

Novel Routes For Heterogenizing Gold Nanoparticles For Catalytic Oxidation Using Molecular Oxygen

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ABSTRACT

Two different methods for preparing gold catalysts have been investigated in this project: deposition precipitation with NaOH (DP NaOH) and urea (DP urea) methods. On a collection of metal oxide materials as supports, gold has been deposited as nanoparticles. Gold particles less than 5 nm in diameter were obtained based on TEM measurements. Various assisted Au catalysts prepared by deposition precipitation with NaOH show unmatched catalytic efficiency for selective nanoparticles. In contrast to the other Au catalysts, alcohol oxidation. Gas chromatography analyzed both of the reactions. The product shows that in the presence of supported nanoparticle Au catalyst provided by the DP NaOH process, the selective benzyl alcohol oxidation to benzaldehyde in air could be completed with elevated conversion and selectivity at 403 K.

Keywords: Nanoparticles of Gold; Transmission Electron Microscopy; Manufacture Catalyst

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INTRODUCTION

Heterogeneous catalysis refers to the form of catalysis in which the catalyst phase differs from the reactant phase. The majority of processes using homogeneous catalysts are in the liquid phase, while the catalysts are in solid form for heterogeneous catalysts, and the reaction occurs with liquid or gaseous phase substrates [1]. Recently, there has been an enormous benefit in creating or designing new processes that can mitigate energy exhaustion and contamination of the chemical structure and processing because of rising concern about the environmental effects [2]. Heterogeneous catalysis is the cornerstone to the effective production of so-called "green chemistry" as it is commonly used to minimize emissions from automotive and stationary combustion sources. For example, the emission of carbon monoxide (CO) from cars is dramatically reduced by heterogeneous catalysts[3][4]. In addition, heterogeneous catalysts play major role in chemical output and treatment in the petroleum industries [5] [6].

Gold was historically thought to be inefficient as a catalytic metal. However, gold, as small nanoparticles, has shown an improvement in catalytic activity in many chemical reactions when these particles are deposited on a high surface area with support for oxide[7]. In addition, gold particles serve as active heterogeneous catalysts in both the gas and liquid phases. A broad variety of reactions to be considered can lead to more applications for gold catalysis and its effect in pollution control, chemical processing and fuel unit technology [8].

One of the biggest breakthroughs in the field of gold catalysis is when Haruta et al. have proved that supported gold nanoparticles are active at very low temperatures in the oxidation of CO [7]. Due to this discover, nowadays supported gold nanoparticles are more used in many industrial applications, such as pharmaceutical, perfumery and fuel cells operating in electric vehicles applications.

In this work, oxidation of benzyl alcohol and cyclohexanol, has been carried out with different supported-gold nanoparticle catalysts, trying to find an appropriate route for selective oxidation with high conversion. Selective oxidation is an important topic for research and as a unit process in the manufacture of chemical intermediates, due to rise atom efficiency that can be obtained by these selective oxidations [9][10]. The oxidation of alcohols to aldehydes and ketones

is important in laboratory and commercial procedures especially when exploiting molecular oxygen in the form of air as 'green' oxidising agent.[9-11]

Gold nanoparticle reactivity has been extensively discussed in the literature due to its significance in catalytic processes. There are different theories about the catalytic activity of the Gold Particles, the first form of these theories suggests that the catalytic activity of the Gold Particles is due to the existence of the Gold Atoms in these particles. In both the theoretical and experimental parts, the value of low-coordinated auto atoms and their position as active sites [12-13]. Another explanation considers that the catalytic performance of gold particles is due to indirect effects of the support; charge transfer to or from the support, [14-15] or support-induced strain [16].

The third theory explicitly implies the impact of the aid. This applies to the movement of activated oxygen from the help or to particular active sites at the metal oxide boundary [16]. The morphology of the golden particles could be described by the interaction of the gold-bearing, which could have an effect on the number of low organized atoms or strains[17]. In other studies, it was addressed that catalytic activity should be scaled to the number of low-coordinated atoms in nanoparticles in the case of low-coordinated corner sites, active sites and not surface areas[18].

