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# Oxidation of benzyl alcohol catalyzed by ligand-stabilized Au nanoparticles in the presence of weak bases

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## ABSTRACT

Ligand-stabilized gold nanoparticles (tetrakis(hydroxymethyl)phosphonium chloride-Au, citrate-Au, cetrimonium bromide-Au) were synthesized and mixed with several weak-base solids (barium carbonate, Amberlite IRA-900) and acidic solid (Dowex 50WX2 resin). Those catalysts were applied for the oxidation of benzyl alcohol in water at 80 °C. Almost ligand-stabilized Au nanoparticles/weak-base solids showed good conversion of benzyl alcohol and high selectivity of benzoic acid, whereas ligand-stabilized Au nanoparticles/acidic solid were catalytically inactive. Nanoparticles were characterized by transmission electron microscopy, zetapotential measurement, and dynamic light scattering. The catalytic activity and product selectivity were determined by using a gas chromatography coupled with a mass selective detector. Our study suggests that the oxidation reaction in water could be catalyzed by gold with the presence of weak-base solids.

## Introduction

Metallic gold has been considered as an inert material and could not be used as a catalyst. However, the discovery of catalytic ability of gold for hydrogenation of olefins in 1973 has changed the aforementioned point of view regarding metallic gold [1]. Following this finding, the study performed by Hutchings and Haruta et al have revealed that gold could catalyze the acetylene hydrochlorination and aerobic oxidation of carbon monoxide [2, 3]. After that, the use of gold as a catalyst has been quickly increased, and it has been employed in many catalytically transformations regarding reactions in organic chemistry such as oxidation of aldehydes, alcohols, and organosilanes; amine transformations; and transformations of alkylaromatic compounds [4, 5]. Gold catalyst can be utilized in the form of ligand-capped gold nanoparticles or metallic gold dispersed on solid materials. The former is often used in reactions in liquid phase, and the latter is usually employed in both liquid and gas phases reactions [6-10].

The addition of bases to liquid-phase oxidations reactions is essential to enhance the reaction kinetics and may increase the reaction rate several hundredfold. However, addition of bases results in complicated and time-consuming purification protocols to isolate products. The visible conversions of benzyl alcohol oxidation using supported gold catalysts are only obtained in the presence of base

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promoters in aqueous reaction media [11-16] and in non-aqueous media. Hydroxides and carbonates of alkaline metals are often used in the oxidation of alcohols (aliphatic and aromatic) in water-based reaction medium. The ratio of base to substrate has been selected in a range of 0.5-3.0. The catalytic activity of gold catalyst with base addition is an order of magnitude higher than that without catalyst addition. This observation implies the critical role of base addition in the oxidation reaction of benzyl alcohol in aqueous medium [17].

The addition the bases may be omitted by supporting Au nanoparticles on a basic support. For example, gold nanoparticles dispersed on magnesium oxide well catalyzed the selective oxidation of glucose to gluconic acid in aqueous reaction medium without the addition of a base [18, 19]. The most recent study utilizing the Au nanocomposite catalyst on the SBA-15 material, where the SBA-15 was alkalized with amine, resulted in a significant reduction in the amount and strength of the base used in the oxidative alkyne coupling to 1,3-diynes [20]. However, the identity and concentration of bases affecting both catalytic activity of gold and product distribution have not been well understood.

We want to contribute to fundamental understanding of the role of bases in oxidation reactions in aqueous reaction media, using Au as catalyst. To this end, we select very weak basic supports, $BaCO_3$ with positive charge or anionic exchange resins (Amberlite-positive charge or Dowex-negative charge), to interact with Au nanoparticles with negative or positive charge. This design enable us to understand the influence of intimate or loose contact, between Au nanoparticles and supports, on catalytic activity. This will provide information if basic species in bulk liquid or basic species on the surface of support is crucial for oxidation reactions.

