Supported nano gold as a recyclable catalyst for green, selective and efficient oxidation of alcohol using molecular oxygen

Bashir Ahmad Dar\textsuperscript{a,b} and Mazahar Farooqui\textsuperscript{a}

\textsuperscript{a}Post Graduate and Research Center Maulana Azad College Aurangabad India 431001
\textsuperscript{b}Indian Institute Of Integrative Medicine(CSIR) Canal Road Jammu India 180001

Received: 07 October 2010; revised: 20 January 2011; accepted: 23 April 2011. Available online: 12 September 2011.

**ABSTRACT:** The myth that gold cannot act as a catalyst has been discarded in view of recent studies, which have demonstrated the high catalytic efficiency of pure nano-gold and supported nano-gold catalysts. In recent years, numerous papers have described the use of supported nano-gold particles for catalysis in view of their action on CO and O\textsubscript{2} to form CO\textsubscript{2}, as well as a variety of other reactions. Special emphasis is placed on the oxidation studies undertaken on model nano-Au systems. In this work a solvent free oxidation of 1-phenyl ethanol was carried out using gold supported on ceria-silica, ceria-titania, ceria-zirconia and ceria-alumina at 160 °C. Almost 88-97% conversion was obtained with >99% selectivity. Temperature screening was done from 70 to 160 °C. Catalysts were prepared by deposition co-precipitation method and deposition was determined by EDEX analysis.

**Keywords:** ceria-silica; ceria-titania; ceria-zirconia; ceria-alumina; gold supported catalyst; catalytic oxidation

**Introduction**

As compared to their bulk counter parts, the tiny size of nano-materials instruct considerably different fundamental properties (e.g. adsorption properties, melting point, etc.) to these systems, which makes it applicable to several processes such as catalysis, chemical and bio-detectors, advanced drug delivery systems, enhanced computing systems and opto-electronics etc. In recent years there has been a mounting attention in nano-gold systems [1-6] since particle size is known to have an immense influence on the catalytic properties of gold [7]. Gold exhibits catalytic activity but its use as catalyst...
is very recent compared to the other metals such as metals those belonging to VIII and IB group (Cu, Ag) of the periodic table [8]. The gold catalyst supported on ceria-alumina promoted by presence of vanadia and molybdlena exhibit a high and stable activity in complete oxidation of benzene at low temperature [9]. It has been reported that oxide supported gold has superior catalytic activity over the colloidal form [10]. The oxides like ceria have high oxygen storage capacity [11], which can be enhanced by doping it with some metals like Al and Sm etc. Gold nanoparticles supported on ceria promote the selective oxidation of oximes into the corresponding carbonyl compounds [12]. Therefore we decided to study oxidation of alcohol using oxide supported gold as a catalyst, since catalytic activity of oxide supported gold depends on various factors such as the method of preparation, the solid support, the pre-treatment etc. The catalytic property of gold/metal oxide interface strongly depends on the nature and textual structure of the support [13]. The present study investigates the oxidation of 1-phenyl ethanol as a model using gold supported on mixed oxides as catalyst.

Ceria was chosen as main constituent of catalyst support for the reason that CeO$_2$ is having many beneficial properties in catalysis, such as improving the dispersion of surface metals, and store and release oxygen. The later property is expected to help minimizing the pyrophorocity of the metal supported on CeO$_2$ [14] the two unique features which are responsible for making CeO$_2$ a talented substance for exercise either as a support or as an active catalyst are (a) the Ce$^{3+}$/Ce$^{4+}$ redox couple, with its ability to shift between CeO$_2$ and Ce$_2$O$_3$ under oxidizing and reducing environments, respectively, and (b) the ease of formation of labile oxygen vacancies [15]. However, the oxygen storage capacity of pure ceria is inadequate for practical uses. CeO$_2$ crystallizes in the fluorite structure in which each cerium ion is coordinated to eight oxygen neighbours, making CeO$_2$ more stable and the reduction of Ce (IV) to Ce (III) is unfavourable. To tackle this problem, one of the best approaches is replacing of another metal/metal oxide into the ceria lattice thus facilitating the formation of composite oxides and replacement of cerium ions by cations of different size and/or charge modifies ionic mobility within the lattice ensuing in the formation of a defective fluorite structured solid solution. Such modifications in the structure of ceria impart new properties to the catalysts, such as density, ionic conductivity and lattice parameters, improved thermal stability, high catalytic activity [16-18]. Supported metals are used in large scale in heterogeneous catalysis. The role of the support is to disperse the metal particles and preserve them from sintering. The supports widely used are SiO$_2$, Al$_2$O$_3$, TiO$_2$, Nb$_2$O$_5$, CeO$_2$ and ZrO$_2$. In addition to the dispersion of the metallic components the support can influence the electronic and catalytic properties of the supported metal particles by electron transfer or chemical bond formation. Metal support interactions have been extensively studied by using chemisorptions techniques after the discovery of the strong metal support
interaction (SMSI) effect by Tauster et al. The occurrence of SMSI has been well established for reducible support such as TiO$_2$ and Nb$_2$O$_5$ using chemisorption of hydrogen and carbon monoxide as probe molecules. Ceria supported metals have been investigated for metal support interactions and catalytic applications [19]. Despite large number of investigations, no clear picture seems to have emerged on metal-ceria interactions.