The general goal of this project is developed an efficient gold catalyst for catalytic oxidation of different types of alcohols. Molecular oxygen in the form of air was chosen as the oxidant, which is both abundant and inexpensive and offers high atom efficiency.

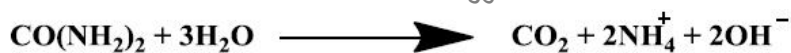
EXPERIMENTAL AND CHARACTERIZATION

Catalysts Preparation

Initially, batches of gold nanoparticle catalysts were prepared by deposition-precipitation (DP) method which can be divided into two ways: DP with urea and NaOH. Commercial metal oxides were used as supports for Au particles such as titania, alumina, silica and ceria powders.

Deposition Precipitation with urea (CO (NH₂)₂)

The deposition precipitation method developed by Geus using urea (CO(NH₂)₂) as a precipitation base allows the gradual and homogeneous addition of hydroxide ions in the solution (equation 1): [19]



A suspension of 1 g of help in 100 mL of distilled water was added into an Erlenmeyer flask heated at 353 K, followed by 0.20 g of gold precursor (HAuCl₄.3H₂O). A new color for the suspension was observed: after the addition of urea to the suspension in the chloroauric acid solution at 353 K, the pale yellow color of the suspension becomes pale orange within less than 1 min for the entire catalyst[22].

Deposition precipitation with NaOH

This method has been developed by Haruta using NaOH as a precipitating agent. [23] In the standard preparation conditions (similar to Haruta's preparations), [24] 100 ml of HAuCl₄ aqueous solution (2.1 × 10⁻³ M) was heated to 343 K. The pH of the solution was modified (7.5-8.5) with a dropwise addition of NaOH aqueous solution (0.5 M). Then 1 g of metal oxide brackets was added with a vigorous

stirring at 343 K for 2 h; the pH value of NaOH solution was maintained during stirring.

After cooling to room temperature, all the solids obtained were treated as DP urea (separation, four washes with deionized water, 353 K dry overnight and 573 K calcination under air for 4 h). Solutions of aqueous containing Au can be easily photoreduced by natural light, and it is recommended that all preparations be made in the dark.

Catalysts testing

The general procedure followed for all oxidation reactions was as follows:

Au catalyst has been screened for the oxidation of two types of alcohols, benzyl alcohol and cyclohexanol (Figures 1 and 2, respectively).

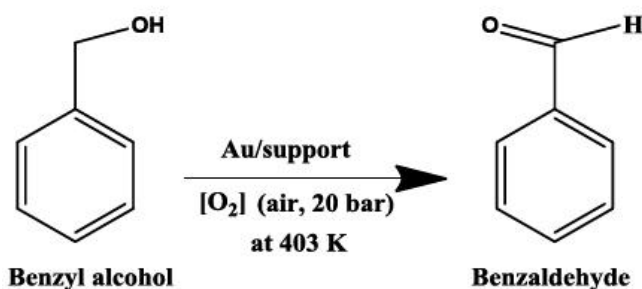


Fig. 1. Scheme for the benzyl alcohol oxidation to Benzaldehyde over supported gold catalysts

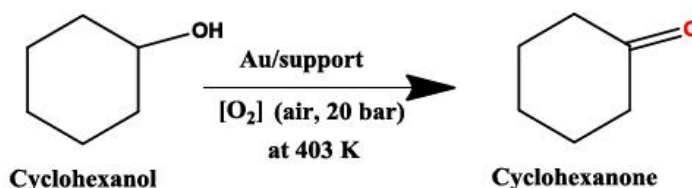


Fig. 2. Scheme for the benzyl alcohol oxidation to cyclohexanone over supported gold catalysts.

Alcohol oxidation reactions were Performed in a stirred reactor. The Teflon liner was filled with alcohol (1 g) and a catalyst (0.1 g). Subsequently, tert-butanol (35 mL) and monoglyme (0.9 g) were used as solvent and internal norm, respectively. The stirrer was set at (800 rpm) and the reaction mixture was raised to the appropriate temperature (403 K). The reaction time was started when the reactor pressurized with air (as an oxidant) at about 20 bar.

