



## Selectivity of Gold Catalysts for Selective Hydrogenation of Cinnamaldehyde

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Gold nanoparticles (AuNPs), SiO<sub>2</sub> and TiO<sub>2</sub> supported AuNPs prepared by colloid deposition method and Au/TiO<sub>2</sub> prepared by deposition-precipitation method (Au/TiO<sub>2</sub>-DP) were used for the liquid-phase selective hydrogenation of cinnamaldehyde. The catalysts were characterized by HRTEM, H<sub>2</sub>-TPR and XPS. Results showed that AuNPs, AuNPs/SiO<sub>2</sub> and AuNPs/TiO<sub>2</sub> in dried form selectively hydrogenated the C=C bond, whereas AuNPs/TiO<sub>2</sub> treated in H<sub>2</sub> and Au/TiO<sub>2</sub>-DP preferentially hydrogenated the conjugated C=O bond. From our data, high selectivity toward cinnamyl alcohol could be mainly attributed to an electron transfer from the reduced support to gold, which creates more electron-enriched gold particles, favouring C=O hydrogenation.

**Key Words:** Gold catalyst, Cinnamaldehyde, Selective hydrogenation, Cinnamyl alcohol.

### INTRODUCTION

The selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to the corresponding unsaturated alcohols, an important procedure in the synthesis of fine chemicals and pharmaceuticals, is a difficult task, since thermodynamics favours C=C hydrogenation over the conjugated C=O bond<sup>1-3</sup>. Most of the classical heterogeneous hydrogenation catalysts (Pt, Pd, Ru, Ni, *etc.*) show no or low selectivity toward C=O hydrogenation<sup>3</sup>. In recent years, it has been found that supported gold catalysts show remarkable selectivity toward unsaturated alcohols in the hydrogenation of  $\alpha,\beta$ -unsaturated compounds<sup>4-27</sup>. Many researchers have investigated the factors affecting on the selectivity of gold catalysts to unsaturated alcohols and given different opinions.

Bailie *et al.*<sup>4</sup> proposed that active and selective sites for but-2-enal hydrogenation on Au/ZnO catalysts are associated with the presence of large gold particles. Claus *et al.*<sup>5,6</sup> reported that the selectivity of Au/TiO<sub>2</sub> and Au/ZrO<sub>2</sub> to unsaturated alcohols is favoured by face gold atoms in the larger gold particles. Claus *et al.*<sup>7</sup> identified that the edges of single crystalline gold particles are active sites for C=O hydrogenation through the decoration of gold particle faces by a second metal indium. This conclusion is in contradiction to the earlier predictions. Lenz *et al.*<sup>8</sup> reported that the selectivity of iron oxides modified alumina supported gold catalysts to unsaturated alcohols is independent of the gold particle size and is related to morphological aspects of gold particles.

Chen *et al.*<sup>9,10</sup> found a correlation between the gold states (Au<sup>3+</sup>/Au<sup>0</sup>) of Mg<sub>x</sub>AlO hydrotalcite supported gold catalysts and the catalytic performance. The activity and selectivity to unsaturated alcohols increase with increasing the Au<sup>3+</sup>/Au<sup>0</sup> ratio of the catalysts.

Some have proposed that the selectivity of gold catalysts towards unsaturated alcohols is strongly influenced by the nature of the support. Reducible oxides (TiO<sub>2</sub>, ZrO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, *etc.*) supported gold catalysts selectively hydrogenate the C=O bond, while inert oxides (such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) supported gold catalysts show no or low selectivity toward C=O hydrogenation<sup>11-16</sup>. For example, Bailie and Hutchings<sup>11</sup> found that the selectivity toward crotyl alcohol in crotonaldehyde hydrogenation is greater than 50 % over Au/ZrO<sub>2</sub> and Au/ZnO, whereas it is zero over Au/SiO<sub>2</sub>. Milone *et al.*<sup>14,15</sup> reported that the activity and selectivity of FeOOH,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> supported gold to unsaturated alcohols increase with increasing the reducibility of the support in the hydrogenation of benzalacetone and cinnamaldehyde. They argued that active and selective sites are formed by electron-enriched gold particles formed through an electron transfer from the reduced support to gold. Claus *et al.*<sup>12</sup> reported that the presence of electron-enriched gold particles favours C=O adsorption in the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes.