## Experimental

### Chemicals

Gold (III) chloride solution (99.99% trace metals basis, 30 wt. % in dilute HCl), trisodium citrate dehydrate (ACS reagent, ≥ 99.0%), hexadecyltrimethylammonium bromide (BioXtra, ≥ 99.0%), benzyl alcohol (≥ 99.0%), hydrogen peroxide solution (30 wt. % in water), barium carbonate (ACS reagent, (≥ 99.0%) Tetrakis(hydroxymethyl)phosphonium chloride (80% w/w in water), Dowex 50WX2-$Na^+$ (100-200 mesh), Amberlite IRA-900 chloride form, calcium chloride (Vetec™ reagent grade, 96%), sodium hydroxide (BioXtra, ≥ 98%, pellets), sodium carbonate (BioXtra, ≥ 99.0%), ammonium hydroxide (ACS reagent, 28.0-30.0% $NH_3$ basis), hydrochloric acid (AR, 35-37%), ethyl acetate (anhydrous, 99.8%), benzaldehyde (≥ 99.0%), benzoic acid (ACS reagent, ≥ 99.5%), benzyl benzoate ( ≥ 99.0%).

### *Synthesis of THPC-, citrate-, and CTAB-stabilized Au nanoparticles*

The Au nanoparticles stabilized with tetrakis(hydroxymethyl)phosphonium chloride (THPC-Au) were synthesized following the published procedure from Tan et al [21] with minor modification. One milliliter of THPC (12 ul of 80% THPC in 1 mL of water) and 0.5 mL of 1M NaOH were added to 45 mL of deionized water. The mixture was vigorously stirred for 5 min at 25 °C. After that, 1 mL of aqueous $HAuCl_4$ solution (50 microliter $HAuCl_4$ 30% in 2 mL water) was added to the above solution to form the THPC-stabilized Au nanoparticles.

Citrate-stabilized Au nanoparticles were synthesized using the previously published work by John. Turkevich [22]. The Au nanoparticles stabilized by cetyltrimethylammonium bromide (CTAB-Au) were made as follows: CTAB (0.1 g) was added into a reaction vial containing a solution of water (100 mL)-ethanol (5 mL). Stirring was maintained for 30 min to ensure a clear solution. Thirty microliters of an aqueous solution of $HAuCl_4$ 30 wt. % was injected into the above mixture). Stirring was maintained for another 30 min to obtain a homogeneous solution. The transformation of cationic gold to metallic gold was assisted with an addition of an aqueous solution of $NaBH_4$ 0.14 M (1.5 mL). This reduction process was lasted for 5h at room temperature to obtain CTAB-Au.

### *Treatment of anion-exchange resin*

The chloride anion in anion-exchange resin (Amberlite IRA-900, Cl form) is exchanged with hydroxyl or carbonate anion by the following procedure: 5 g of IRA-900 was added to a solution of NaOH (2 g in 40 mL of de-ionized water) or of $Na_2CO_3$ (2 g in 40 mL de-ionized water), and the resin was soaked in the alkaline solution for 3h before it was separated by a centrifuge at 1,000 rpm and washed with de-ionized water until residue of chlorine anion was not detected (checked by $AgNO_3$ solution) in the supernatant and the pH of the supernatant is neutral.

### *Oxidation of benzyl alcohol*

0.1 g of barium carbonate, 2 g of anion-exchange resin (Amberlite IRA-900-OH or Amberlite IRA-900-$CO_3$), or 5 g of cation-exchange resin (Dowex 50WX2-Na) was added to 5 mL of aqueous solution of nanoparticles (THPC-Au, citrate-Au, or CTAB-Au). 0.1 mL of benzyl alcohol and 1 mL of aqueous solution of hydrogen peroxide were added to the above mixture of gold nanoparticles and basic support. The reaction vial was seal by a septum and the reaction was performed at 80 $^{o}$C for 2.5 hours with stirring. After reaction was completed, catalyst was separated from the reaction solution by a centrifuge at 7,800 rpm for 15 min. The supernatant was acidified with 0.3 mL of aqueous HCl solution ($HCl:H_2O$ = 1:1), and then 5 mL of ethyl acetate was added to extract the product. The Table 1 shows the experimental design for the reactions using a variety of catalysts. The influence of calcium chloride on the oxidation reaction catalyzed by THPC-Au/$BaCO_3$ or citrate-Au/$BaCO_3$ was performed under the same conditions described in Table 1. However, different volumes of solution of calcium chloride were added. The nominal Au contents in 1 mL of THPC-Au, CTAB-Au, and citrate-Au solutions are 7.3 x $10^{-2}$, 7.8 x $10^{-2}$, and 5.0 x $10^{-2}$ mg, respectively.