RESULTS

Electron Microscopy results

Transmission electron microscopy (TEM) was used to evaluate the scale, form and distribution of gold nanoparticles deposited on various metal oxide supports. TEM has shown a variety of sizes and morphology nanoparticles of gold on the catalytic converters made. The gold particles on the catalysts have been tested individually (Table 1).

Table 1: Gold mean particles size from TEM micrographs

Catalysts	Preparation Method	Particles Counted	Average Of Particle Size
Au/CeO ₂	DP urea	85	2.7 nm
Au/CeO ₂	DP NaOH	76	4.5 nm
Au/TiO ₂	DP NaOH	48	3.3 nm
Au/SiO ₂	DP urea	21	23.1 nm

The catalyst powder was prepared for the TEM analysis by processing in high-purity ethanol using an agate pestle and mortar. A drop in the suspension was then deposited on a hollow carbon grid and allowed to evaporate to dry.

Figure 3 displays representative micrographs of Au / CeO₂ catalytic converter after calcination at 673 K. As seen in the

figure 3, the gold particles are homogeneously distributed on the assistance of CeO₂. The majority of these particles are uniform. The average particle size was less than 5 nm in diameter, with an average of 2.7 nm observed. This average was determined by measurement of at least 85 particles (Table 1).

Novel Routes For Heterogenizing Gold Nanoparticles For Catalytic Oxidation Using Molecular Oxygen