The understanding of the main factors affecting on the selectivity of gold catalysts is necessary for development of tailor-made gold catalysts for the hydrogenation of  $\alpha,\beta$ -

unsaturated compounds. The aim of the present work is to gain a deeper insight into the role of the support in the selectivity of gold catalysts in cinnamaldehyde hydrogenation, an important reaction in the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes, by investigating the performances of Au nanoparticles (AuNPs), SiO<sub>2</sub> and TiO<sub>2</sub> supported AuNPs prepared by colloid deposition method and Au/TiO<sub>2</sub> catalyst prepared by deposition-precipitation method. Combined with the results of characterization and activity/selectivity, the origin of the selectivity of gold catalysts to cinnamyl alcohol was proposed.

## EXPERIMENTAL

**Catalyst preparation:** Gold nanoparticles were prepared by the reduction of AuCl<sub>4</sub><sup>1-</sup> ions using KBH<sub>4</sub> (molar KBH<sub>4</sub>/Au = 3:1) in water-isopropanol solutions containing a certain amount of PVP (molar PVP/Au = 20:1) at 30 °C under vigorous stirring. After 1 h, a brown solution was obtained, indicating the formation of gold colloid<sup>28</sup>.

Supported AuNPs were prepared by colloid deposition method as follows: adding a desirable amount of SiO<sub>2</sub> (Qingdao Haiyang Chem, 400 m<sup>2</sup> g<sup>-1</sup>) or TiO<sub>2</sub> (prepared as in Ref.<sup>23</sup>, 60 m<sup>2</sup> g<sup>-1</sup>) to the colloidal gold solution under stirring until total adsorption (2 wt. % Au) occurred, indicated by decoloration of the solution. The solids were separated, washed with deionized water and dried in air at 100 °C for 2 h. The as-prepared catalysts were named as AuNPs/SiO<sub>2</sub>/dried and AuNPs/TiO<sub>2</sub>/dried. A part of the two samples were then treated in hydrogen flow at 200 °C for 3 h and named as AuNPs/SiO<sub>2</sub>/reduced and AuNPs/TiO<sub>2</sub>/reduced.

Au/TiO<sub>2</sub>-DP catalyst was prepared by deposition-precipitation method as in Ref.<sup>29</sup>. The gold content was measured by an Elan DRC-e ICP-MS instrument of PE Inc. USA.

**Catalyst characterization:** High-resolution transmission electron microscopy (HRTEM) analysis was performed on a Tecnai G2 F30 S-Twin equipment. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) of the catalyst was carried out in a FINESORB-3010 chemical adsorption instrument, heating the sample (0.1 g) from room temperature to 700 °C at a rate of 10 °C min<sup>-1</sup> under 20 H<sub>2</sub>/Ar (vol %) at a flow rate of 40 mL min<sup>-1</sup>. The effluent hydrogen concentration was detected with a thermal conductivity detector (TCD). X-Ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos AXIS Ultra DLD instrument equipped with a monochromatic AlK<sub>α</sub> X-ray excitation source (1486.6 eV).

**Catalytic activity test:** The liquid phase selective hydrogenation of cinnamaldehyde was carried out in a 100 mL stainless

steel autoclave equipped with magnetic stirring at 100 °C and 2.0 MPa H<sub>2</sub>. The following conditions were applied over all the supported gold catalysts: cinnamaldehyde 2.5 mL, isopropanol 50 mL, catalyst 0.5 g. Over AuNPs, the reaction was carried out in 50 mL isopropanol using 0.5 mL cinnamaldehyde and 0.125 mmol catalyst (molar cinnamaldehyde/Au = 30). The reaction products were analyzed using a gas chromatograph equipped with a HP-5 capillary column and a flame ionization detector.