Table 1: The experimental setup for the oxidation of benzyl alcohol in water using different catalysts

| Nanoparticles, mL | Resin (2 g) or $BaCO_3$ (0.1 g) | Reaction time, h |
|---|---|---|
| THPC-Au | $BaCO_3$ | 2.5 |
| THPC-Au | Amberlite IRA-900, $OH^-$ | 2.5 |
| THPC-Au | Amberlite IRA-900, $CO_3^{2-}$ | 2.5 |
| THPC-Au | No | 2.5 |
| CTAB-Au | $BaCO_3$ | 2.5 |
| CTAB-Au | Amberlite IRA-900, $OH^-$ | 2.5 |
| CTAB-Au | Amberlite IRA-900, $CO_3^{2-}$ | 2.5 |
| CTAB-Au | No | 2.5 |
| Citrate-Au | $BaCO_3$ | 2.5 |
| Citrate-Au | Amberlite IRA-900, $OH^-$ | 2.5 |
| Citrate-Au | Amberlite IRA-900, $CO_3^{2-}$ | 2.5 |
| Citrate-Au | No | 2.5 |
| Citrate-Au | Dowex 50WX2-Na$^{(*)}$ | 5 |
| THPC-Au | Dowex 50WX2-Na$^{(*)}$ | 5 |

0.1 mL benzyl alcohol and 1mL $H_2O_2$ were used in all reactions.

### *Chemical analyses and characterizations of materials*

The conversion and product distribution of the oxidation reaction of benzyl alcohol catalyzed by gold catalysts were determined by gas chromatography coupled with mass analyzer (Agilent 7820A-5975C). The non-polar column DB-5MS (30m x 0.25 mm x 25 μm) was used to separate the reaction products. Chlorobenzene was used as an internal standard. The content of gold was determined by ICP-OES equipment (Varian, 720-ES). The hydrodynamic diameter and zeta potential of ligand-stabilized gold nanoparticles were determined by dynamic light scattering equipment (Zetasizer Nano NS) with a 632.8 nm He-Ne laser. The particle size of gold was characterized by transmission electron microscopy (Titan G2 80-300 kV TEM, FEI Company).

## Results and discussion

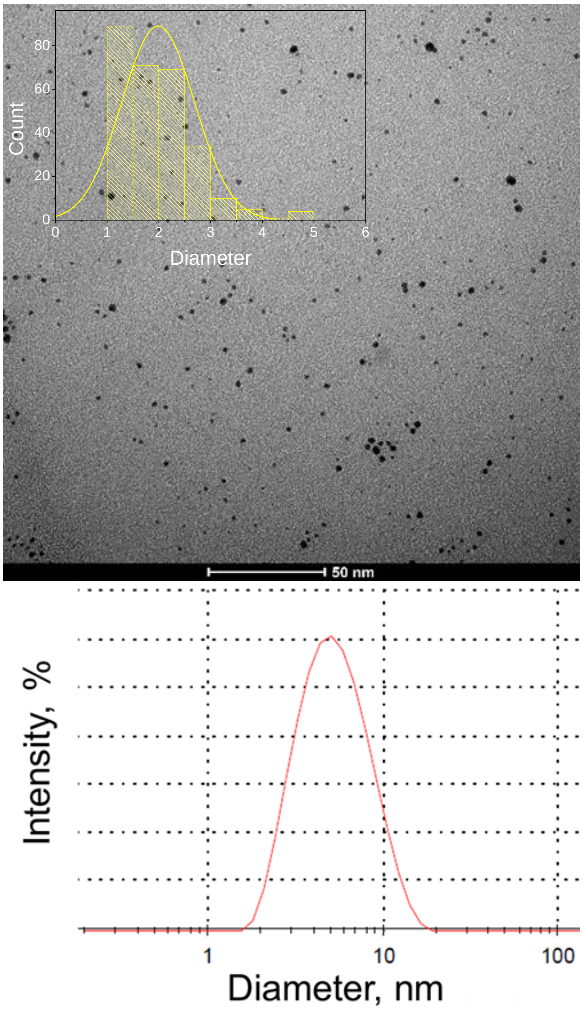

Figure 1: (top) TEM image of THPC-Au and diameter distribution of Au particles (inset), (bottom) size distribution of THPC-Au determined by dynamic light scattering