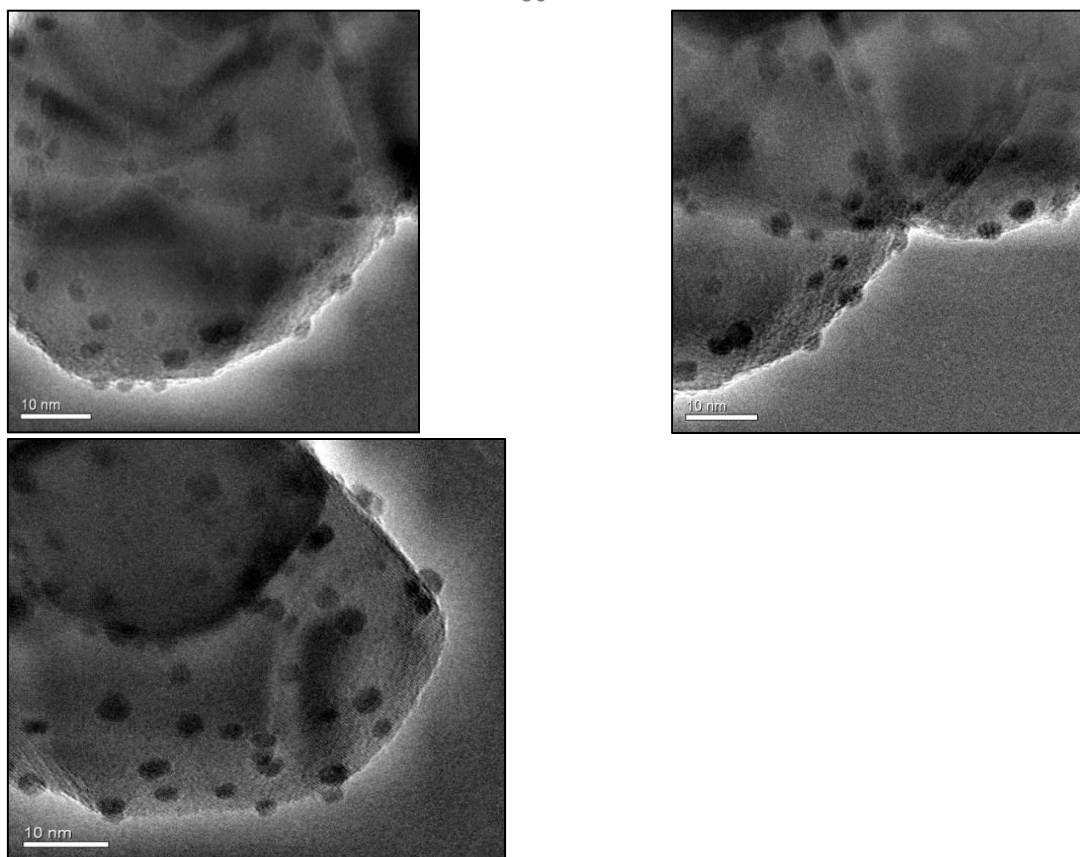


Fig. 3. TEM images for Au / CeO₂ Catalyst produced using the DP urea process.

In Figure 4, similar gold particles were obtained for Au/CeO₂ catalyst, which is prepared by DP NaOH method. The catalyst was calcined at 573 K; therefore the calcination temperature was lower than that prepared by DP urea method.

However, it can be clearly seen that the size of particles is larger than that of Au/CeO₂ catalyst produced by DP urea method and more visible. Additionally, more particles are deposited on the surface of ceria.

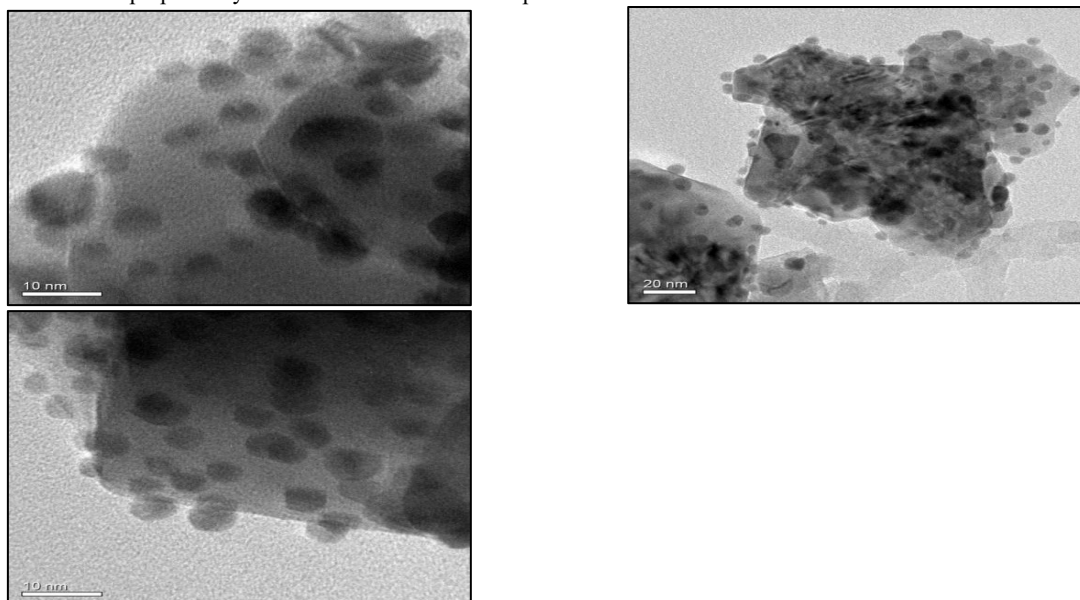


Figure 4: TEM images for Au / CeO₂ Catalyst produced using the DP NaOH process

Whereas, in Figure 5, the TEM images clearly demonstrate that the Au particles are distributed on the TiO₂ support, prepared by DP NaOH. Furthermore, the nanoparticles of the Au/TiO₂ catalyst have a different support morphology from

those obtained with Au/CeO₂ catalysts. The particle sizes mean of Au/TiO₂ catalysts is also smaller than 5 nm (average ~3.3 nm).