**Material and Methods**

**Preparation of the samples**

The first step was to perform a co-precipitation of the metal oxides from metal nitrate solutions. To accomplish this, a solution containing Ce(NO$_3$)$_3$.6H$_2$O (9.314 g) and SiO(NO$_3$)$_2$ (3.6052 g) was treated with a NH$_4$OH solution at constant pH 9.0 and room temperature with constant mechanical stirring. The resulting precipitates were aged at the same temperature for 12 h, then filtered and washed until the removal of nitrate ions. The washed precipitates were dried at 100 °C and calcined under air at 500 °C for 5 h. The support prepared in this way was denoted as CS. Similarly we prepared ceria-titania (CT) using solution containing 8.6112 g Ce(NO$_3$)$_3$.6H$_2$O and 3.7276 g TiO(NO$_3$)$_2$: ceria-zirconia (CZ) by using 7.3004 g Ce(NO$_3$)$_3$.6H$_2$O and 3.915 g ZrO(NO$_3$)$_2$ and ceria-alumina (CA) by using 7.9169 g Ce(NO$_3$)$_3$.6H$_2$O and 6.8432 g Al(NO$_3$)$_3$.9H$_2$O. The normal molar ration for all solid supports was 1:1.

To prepare the catalysts Au/CS, Au/CZ, Au/CT and Au/CA, aqueous solutions of HAuCl$_4$.3H$_2$O were precipitated by adding 1 N aqueous NaOH at constant pH and temperature upon mixed metal oxides preliminary suspended in water by mechanical stirring. The resulting precipitate was aged at room temperature for 12 h, then filtered and washed carefully until complete elimination of Cl$^-$ ions as detected by using silver nitrate as precipitating agent. The sample was dried at 80 °C and then calcined at 200 °C. The samples contained Au/CS = 1.01, Au/CZ = 1.15, Au/CT = 1.79 and Au/CA = 1.34 Wt% gold, as determined by SEM EDEX using instrument SEM Hitachi- S520, Japan; Oxford Link ISIS-300 UK with instrument operated at 98 eV resolution. The results were further confirmed by fluorescence X-ray crystallography using D8 – Advance, Bruker, Germany MultiRes-Vac34 method. So it may be concluded that maximum deposition of the metal is on ceria-titania and this may be the cause of highest percentage conversion by Au/CT as shown in Table 1. The metal loading on these supports depends on the surface area of support and the available sites. Thus ceria-titania avails it better than the other supports used.

**Catalytic tests**

The reactant used for the present work was of analytical grade obtained from SD
fine chemicals. The reaction was carried out in two neck glass reactors fitted with a condenser in one neck whilst the other neck was closed by a rubber septum through which a syringe needle was passed to supply oxygen (O₂). Reactant (2 mL) was placed in the reactor without solvent, together with 50 mg of catalyst with constant stirring. Molecular oxygen was passed through syringe needle. The reaction was run for 4 h at 160-170 °C. The quantitative analysis was done by using HPLC C-R8A chromatopac shimadzu model SPD-10A with UV-Visible detector and LC 18. A Shimadzu column and methanol as eluent.

**Results and Discussion**

As a first stage of our work, we selected 1-phenylethanol as a model compound to study the activity of ceria based mixed oxide supported nano-gold catalyst for selective oxidation using molecular oxygen in solvent free conditions.

For the present work, temperature screening was done from 70 to 160 °C and no reaction was observed even up to 155 °C and therefore 160 °C is the threshold temperature for this reaction. The catalyst was recycled for many times and it was observed that there is little activity lost which was recovered by washing the catalyst with piranha solution [20]. Almost 97 % conversion is achieved by using these catalysts (Table 1) which is much better than previously reported [21-22].

![Scheme 1](image)

**Table 1.** Percentage conversion using catalyst over different supports

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time in hours</th>
<th>Percentage conversion</th>
<th>Selectivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/CS</td>
<td>4</td>
<td>92</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Au/ CT</td>
<td>4</td>
<td>97</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Au/ CZ</td>
<td>4</td>
<td>88</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Au/ CA</td>
<td>4</td>
<td>96</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

**Conclusion**

Hence it can be concluded that nano gold supported on CeO₂-M₂O₃ is a suitable, efficient, and selective catalyst for the oxidation of organic compounds in aerobic conditions. The process is heterogeneous solvent free, and catalysts can be reused without decay. Over and above we can propose that the process is environment friendly, economic and thus green.

**Acknowledgments**
We are grateful to CSIR, New Delhi, for generous financial support to accomplish this work.

References and Notes