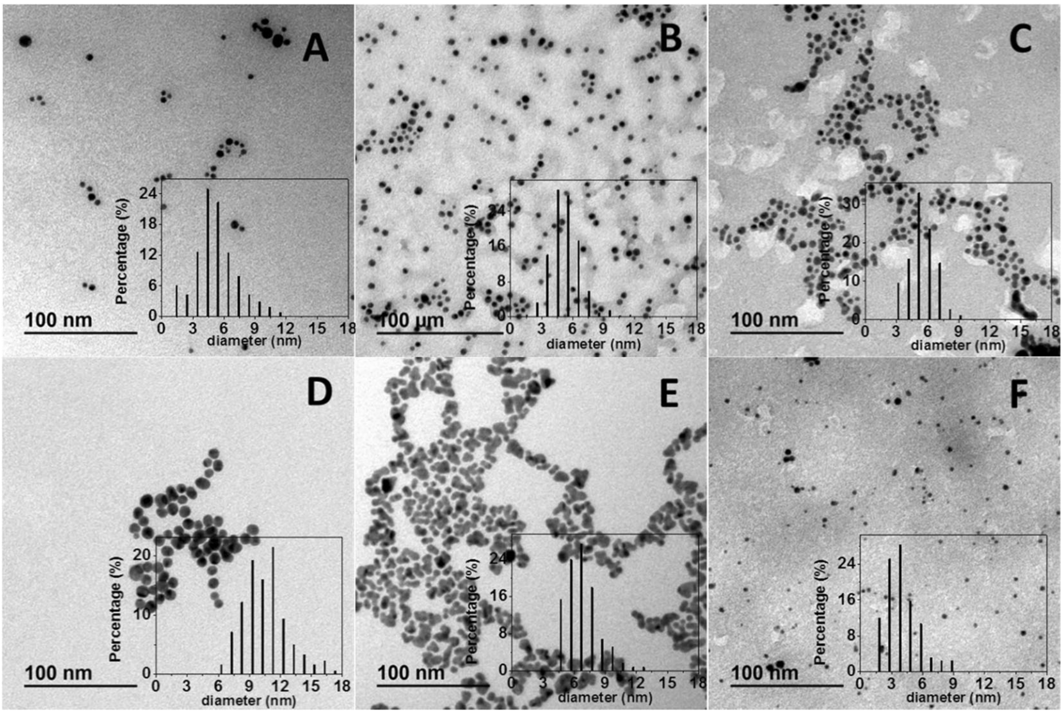


Fig. 1 TEM images of **a** AuNP-CB[6], **b** AuNP-CB[7], **c** AuNP-α-CD, **d** AuNP-β-CD, **e** AuNP-metastable and **f** AuNP-S-β-CD

Results and discussion

Metal-nanosystems characterization

As described in the "Experimental" section, the synthetic procedure followed for the six gold nanoparticles systems depicted in the Scheme 1 was similar except for the so-called metastable nanoparticles. In this case, the gold nanoparticles are stabilized with the same BH_4^- employed in the reduction of gold during the synthesis. The TEM images obtained from the different AuNPs synthesized and the average of nanoparticles diameter size are depicted in Fig. 1 and Table 1, respectively. From the images, it is observed that, in all cases, spherical nanoparticles were predominantly obtained with different distribution depending on the macrocycle employed.

In general, CDs and CB[n]s systems tend to form assemblies of nanoparticles grouped together. This is specially noted in case of AuNP-α-CD and AuNP-β-CD systems, while AuNP-CB[7] result less associated and more uniformly distributed.