Novel Routes For Heterogenizing Gold Nanoparticles For Catalytic Oxidation Using Molecular Oxygen

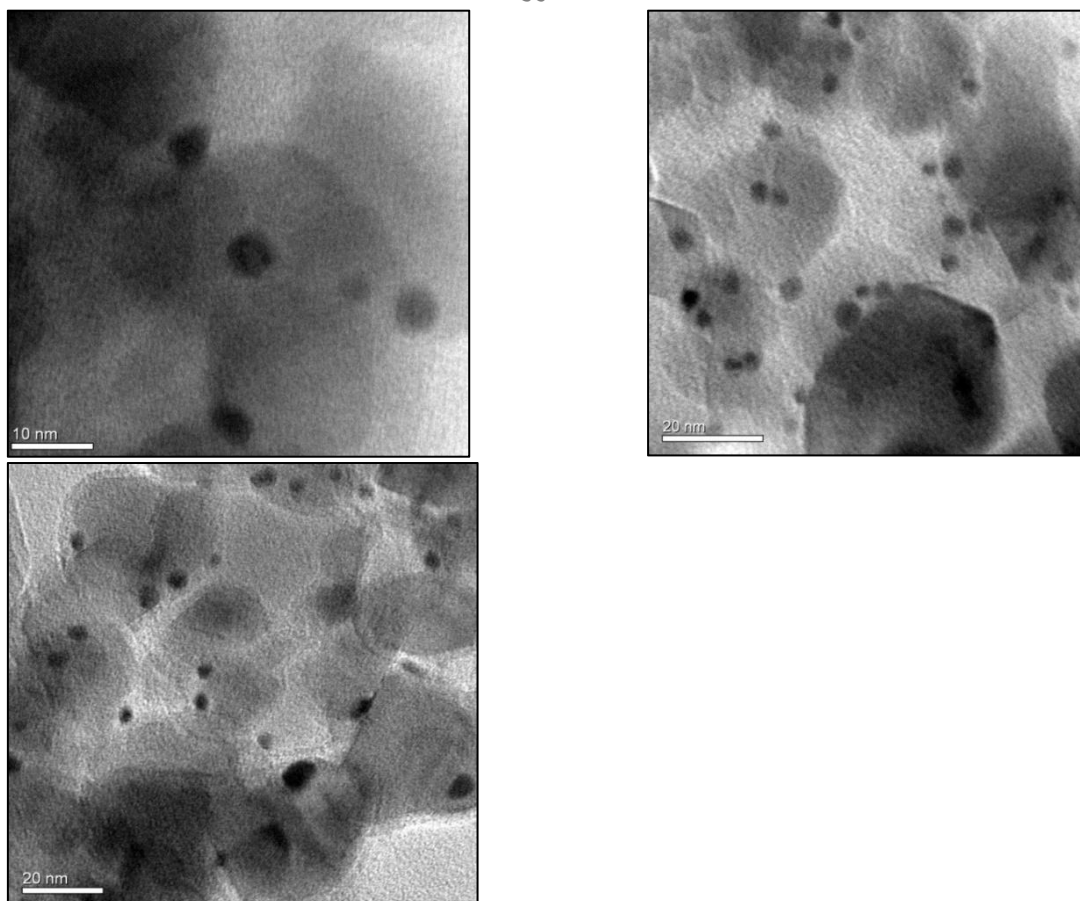


Fig. 5. TEM images for Au/TiO₂ catalyst produced using the DP NaOH process.

On the other hand, larger gold particles were observed in Au/SiO₂ catalyst produced by urea show a totally different support morphology. The Au/SiO₂ catalyst prepared by urea was the lowest conversion in the oxidation of alcohols among other catalysts and this is due to the large size of particles (this will be discussed more in catalysis work). Also

agglomeration has also produced some large irregular structures as shown in Fig. 6. The TEM has not really shown evidence for the shape of the gold particles being hemispherical, instead of that, they appear as spheres for the most part.