Average diameter of Au nanoparticles stabilized with CTAB and citrate, measured by TEM, are 25.5 nm and

13.5 nm, respectively. Their diameters confirmed by DLS are 25.45 nm (CTAB-Au) and 17.25 nm(citrate-Au) [23]. The diameter of THPC-Au determined by TEM and DLS is 2.0 nm and 4.8 nm, respectively (Figure 1). The surface charge of each type of ligand-capped Au nanoparticles was determined and is shown in Figure 2 and summarized in Table 2. As seen in Table 2, the zeta potential of barium carbonate in deionized water (pH~8.0) is positive at +15.3 mV, which agrees with the previous reports [24, 25] showing positive zeta potentials of barium carbonate at a pH value smaller than the isoelectric point of barium carbonate (at pH~10).

The value of isoelectric point may depend on the nature of barium carbonate; for example, the synthesis of barium carbonate using a high-gravity technique produced submicron particles with isoelectric point ca. pH~8.2 [26]. The THPC-Au nanoparticles show the zeta potential at -36 mV, and this negative zeta potential likely contradicts the chemical structure of THPC with a positive charge at the phosphorus atom.

In the original synthetic procedure for THPC-Au, due to the reaction conditions were under the alkaline medium, the cationic $P(CH2OH)_4^+$ species was proposed to react with OH- anion to produce the $P(CH_2OH)_3$ molecule. As a result of the extensive hydrolysis, the $P(CH_2OH)_3$ molecule transforms to the pentavalent $O_2(CH_2OH)_3$ molecule [27].

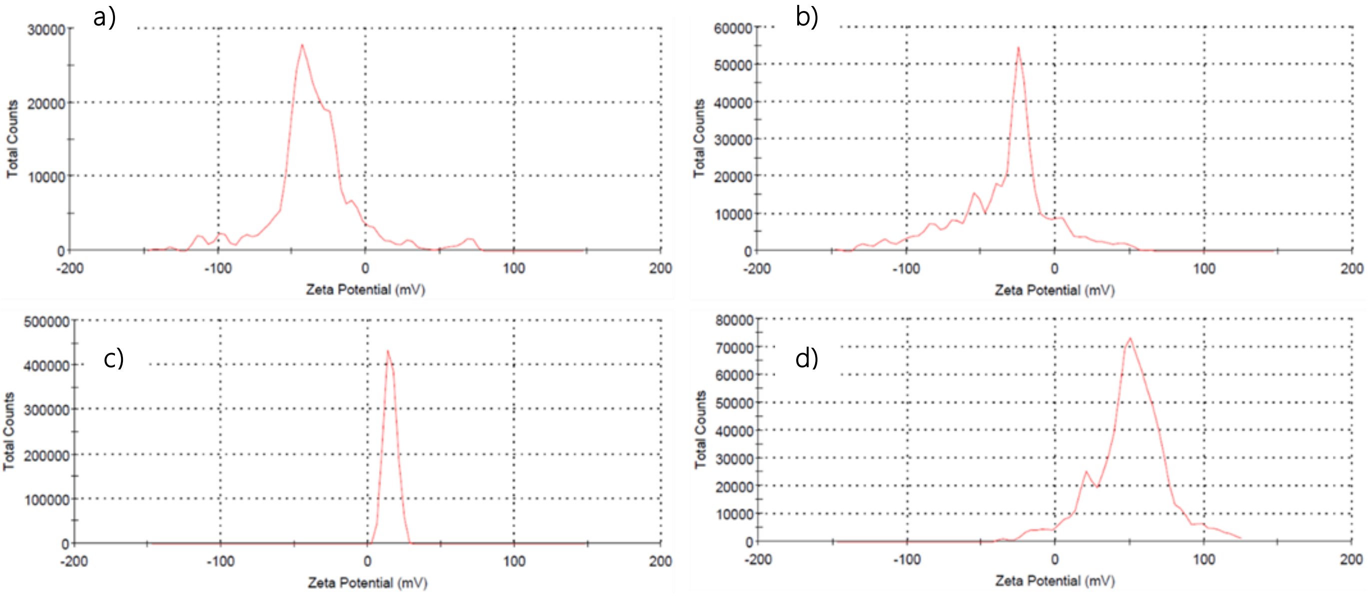

**Figure2:** The measurements of zeta potentials of a) THPC-Au, b) citrate-Au, c) $BaCO_3$, and d) CTAB-Au

**Table 2:** The zeta potentials of ligand-capped Au nanoparticles and barium carbonate

| Sample | $BaCO_3$ | THPC-Au | Citrate-Au | CTAB-Au |
|---|---|---|---|---|
| pH | 8 | 8 | 6 | 7 |
| Zeta, mV | + 15.3 | -36.0 | -34.3 | +50.2 |