Moreover, CB[n]s and AuNP-α-CD systems (Fig. 1a–c) present similar particle sizes (in the 5.2–5.8 nm range, see Table 1) with around the 75–90% of the nanoparticles with size lower than 6 nm as shown in the corresponding histograms inserted (Fig. 1). In particular, α-CDs seem to lead to slightly higher nanoparticle sizes (5.8 nm in average). It is noticed that the use of β-CDs and S-β-CDs as capping agents lead to obtain the biggest and smallest nanoparticles, respectively. Usually, CDs and CB[n]s are compared on the base of their cavity size. α-CDs and CB[6] present similar cavity volume size values (164 and 174 Å^3) like β-CDs and CB[7] do (279 and 262 Å^3, respectively), however, they present differences in their portal diameter values. The diameter of the portals of CB[6], CB[7] and α-CDs are similar: 3.9, 5.4 and 4.7–5.2 Å, respectively. However, the β-CDs present higher portals diameters up to 6.4 Å in the larger entrance. These variations in their portal diameter values and the truncated cone shape of CDs (unlike the symmetrical structure of the CB[n]s) could play a relevant role in the orientation and arrangement of the macrocyclic compound around the metal and, therefore, in the final nanoparticle size.

As stated before, the use of thiolated-β-CDs leads to the smallest nanoparticles around 3.7 nm. In this macrocycle, all the oxygen groups located at the small portal are derivatized with a thiol group. Assuming the LaMer mechanism, which state that the formation of gold nanoparticles consists on an initial stage (focusing period in which nanoparticles with quite similar diameter are produced) followed by a defocusing period (where different nanoparticles growth rate leads to differences in their diameter) (Bastus et al. 2011), the stronger covalent bond between gold and thiolate groups would block the surface at the initial stage preventing the nanoparticle growth. This mechanism would explain the smallest nanoparticle size obtained for these nanoparticles.

Table 1 AuNPs diameters obtained from TEM images. $n \geq 150$

AuNPs stabilizer	BH_4^-	CB[6]	CB[7]	α-CD	β-CD	S-β-CD
Diameter (nm)	6.6	5.4	5.2	5.8	10.7	3.7
± SD	± 1.6	± 2.2	± 1.4	± 1.3	± 2.2	± 1.6

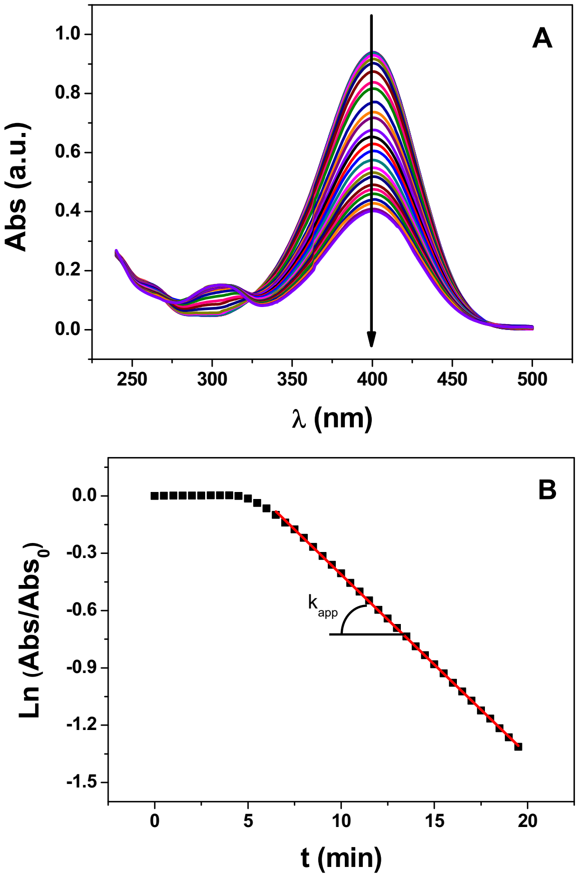


Fig. 2 **a** UV-Vis spectra of 4-Np reduction catalyzed by AuNP-CB[6] system. **b** Ln (Abs/Abs$_0$) vs. time. $\lambda = 400$ nm. $V_{cat} = 15$ µL