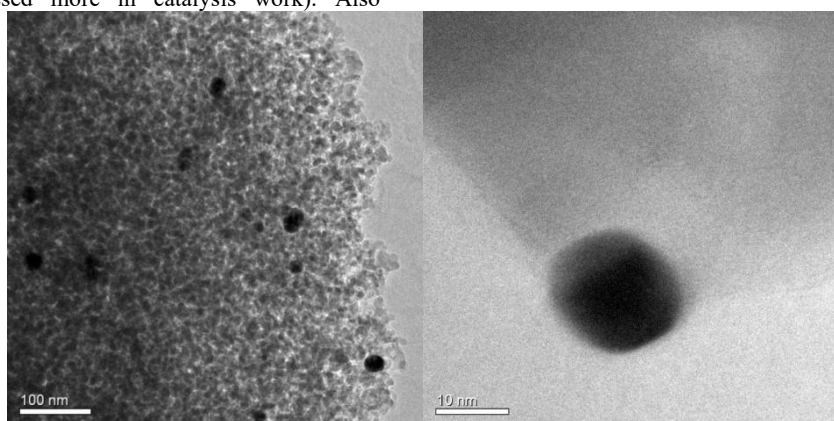


Fig.6. TEM images for Au/SiO₂ catalyst produced using the DP urea process

Catalysis Results

In this study, two separate substrates (benzyl alcohol and cyclohexanol) were used to test the catalytic efficiency of the catalysts. Eight gold catalysts were produced by DP urea and DP processes, using four different supports CeO₂, TiO₂, Al₂O₃ and SiO₂. The oxidation reactions of benzyl alcohol and cyclohexanol were both investigated catalysts. These reactions were conducted at 403 K for 8 h, using air as an oxidant.

benzyl alcohol oxidation to Benzaldehyde

- Using catalysts prepared by DP NaOH method

As shown in Figure 7, the nanoparticle Au catalysts exhibiting some catalytic activity and benzaldehyde selectivity. Both good conversion and benzaldehyde selectivity were observed using Au / CeO₂ catalysts, while the highest selectivity (95 percent) was observed for Au / TiO₂ catalysts with a conversion rate of 83.9 percent. Gold sponsored by the Al₂O₃ catalyst shows high response and selectivity values of 78.2 percent and 75 percent respectively. In contrast, the lowest rates for the oxidation of benzyl alcohol were obtained with Au/SiO₂ catalyst; the catalytic performance and selectivity were not satisfactory: 22% and 37%, respectively.

Using catalysts prepared by DP urea method

Similarly, both gold catalysts prepared by DP urea have also been investigated for the benzyl alcohol oxidation. The Au / CeO₂ catalyst shows high selectivity for benzaldehyde with strong conversion (93 percent) and (64 percent) respectively. On the other hand, poorer catalytic efficiency for Au / TiO₂ catalysts compared with Au / TiO₂ catalysts produced by DP NaOH. While Au / Al₂O₃ and Au / SiO₂ catalysts exhibit identical conversion and selectivity values with Au / Al₂O₃ and Au / SiO₂ in DP NaOH. (Fig. 8).

Oxidation of cyclohexanol to cyclohexanone

All four gold nanoparticles catalysts have been screened for the catalytic benzyl alcohol oxidation to cyclohexanone, which are very important intermediates for the production of Nylon. The chart below indicates the conversion and selectivity of gold nanoparticles catalysts for cyclohexanol oxidation to cyclohexanone. The reactions were carried out at 403K, 20 bar of air and in the presence of t-butanol solvent for 8 hours. Gas chromatography (GC) was used for reactions analysis.

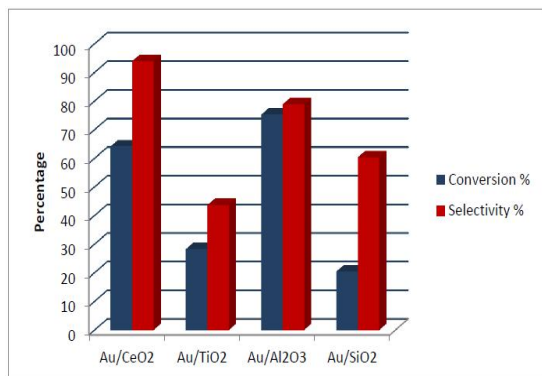


Fig. 8. Conversions and selectivities of benzyl alcohol oxidation over different supported gold catalysts prepared by DP urea method (20 bar of air, 403 K).