## RESULTS AND DISCUSSION

The results of cinnamaldehyde hydrogenation over different gold catalysts are listed in Table-1. The catalytic activity is expressed as the initial rate of cinnamaldehyde hydrogenation per gram of gold. It can be seen that the activity of the gold catalysts investigated was affected by the support and the preparation method, following the order: AuNPs < AuNPs/SiO<sub>2</sub>/reduced < AuNPs/SiO<sub>2</sub>/dried < AuNPs/TiO<sub>2</sub>/dried < Au/TiO<sub>2</sub>-DP < AuNPs/TiO<sub>2</sub>/reduced.

Table-1 showed that the gold catalysts investigated showed remarkably different selectivity. Unsupported and inert SiO<sub>2</sub> supported AuNPs in dried form as well as in reduced form showed high selectivity toward hydrocinnamaldehyde (HCAL), the product of C=C hydrogenation in cinnamaldehyde, with lower than 7 % selectivity toward cinnamyl alcohol (COL), the product of C=O hydrogenation. This result is in agreement with that reported by Xu *et al.*<sup>30</sup> in which SiO<sub>2</sub> supported gold nanoparticles prepared by colloid deposition method show high selectivity to C=C hydrogenation in cinnamaldehyde. It is worth noting that TiO<sub>2</sub> supported AuNPs showed a significant difference in selectivity before and after being treated in H<sub>2</sub> at 200 °C for 3 h. AuNPs/TiO<sub>2</sub>/dried showed higher preference for C=C hydrogenation over C=O, similar to the unsupported and SiO<sub>2</sub> supported AuNPs. However, AuNPs/TiO<sub>2</sub>/reduced preferentially hydrogenated the C=O bond, similar to Au/TiO<sub>2</sub>-DP. These results suggest that TiO<sub>2</sub> by itself is not sufficient to enhance C=O hydrogenation with respect to the C=C bond in cinnamaldehyde hydrogenation and the catalytic behaviour arises from a synergetic effect between gold and TiO<sub>2</sub>.

Fig. 1 shows the TEM and STEM images of the catalysts. The average particle sizes of gold are listed in Table-2. Different particle sizes were obtained on the samples. For AuNPs [Fig. 1(a)], gold particles with an average size of 10.6 nm were observed. After being supported on SiO<sub>2</sub>, the average size grew to ca. 16 nm [Fig. 1(b)], significantly larger than the as-prepared

TABLE-1  
CINNAMALDEHYDE HYDROGENATION OVER DIFFERENT GOLD CATALYSTS<sup>a</sup>

| Catalyst                        | Au<br>(wt %) | Activity <sup>c</sup><br>(mmol g <sub>gold</sub> <sup>-1</sup> min <sup>-1</sup> ) | Conversion<br>(%) | Selectivity (%) |      |      |
|---------------------------------|--------------|------------------------------------------------------------------------------------|-------------------|-----------------|------|------|
|                                 |              |                                                                                    |                   | HCAL            | HCOL | COL  |
| AuNPs <sup>b</sup>              | 100          | 0.526                                                                              | 98.8              | 63.8            | 0.4  | 1.6  |
| AuNPs/SiO <sub>2</sub> /dried   | 2.0          | 0.960                                                                              | 14.5              | 42.2            | 12.4 | 6.4  |
| AuNPs/SiO <sub>2</sub> /reduced | 2.0          | 0.715                                                                              | 10.8              | 53.8            | 0    | 6.2  |
| AuNPs/TiO <sub>2</sub> /dried   | 2.0          | 3.455                                                                              | 52.2              | 43.3            | 6.9  | 24.9 |
| AuNPs/TiO <sub>2</sub> /reduced | 2.0          | 4.077                                                                              | 61.6              | 21.4            | 6.7  | 49.3 |
| Au/TiO <sub>2</sub> -DP         | 1.9          | 3.741                                                                              | 53.7              | 23.0            | 13.3 | 48.7 |

HCAL, hydrocinnamaldehyde; HCOL, hydrocinnamyl alcohol; COL, cinnamyl alcohol. <sup>a</sup>Unless otherwise specified, the reaction was carried out in 50 mL isopropanol using 2.5 mL cinnamaldehyde and 0.5 g catalyst under 2.0 MPa H<sub>2</sub> and 100 °C for 5 h. <sup>b</sup>The reaction was carried out in 50 mL isopropanol using 0.5 mL cinnamaldehyde and 0.125 mmol catalyst (molar cinnamaldehyde/Au = 30) under 2.0 MPa H<sub>2</sub> and 100 °C for 5 h. <sup>c</sup>The average rate for 5 h of reaction time.