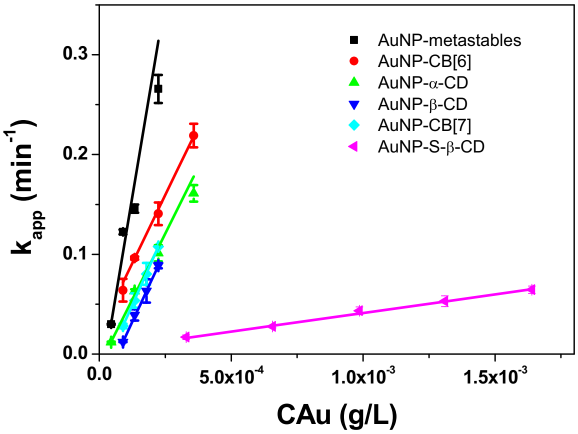


Fig. 3 k_{app} values as a function of gold concentration added. [4-Np] = 5.0×10^{-5} M. [BH_4^-] = 5.0×10^{-3} M

Evaluation of different AuNP-catalyst system in the 4-Np reduction reaction

The aim of this work is to study the effect of different macrocycles as stabilizing agents of gold nanoparticles in the activity of the resulting nanosystems as catalysts of the 4-Np reduction reaction. The choice of the two different macrocyclic receptor families will allow us to evaluate the effect of the interaction between AuNPs and the corresponding chemical group constituting the receptor portal, hydroxyl vs. carbonyl. In addition, the choice of different homologues of each family, will allow us to evaluate the effect of the capping agent size. The 4-Np reduction reaction was selected because it is a benchmark for the study of the catalysts properties of gold nanoparticles. In basic aqueous solution, 4-Np is in the 4-nitrophenolate form (yellow) while the reduction reaction product (4-aminophenol) is uncolored. Therefore, the kinetic evaluation of the reaction can be easily performed by means of spectrophotometric measurements in the visible range monitoring the decrease in the absorbance of 4-Np while the reaction takes place (Zhao et al. 2015).

As an example of the experiments carried out, Fig. 2a shows the UV-Vis spectra recorded during the 4-Np reduction reaction catalyzed by the AuNP-CB[6] system. From the absorbance data at 400 nm, Ln (Abs/Abs$_0$) (where Abs and Abs$_0$ are the absorbance at a time t and the initial absorbance, respectively) vs. time is plotted (Fig. 2b) and k_{app} is obtained from the slope.

With the objective of comparing the performance of the different catalysts under investigation, the experiments were accomplished at increasing colloid volumes in the 5 to 40 μL range and the k_{app} was calculated from the corresponding slopes. The results obtained, plotted vs. gold concentration, are depicted in Fig. 3. As expected, in all cases, k_{app} increased with the catalyst amount. However, while the behavior of AuNP-α-CD, AuNP-β-CD, AuNP-CB[6] and AuNP-CB[7] nanosystems seems similar irrespective of the family and the size of the homologue, the AuNP-metastable and AuNP-S-β-CD present the highest and lowest slopes corresponding to the fastest and slowest reactions, respectively. The low dependence of k_{app} with gold concentration exhibited by AuNP-S-β-CD could be explained on the base of the strong bond that exists between gold and the thiol groups. Assuming that the 4-Np reduction mechanism is based on the adsorption of both reactants, 4-Np and BH_4^-, on the nanoparticle surface (Zhao et al. 2015), the stronger the interaction between the stabilizing molecule and the gold is, the slower 4-Np reduction reaction is produced. This argument can also explain the results obtained with the AuNP-metastable system where a weak interaction leaves more active catalytic points and, consequently, higher k_{app} values were obtained (Deraedt et al. 2014). These results can be better understood if the normalized kinetic constants respect to the gold amount (k_c) are evaluated. As $k_{app} = k_c \times C_{Au}$, the k_c values for each system can be calculated from the corresponding slopes in Fig. 3. The k_c values obtained in this way are collected in Table 2.

The AuNP-metastable and AuNP-S-β-CD systems present the highest and lowest k_c values that result quite different to those obtained for the rest of catalyst under investigation. Regarded to this, although similar responses are recorded for these latter four systems, AuNP stabilized with the higher homologues of each family (CB[7] and β-CD) seem to exhibit slightly higher apparent kinetic constant values than their respective homologues.