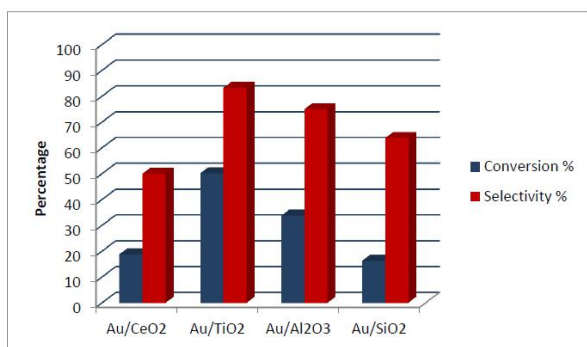


Fig. 9. Conversions and selectivities of cyclohexanol oxidation over different supported gold catalysts prepared by DP NaOH method (20 bar of air, 403 K).

Using catalysts prepared by DP urea method

The results appear that the Au deposited on CeO₂ exhibits good catalytic activity for the benzyl alcohol oxidation when compared with its corresponding analogues on TiO₂, Al₂O₃ and SiO₂. The performance of the Au/CeO₂ (DP urea) is superior to that of the Au/CeO₂ (DP NaOH); the latter showed not only lower selectivity but very poor activity (Fig. 10).

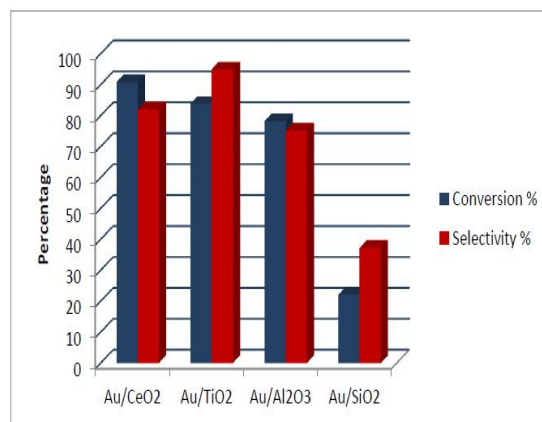


Fig. 7. Conversions and selectivities of benzyl alcohol oxidation over different supported gold catalysts produced by DP NaOH method (20 bar of air, 403 K).

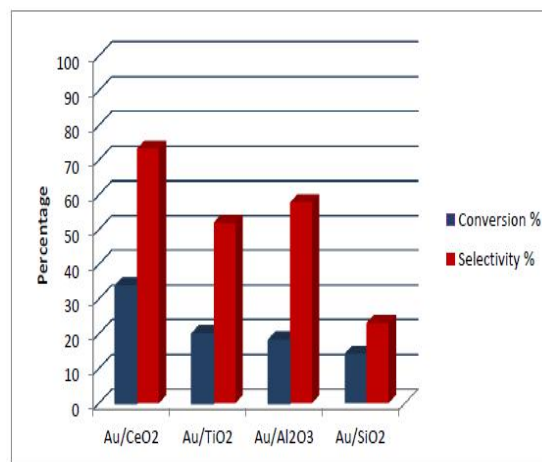


Fig. 10. Conversions and selectivities of cyclohexanol oxidation over different supported gold catalysts prepared by DP urea method (20 bar of air, 403 K).

DISCUSSION

The influence of the support on particle morphology is clearly shown. Four catalysts have been characterized by TEM and gave different particle distributions and sizes depending on the type of support used. Gold particles below 5 nm in diameter can be obtained by using deposition-precipitation with its two directs: NaOH and urea. In the cases of Au supported on Ceria (Figs. 3, 4) a narrow particle size and homogeneously distribution was achieved as expected when using this technique. Mean particle sizes less than 5 nm for Au deposited on CeO₂ and TiO₂ were obtained, however larger particles were observed for Au/CeO₂ and Au/TiO₂ (DP NaOH) than those for Au/CeO₂ (DP urea). As a result, both catalysts (Au/CeO₂ and Au/TiO₂) prepared by DP NaOH method exhibit high catalytic performance for the benzyl alcohol oxidation to benzaldehyde. Furthermore, the preparation method of the catalysts may affect the sizes and the dispersion of particles. In DP NaOH catalyst, more particles are deposited on CeO₂ than DP urea one (Figs 3, 4).