AuNPs in solution, indicating an agglomeration of gold particles during immobilization. Whereas TiO<sub>2</sub> supported AuNPs catalyst [Fig. 1(c)] showed smaller gold particles than unsupported AuNPs. The smallest value of gold particles was found for Au/TiO<sub>2</sub>-DP [Fig. 1(d)], with an average particle size of 3.9 nm. Combined with the results of cinnamaldehyde hydrogenation (Table-1), it can be seen that small gold particle size favours the activity of the gold catalysts for cinnamaldehyde hydrogenation, whereas the selectivity of the gold catalysts toward cinnamyl alcohol is not mainly dependent on the gold particle size.

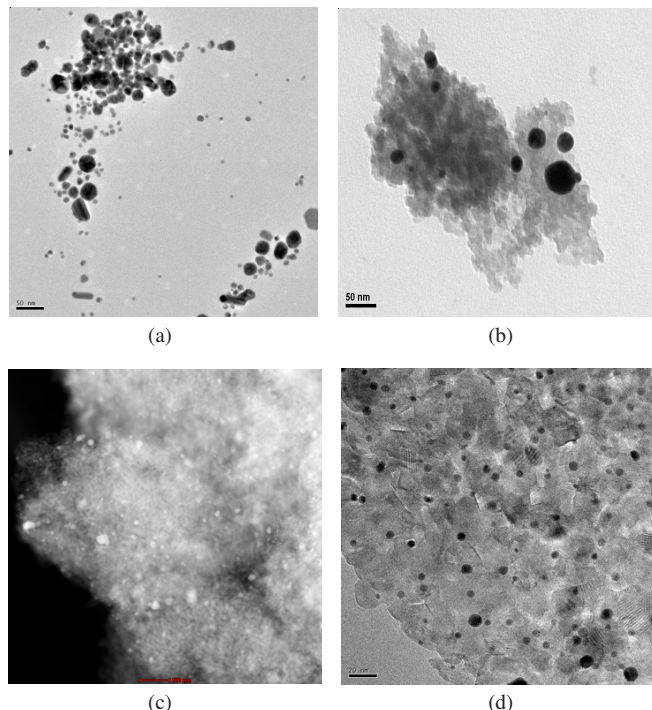


Fig. 1. TEM and STEM images of gold catalysts: (a) AuNPs; (b) AuNPs/SiO<sub>2</sub>/dried; (c) AuNPs/TiO<sub>2</sub>/dried; (d) Au/TiO<sub>2</sub>-DP

TABLE-2  
TEM AND XPS RESULTS OF THE GOLD CATALYSTS

| Catalyst                        | d (nm)<br>TEM | BE (eV) Au<br>4f <sub>7/2</sub> | BE (eV) Au<br>4f <sub>5/2</sub> |
|---------------------------------|---------------|---------------------------------|---------------------------------|
| AuNPs                           | 10.6          | 83.8 (69 %)<br>85.1 (31 %)      | 87.4 (69 %)<br>88.6 (31 %)      |
| AuNPs/SiO <sub>2</sub> /dried   | 16.1          | —                               | —                               |
| AuNPs/TiO <sub>2</sub> /dried   | 8.0           | 83.2 (100 %)                    | 86.8 (100 %)                    |
| AuNPs/TiO <sub>2</sub> /reduced | —             | 83.0 (100 %)                    | 86.6 (100 %)                    |
| Au/TiO <sub>2</sub> -DP         | 3.9           | 82.8 (100 %)                    | 86.2 (100 %)                    |

Fig. 2 shows the TPR profile of Au/TiO<sub>2</sub>-DP catalyst before reduced in H<sub>2</sub>. The profile showed two overlapping reduction peaks at higher temperature (500–600 °C), which was assigned to the partial reduction of TiO<sub>2</sub> to TiO<sub>2-x</sub><sup>31</sup>. Generally, TiO<sub>2</sub> is difficult to be reduced. It has been reported that the reduction temperature of TiO<sub>2</sub> in H<sub>2</sub> is at 1300 °C<sup>32</sup>. Our result indicates that the presence of gold enhances the reducibility of Ti<sup>4+</sup> species, which is in accordance with the literature<sup>31</sup>.