However, this mechanism does not support the negative zeta potential of the THPC-Au nanoparticles. There has been recently evidence showing that the $P(CH_2OH)_4^+$ species is transformed to the pentavalent -$OP(CH_2OH)_4$ anion. The observation was supported by the $^{13}P$ NMR and XPS techniques [28]. This pentavalent anion seems responsible for the negative zeta potential of THPC-Au nanoparticles. The citrate-Au nanoparticles have the negative zeta potential at -34.3 mV (at pH~6.0). This zeta potential value of our citrate-Au is consistent with that of citrate-Au synthesized by the same procedure, which is -39.7 mV (at pH~9.3) [29] and -38.4 mV [30]. Three carboxylate groups in citric acid molecule also support the negative zeta potential of citrate-Au. The CTAB-Au nanoparticles show the positive zeta potential at +50.2 mV (at pH~7.0). This positive zeta potential value is consistent with the cationic nature of this surfactant and also with the previous reports on its positive zeta potential [31]. This positive surface charge is as a result of the formation of bilayer structure of the CTAB molecules on the gold surface [32].

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We have not measured the surface charge of the Amberlite IRA-900 ($OH^-$ or $CO_3^{2-}$ form) because their sizes are quite large (650 – 820 um) so that they settled down during the measurements for their zeta potentials. However, according to the information from the specifications provided by the supplier, the original Amberlite IRA-900 ($Cl^-$ form) is an anionic resin, so one expects that the charge on the resin surface should be positive.

To sum up, the supports ($BaCO_3$, anion-exchange Amberlite IRA-900 resin) have the positive charge on their surface while ligand-capped Au nanoparticles (THPC-Au, citrate-Au) have the negative charge on their surfaces. The CTAB-Au nanoparticles have the positive charge on their surface. Figure 3 shows the interaction models of ligand-capped Au nanoparticles with supports. According to the proposed models, $BaCO_3$ well interacts with THPC-Au or citrate-Au because its surface charge is positive while surface charge of citrate-Au or of THPC-Au is negative. However, the surface charge of CTAB-Au is positive; therefore, CTAB-Au and $CaCO_3$ repulse each other.

The Amberlite resin ($OH^-$, $CO_3^{2-}$) attracts THPC-Au or citrate-Au because they have opposite charge. However, the situation between CTAB-Au and Amberlite resin is different from that between CTAB-Au and $BaCO_3$. The chemical structure of the cationic part of Amberlite resin is similar to that of CTAB (Figure 3); therefore Amberlite resin attracts CTAB-Au via trimethyl ammonium head.

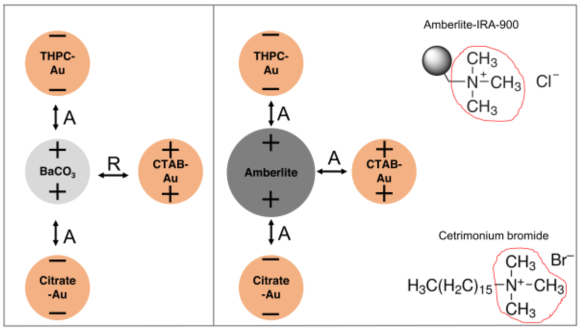

Figure 3: Interaction models of ligand-Au nanoparticles with supports based on the measurements of zeta potentials. A and R stand for the attraction and repulsion, respectively