Table 2 k_c (± SD)$_{n=3}$ constants obtained from the slope of k_{app} vs. C_{Au}

Stabilizer	BH_4^-	CB[6]	CB[7]	α-CD	β-CD	S-β-CD
k_c (L g^{-1} min^{-1})	1581	547.0	592.2	529.4	570.8	37.2
± SD	±268	± 27.5	±1.5	±34.8	±4.3	±1.6

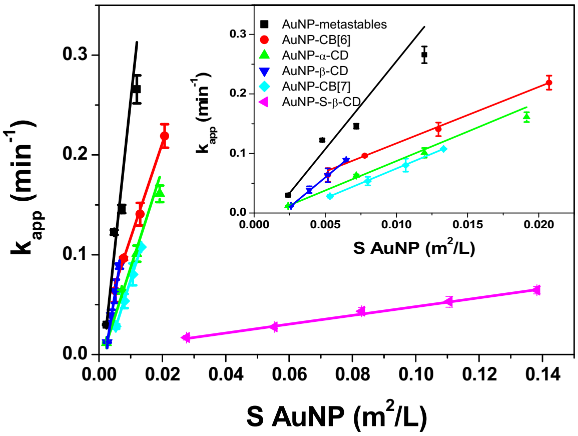


Fig. 4 k_{app} vs. total nanoparticle surface for each system

As the efficiency of the catalyst can be influenced by several factors related to the different capping agents employed, the experimental results were also evaluated in terms of the total gold surface of the catalyst ($k_{app} = k_s \times S$) and the results are depicted in Fig. 4.

As observed, AuNP-metastable again results in the most catalytic system with the highest slope, followed by the AuNPs stabilized with β-CD. From the analysis of the k_s data obtained from the corresponding slope values (Table 3), it can be observed that this latter catalyst presents a value twofold higher than the rest of the systems prepared with similar macrocycles that, in addition, show quite similar values among them. This fact could be explained because AuNP-β-CD, with the highest diameter of nanoparticle, would exhibit higher surface available as active catalytic points. These results agree with those previously reported by Ncube et al. (2015). They observed that reducing the nanoparticles size does not always result in increased activity as the large particles do. These last provide more sites for adsorption of reactants and more efficient electron transfer occurs with large particles. These authors confirmed this hypothesis calculating apparent activation energies.

All these results allow us to conclude that, although the gold amount added in solution was the same, the active catalytic surface is different because the nanoparticle diameter. Moreover, bigger homologues could lead to higher active surface probably because of steric factors during their distribution over the nanoparticle. These steric and electronic effects of the ligand on the catalytic performance of a system, have been previously reported by different (Ciganda et al. 2014; Wang et al. 2016; Huang et al. 2009; Liu et al. 2007).

Data obtained at this point suggested testing if the macrocyclic structure benefits in some extent the catalytic activity of these systems. Therefore, a comparison with a non-macrocyclic analog of the CDs herein used was performed. To this end, maltodextrin, as linear model of α- and β-CDs systems, was employed to stabilize AuNP.

The synthesis of AuNP-maltodextrin was carried out following the same procedure as for the rest of non-thiolated macrocyclic AuNP-systems studied in this work. From TEM characterization (data not shown), bigger nanoparticles than any other AuNP-system (15.3 ± 3.3 nm in diameter, see Table 4) were obtained.

Proceeding as before, the catalytic response of 4-Np was studied at different volumes of catalyst in order to obtain both, the catalytic constant in function of gold amount, k_c, and the catalytic constant in function the total gold surface, k_s. The calculated values are included in Table 4. As observed, k_c value obtained in this case is clearly lower (140 L g^{-1} min^{-1}) than those obtained for all the systems stabilized with macrocyclic receptors (non-thiolated) and for the so-called AuNP-metastable (k_c values around 550 L g^{-1} min^{-1}, see Table 2). On the other side, the obtained value is closer (although higher) to that exhibit by the AuNP-S-β-CD system, the strongest stabilized one ($k_c = 37$ L g^{-1} min^{-1}). Similar results were obtained if the catalytic response is analysed respect to Au surface with a k_s value, for the AuNP-maltodextrin system, between non-thiolated systems and the thiolated one (see Table 3). Therefore, although the AuNP-maltodextrin presents better catalytic behavior for 4-Np reduction reaction with higher kinetic constants than the system with the strongest bond between the receptor and the nanoparticle (AuNP-S-β-CD), the catalytic response of AuNP-maltodextrin is worse than that obtained with the rest of the systems based on macrocyclic receptors.