Catalysis work

Novel Routes For Heterogenizing Gold Nanoparticles For Catalytic Oxidation Using Molecular Oxygen

Two symbolic alcohols over gold catalysts have been investigated in this study: benzyl alcohol and cyclohexanol.

Two different methods were used to form supported gold catalysts: deposition precipitation with NaOH and with urea, as precipitating agents. Both methods have illustrated various catalytic activities and selectivities for the catalysts in the oxidation of two alcohol substrates. The TEM micrographs of Au/CeO₂ catalyst (DP NaOH, Fig. 4) prove that a wide range of particles can be deposited on the surface of support rather than DP urea (Au/CeO₂ in Fig. 3).

Generally, as shown in the TEM micrographs (Figs. 3, 4 and 5) different solid supports can disperse and stabilize gold nanoparticles, high conversions and selectivities were observed when using supported Au particles on CeO₂, TiO₂ and Al₂O₃ for the oxidation of alcohol (benzyl alcohol and cyclohexanol), that may be because of the high surface area of these support and the strong interactions with Au particles. However, less catalytic activity was achieved when mesoporous SiO₂ help was used. A significant difficulty with preparing Au catalysts supported on mesoporous silica is the weak interactions between Au and silica, which lead agglomeration of the Au particles and loss of Au from the mesopores (Fig 6).

In comparison with the literature, very similar results were obtained in this work for the benzyl alcohol oxidation to aldehydes or ketones over Au/TiO₂ catalyst prepared by DP NaOH. In addition, a slightly larger average of particle sizes (3.3 nm) was achieved than that in the literature (2.7 nm).

Whereas, gold deposited on CeO₂ and Al₂O₃ catalysts (DP NaOH) observed higher conversions than in the literature for the benzyl alcohol oxidation, although the molecular oxygen in supercritical carbon dioxide (scCO₂) was used as the oxidant while in this work molecular oxygen in the form of air was used as the oxidant.

CONCLUSION

In summary, two methods were used to prepare gold nanoparticle catalysts: NaOH deposition precipitation and urea deposition-precipitation. The difference between these two approaches is the precipitating agent, NaOH and urea. Both methods show that small gold particles (below 5 nm) can be formed, but the DP urea method requires more preparation time (16 h).

Gold particles were dispersed on four different metal oxides used as supports, CeO₂, TiO₂, Al₂O₃ and SiO₂. Supports play an essential role for achieving excellent catalysts, which lead to high conversions and selectivities for the oxidation reactions of alcohols. As shown in catalysis results part, different supported gold catalysts are showing significant difference in catalytic activities. The size of the particles has a great impact on the catalytic efficiency of the catalysts. High catalytic activities were obtained for the oxidation of alcohols when the size of particles is small enough (Au particles deposited on CeO₂, TiO₂ and Al₂O₃), while lower conversions and selectivities have been shown when using Au/SiO₂ catalysts due to their large particles.

Recommendations

- 1- Upon this project would be useful in trying other preparation techniques for gold nanoparticle catalysts.
- 2- More controlled preparation conditions of gold catalysts will enable through study of the role of preparation method on the catalytic performance.
- 3- Furthermore, further study could also focus on the nature and mechanism of the relationship between gold and support by using another variety of supports, such as ZnO, Fe₂O₃ and ZrO₂.

- 4- Further deep investigations should be in the oxidation reactions of alcohols. One such direction would be to use other characterization techniques, such as STEM, XRD and particularly ICP (Inductively Coupled Plasma), which is used to determine the content of gold in the catalyst.

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Novel Routes For Heterogenizing Gold Nanoparticles For Catalytic Oxidation Using Molecular Oxygen

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