Because the oxidation of benzyl alcohol catalyzed by gold catalysts in water was well-known to be affected by the basicity of reaction medium, a higher pH value gives a better conversion of benzyl alcohol. A pH value lower than 7.0 unlikely results in any viable conversion of reactant [15, 17, 33]. The bases used to promote this reaction can be classified into strong bases (sodium hydroxide, potassium hydroxide) and weak bases (potassium carbonate, sodium acetate, sodium borate). The basic supports we used in our study are different from the above-mentioned ones in some aspects: i) $BaCO_3$ is a very weak base with a solubility product of 2.58 x $10^{-9}$ [34] and mostly stays in solid state in de-ionized water. A small and soluble portion dissolves in water to create the basicity of water. However, it will dissolve to compensate the loss of the basicity of a solution upon demand; ii) anion-exchange resins, Amberlite IRA-900 ($OH^-$ or $CO_3^{2-}$ form), do not create the basicity of deionized water because they are not soluble in water unlike other ones (sodium hydroxide or barium carbonate). Their basicity is via hydroxyl or carbonate exchangeable groups on the surface. In other words, water soaked with these anion-exchange resins shows neutral pH.

We tested the oxidation of benzyl alcohol catalyzed by the ligand-capped Au nanoparticles and ligand-capped Au/supports in water as a solvent and hydrogen peroxide as an oxidant. The reaction conditions are listed in Table 1. The performance of each catalyst is presented in Table 3. The control reaction without any catalyst does not show any viable conversion of benzyl alcohol. The reaction catalyzed by THPC-Au shows a conversion of benzyl alcohol of 18.6% and benzoic acid as a main product with a selectivity of 78.9%. In comparison with THPC-Au, the THPC-Au/$BaCO_3$ catalyst significantly enhances the conversion of benzyl alcohol (74.4%), but the selectivity of benzoic acid is comparable (74.5%).

Table 3: The oxidation reaction of benzyl alcohol catalyzed by a variety of catalysts

| Cat | Support | X | A | B | C |
|---|---|---|---|---|---|
| THPC-Au | $BaCO_3$ | 74.4 | 0.5 | 74.5 | 24.9 |
| THPC-Au | Amberlite-OH | 89.6 | 0.5 | 99.5 | 0.0 |
| THPC-Au | Amberlite-$CO_3$ | 68.7 | 1.3 | 95.6 | 3.0 |
| THPC-Au | No | 18.6 | 13.3 | 78.9 | 7.6 |
| Citrate-Au | $BaCO_3$ | 56.8 | 1.5 | 88.8 | 9.6 |
| Citrate-Au | Amberlite-OH | 57.0 | 3.0 | 97.0 | 0.0 |
| Citrate-Au | Amberlite-$CO_3$ | 11.6 | 7.3 | 92.7 | 0.0 |
| Citrate-Au | No | 3.7 | 100 | 0.0 | 0.0 |
| CTAB-Au | $BaCO_3$ | 5.6 | 34.5 | 64.5 | 0.0 |
| CTAB-Au | Amberlite-OH | 98.6 | 0.0 | 100 | 0.0 |
| CTAB-Au | Amberlite-$CO_3$ | 50.8 | 0.8 | 99.2 | 0.0 |
| CTAB-Au | No | N/D | | | |

X: conversion, A: benzaldehyde, B: bezoic acid, C: benzyl benzoate. ND=not detected

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This observation is surprising because this reaction, normally required strong or weak base, could be well promoted by a very weak base – barium carbonate. It should be mentioning that, without addition of the HCl solution to the reaction product prior to extraction with ethyl acetate, analysis by GC/MS did not detect benzoic acid. This is as a result of a high solubility of barium dibenzoate in water (49.6 g barium dibenzoate in 1L water at 20 $^{o}$C) [35].

With a 74.4% conversion, an estimated concentration of barium dibenzoate formed from the reaction is 22 g/L, and this concentration is about a half of maximum solubility of barium dibenzoate in water. Therefore, barium dibenzoate formed from the reaction was completely soluble in aqueous reaction medium. This explains the fact that product had to be converted to benzoic acid by HCl before extracting it with ethyl acetate for GC/MS analysis.