These results allow us to think that the open structure of maltodextrin (employed as linear model of α-CD or

Table 3 k_s (± SD)$_{n=3}$ values obtained from the slope of k_{app} vs. S AuNP

Stabilizer	BH_4^-	CB[6]	CB[7]	α-CD	β-CD	S-β-CD
k_s (L m^{-2} min^{-1})	29.5	9.5	9.97	9.9	19.8	0.44
± SD	± 5.0	± 0.5	± 0.03	± 0.6	± 0.1	± 0.01

Table 4 AuNP diameter, k_c and k_s values obtained for AuNP-maltodextrin system

Diameter (nm) ± $SD_{n \geq 150}$	k_c ($L\ g^{-1}\ min^{-1}$) ± $SD_{n=3}$	k_s ($L\ m^{-2}\ min^{-1}$) ± $SD_{n=3}$
15.3 ± 3.3	140 ± 37.7	6.79 ± 1.2

β-CD) stabilizes gold nanoparticles in a greater extent than the cyclic structure, which seems to provide more active surface for the catalytic reaction.

From the study of the different efficiency as catalysts carried out, it is shown that those AuNP-systems, with relatively weak interactions stabilizer-gold, present better catalytic activity for 4-Np reduction than nanoparticles that have strong interactions with the capping agent employed, i.e., with thiol groups. Therefore, the so-called AuNP-metastable system presents the highest kinetic constant values. Other authors also reported relatively high reaction rates when sodium borohydride and/or its hydrolysis products were used to stabilize AuNPs (Deraedt et al. 2014). However, the use of a capping agent during AuNPs synthesis is required to guarantee the stability in time of the catalyst as it is demonstrated from the results of the experiments corresponding to the study of 4-Np reduction reaction up to 2 months after nanoparticles synthesis. In this case, only nanoparticles stabilized by weak interactions and cyclic structure were considered. As depicted in Table 5, the variation of k_c values shows a general trend towards the loss of catalyst activity, which is really more noticeable in the case of the AuNP-metastable system even during the first month. Unexpectedly, AuNP-CB[6] system displays low stability respect to the rest of catalysts. As salts are needed to solubilize this homologue, significant NaCl amounts are present during the synthesis that could affect to the stabilizer-AuNP bond as a consequence of the Na^+ interaction with the CB[n]s portals or because the chloride surface poisoning. Therefore, we dealt with the AuNP-CB[6] synthesis decreasing the amount of cations in solution (around fivefold) and we tested the performance of this new system (named AuNP-CB[6] low Na^+) in the 4-Np reduction reaction. The results obtained are also included in Table 5, last line. We can observe, the loss of the catalyst efficient during 1 month is greater for the less stabilized nanoparticles (around 79 and 75% for metastable and CB[6] systems, respectively) than for those stabilized with the macrocyclic receptors.

Table 5 Comparison of AuNPs stability referred to the catalytic performance (k_c) in the 4-Np reduction reaction

Stabilizer	Loss of efficiency (%) 1 month	Loss of efficiency (%) 2 months
BH_4^-	78.9	77.6
CB[6]	74.9	84.1
CB[7]	28.5	31.6
α-CD	37.4	58.2
β-CD	58.9	79.1
CB[6] low Na^+	26.4	71.9

It is clear the influence of cations in the AuNP-CB[6] interaction. If this effect is eliminated, the resulting nanoparticles (AuNP-CB[6] low Na^+) remain stables for a longer time than AuNP-metastable system does. Moreover, excellent k_c and k_s values were obtained for this latter system (853 and 12.53 L g^{-1} min^{-1}, respectively). As shown in Fig. 5, these values are higher than most of the macrocyclic capping agents assayed. So, although AuNP-metastable could produce the 4-Np reduction faster than any of them, the presence of a capping agent ensures the longer durability of its original catalytic activity. Finally, higher stability in time for the AuNP stabilized with CB[n]s systems than that exhibited by the AuNPs-CDs ones is observed.