The concentration of carbonate anion in water, calculated from the product solubility of $BaCO_3$, is 5 x $10^{-5}$ mol/L. This calculation does not account for the complexity of the reaction medium but is just for the comparison purpose. Gold nanoparticles stabilized by carboxylate modified polyvinylpyrrolidone required 0.2 mol/L of $K_2CO_3$ to have a good conversion (83% at 4h and 22 $^{o}$C, dioxygen as an oxidant) and selectivity of benzoic acid (81.0 %) [15]. The PVA-Au/$TiO_2$ catalyst required 10.86 x $10^{-3}$ mol/L $K_2CO_3$ to have a conversion of 72% and selectivity of benzoic acid of 87.0 % (reaction at 100 $^{o}$C, 1h, and dioxygen as an oxidant) [17]. Gold nanoparticles in ordered mesoporous carbons required 1.44 mol/L of KOH to achieve almost 100% conversion and 100 % selectivity towards benzoic acid (reaction at 90 $^{o}$C, 1h, and dioxygen as an oxidant) [36]. The Au clusters (~ 1 nm) within mesoporous silicas (SBA-15, MCF, HMS) needed 0.075 mol/L of $K_2CO_3$ to have 100% conversion and 91% selectivity of benzoic acid (reaction at 80 $^{o}$C, 1h, $H_2O_2$ as an oxidant) [37, 38]. The comparison between the aqueous concentration of the base used in our study with that used in the other work indicates that the oxidation of benzyl alcohol in water catalyzed by gold catalyst can take place with the presence of a very weak base like barium carbonate.

This observation can be explained that the strength of a base does not seem important than the availability of a base that can provide the basic species to the reaction media once needed.

The characteristic of the oxidation reaction of benzyl alcohol in water catalyzed by a variety of gold catalysts is that the main product is benzoic acid but not benzaldehyde and that a base must be present to achieve a viable conversion. On the contrary, the oxidation of benzyl alcohol in organic solvents or in the absence of any organic solvents (solvent-free) catalyzed by gold catalysts do not need the presence of any base to achieve a good conversion of benzyl alcohol. The main product in those cases is benzaldehyde while benzoic acid is a minor product, regardless of oxidant, reaction temperature, size of gold, and support [39-47].

It has been proposed that the role of a base in the oxidation reaction of benzyl alcohol in water is to convert benzoic acid to a salt of benzoic acid. The deactivated gold catalyst could be also restored by washing it with a base. This prevents gold surface from being poisoned by benzoic acid and therefore from being deactivated [48-50]. However, this proposed poison mechanism does not sound logical because most carboxylic acids or their salts bind to the surface of gold nanoparticles via carboxylate functional groups. Therefore, after neutralizing benzoic acid with a base, the carboxylate functional groups are still available to poison the surface of gold. For example, trisodium citrate is a well-known ligand to stabilize gold nanoparticles because carboxylates well bind to the surface of gold nanoparticles [22].

The catalytic performances of THPC-Au/Amberlite-IRA-900 ($OH^-$) and THPC-Au/Amberlite-IRA-900 ($CO_3{}^2$) for the oxidation reaction of benzyl alcohol are presented in Table 2. Unlike $BaCO_3$ or other soluble bases (NaOH, $K_2CO_3$), the anion-exchange resin has hydroxyl or carbonate species on its surface, which is responsible for the basicity. Two resins show very good conversions of benzyl alcohol and good selectivities towards benzoic acid. In these cases, benzoic acid formed was not converted into a salt of benzoic acid because there are not available counter ions in the reaction media. This free benzoic acid being available in the reaction solution was confirmed by the fact that a solution of HCl was not needed to add into the reaction solution prior to extracting with ethyl acetate for analysis (the extraction of product with ethyl acetate with or without an addition of HCl solution gave the same conversion of benzyl alcohol and selectivity of benzoic acid). However, the benzoic acid exchanged with hydroxyl or carbonate ion on the surface of resin cannot be excluded because there was an evidence that benzoic acid tends to adsorb on the surface of anion-exchange resin having the same nature as Amberlite-IRA-900 (e.g. $-N^+-(CH_3)_3$) [51]. In other words, Amberlite-IRA-900 ($OH^-$ or $CO_3^{2-}$) resin can be a scavenger for benzoic acid. However, the adsorption is an equilibrium process, and thus free benzoic acid should be always available in the solution. Therefore, if free benzoic acid is responsible for the deactivation of gold catalysts, Au-THPC/Amberlite-IRA-900 ($OH^-$ or $CO_3^{2-}$) would be deactivated due to free benzoic acid. The oxidation reaction of benzyl alcohol catalyzed by citrate-Au/$BaCO_3$ or citrate-Au/Amberlite-IRA-900 ($OH^-$ or $CO_3^{2-}$) catalyst shows a similar characteristic to that catalyzed by Au-THPC/$BaCO_3$ or THPC-Au/Amberlite-IRA-900 ($OH^-$ or $CO_3^{2-}$) catalyst. Amberlite-IRA-900 ($OH^-$) gives a better conversion of benzyl alcohol than Amberlite-IRA-900 ($CO_3^{2-}$). This probably can be attributed to a weaker basic nature of the carbonate ion than the hydroxyl ion on the surface of resin. This observation is also true for the CTAB-Au/Amberlite-IRA-900 ($OH^-$ or $CO_3^{2-}$) catalyst. Once we compare the catalytic activities of CTAB-Au/$BaCO_3$ and CTAB-Au/Amberlite-IRA-900 ($CO_3^{2-}$), one recognizes that the activity of the CTAB-Au/Amberlite-IRA-900 ($CO_3^{2-}$) catalyst is almost ten times higher than that of the CTAB-Au/$BaCO_3$ catalyst although two catalysts have the same carbonate species. This implies that the reaction mechanism of the oxidation of benzyl alcohol over gold-based catalysts is quite complicated, and further mechanistic studies should be investigated to comprehend.