In summary, if a global comparison of the obtained results is made (Fig. 5), we can observe that, the nature of chemical groups (atoms) constituting the macrocyclic portals as well as the receptor size, influence the global catalyst efficiency. AuNPs stabilized by capping agent with strong gold interactions (AuNP-S-β-CD system)

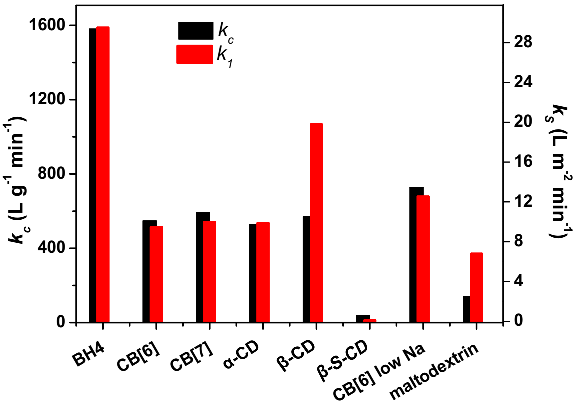


Fig. 5 Comparative of k_c and k_s values obtained for each AuNP system

and non-cyclic structure lead to the lowest catalytic activities. α-CDs and β-CDs k_c values are slightly lower than that obtained for CB[n]s of comparable sizes (CB[6] and [7], respectively) which could denote stronger AuNP-CD interactions than AuNP-CB[n] do. For this latter system, it is also observed, a great influence of the salts presented in solution as it can be expected for the chemical structure of these macrocyclic compounds. On the other hand, from the experimental data of k_s values obtained, homologues with higher size seem present higher catalytic surface obtaining higher kinetic rates for both receptors families. Therefore, the global performance of the catalytic system designed is the result of a great number of factors related with the capping agent employed.

Conclusions

In this work, we showed a novel comparison between two families of macrocyclic receptors employed as stabilizers of AuNPs that were used as catalysts for the 4-Np reduction reaction. To support our conclusions obtained for the macrocycle-stabilized systems proposed (AuNP-CB[6], AuNP-CB[7], AuNP-α-CD and AuNP-β-CD), non-stabilized AuNPs (called AuNPs-metastable) and highly-stabilized AuNPs (the stabilizer contained SH groups) were also included in the assays.

It was found that the efficiencies as catalyst showed by our relatively soft-stabilized AuNPs are between the efficiency exhibited by AuNPs-metastable (the best ones) and that obtained with AuNP-S-β-CD, which presented the slowest response for this reaction. Although AuNPs-metastable showed the greatest catalytic response, its performance was quickly lost in 1 month. So, the use of a stabilizing agent during the nanoparticles synthesis is required in order to avoid the loss of catalyst efficiency.

As catalysts are frequently found in industrial processes based on chemical reactions, the balance between cost and performance should be kept in mind. Therefore, in this work the experimental kinetic rate constants were normalized respect to the catalyst mass concentration in the reaction medium (k_c). In this comparison, although non-significant differences in the k_c values were obtained, the bigger homologues of CD and CBs families showed slightly higher efficiency than the smaller counterparts synthesized in the same conditions. In addition, the k_c values for α- and β-CDs are slightly lower than that obtained for CB[n] which allow to conclude that the interaction between AuNP and CDs could be relatively stronger than that between AuNP and CBs. The highest reaction rate respect to the catalyst concentration was obtained for AuNP-CB[7] which would be the best in terms of cost-efficiency.

From a physical-chemistry point of view, the efficiency of the catalysts was normalized respect to the AuNPs medium-exposed surface. It was found that bigger homologues showed higher reaction rates than smaller equivalents. This fact could be explain because CB[7] and β-CD showed a lower surface coverage leading to higher active surface available for the 4-Np reaction. When β-CD was used as stabilizer, the differences with the group CB[6], CB[7] and α-CD were twofold higher. From this point of view, AuNP-β-CD would be the best catalyst system.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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