We also performed the oxidation of benzyl alcohol over the THPC-Au/Dowex 50WX2-Na and citrate-Au/Dowex 50WX2-Na catalysts (Dowex 50WX2-Na is a cation-exchange resin). Both catalysts are almost inactive, in comparison with control reactions without catalysts, for the oxidation of benzyl alcohol using the same reaction conditions described in Table 4.

Table 4: The oxidation reaction of benzyl alcohol catalyzed by gold catalysts with Dowex 50WX2-Na resin

| Cat | Resin | X | A | B | C |
|---|---|---|---|---|---|
| THPC-Au | Dowex 50WX2-Na | 6.19 | 100 | 0 | 0 |
| Citrate-Au | Dowex 50WX2-Na | 4.13 | 100 | 0 | 0 |

X: conversion, A: benzaldehyde, B: bezoic acid, C: benzyl benzoate.

The influence of the acidic modifier on the performance of catalysts was investigated using $CaCl_2$ as a pH modifier. The catalytic performances of the TPHC-Au/$BaCO_3$ and citrate-Au/$BaCO_3$ catalysts with the presence of different amounts of $CaCl_2$ added are listed in Table 5. As seen in Table 5, the conversion of benzyl alcohol decreases with an increase in the amount of $CaCl_2$. This observation clearly shows that a decrease in pH results in lower conversion.

Table 5: The influence of the acidic modifier on the performance of gold catalysts

| Cat | $CaCl_2$ added(*), mL | X | A | B | C |
|---|---|---|---|---|---|
| THPC-Au | 0.0 | 74.4 | 0.5 | 74.5 | 3.4 |
| THPC-Au | 0.2 | 66.5 | 1.9 | 94.6 | 2.1 |
| THPC-Au | 0.6 | 47.1 | 3.1 | 94.7 | 9.6 |
| Citrate-Au | 0.0 | 56.8 | 1.5 | 88.8 | 2.5 |
| Citrate-Au | 0.2 | 54.2 | 1.6 | 95.9 | 3.0 |
| Citrate-Au | 0.4 | 21.5 | 7 | 90.0 | 13.7 |

X: conversion, A: benzaldehyde, B: bezoic acid, C: benzyl benzoate. (*)$CaCl_2$ solution: 1g dissolved in 5 mL DI water. Base added is $BaCO_3$

## Conclusion

In summary, we have succefully synthesized ligand-stablized gold nanoparticles (CTAB-Au, citrate-Au, and THPC-Au). They were mixed with weakly basic solids ($BaCO_3$, Amberlite IRA-900 ($OH^-$ or $CO_3^{2-}$ form)) and acidic solid (Dowex 50WX2-Na) to serve as catalysts in oxidation of benzyl alcohol in water. Our study shows that very weak bases promote catalytic activity of ligand-stabilized Au nanoparticles. Because benzoic acid is a main product and conversion is siginificantly high, catalyst cannot be poisoned by benzoic acid. The ligand-stabilized Au nanoparticles with acidic support does not show any catalytic activity. An increase in acicidity of reaction medium leads to deterioration of catalytic activity of ligand-stablized Au/weak bases. Therefore, bases are still needed for the oxidation reaction catalyzed by gold in water phase. However, strong bases are not necessary, as indicated by our study.

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