Fig. 3 shows the XPS spectra of Au 4f in AuNPs, AuNPs/TiO<sub>2</sub>/dried, AuNPs/TiO<sub>2</sub>/reduced and Au/TiO<sub>2</sub>-DP. The corresponding XPS data are summarized in Table-2. XPS data for AuNPs revealed the presence of two different gold species,

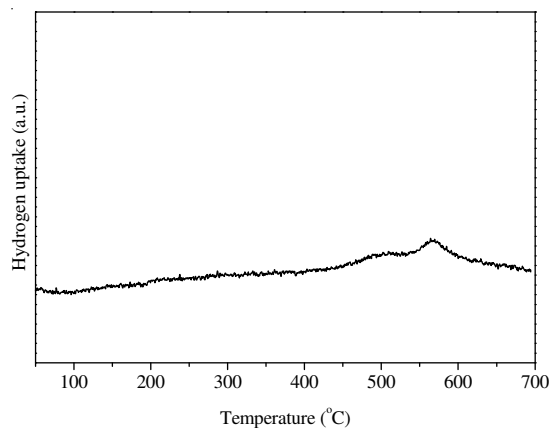


Fig. 2. TPR profile of Au/TiO<sub>2</sub>-DP catalyst before reduction

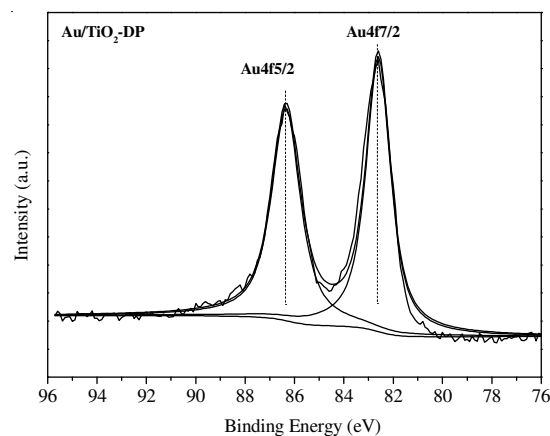
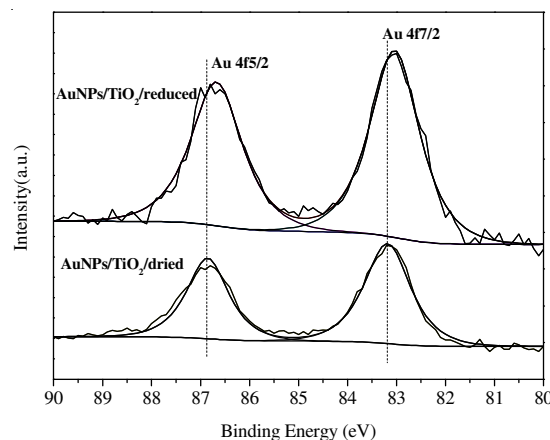
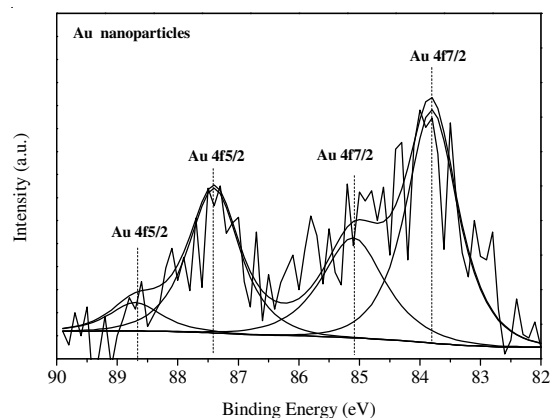


Fig. 3. XPS spectra of Au 4f in AuNPs, AuNPs/TiO<sub>2</sub>/dried, AuNPs/TiO<sub>2</sub>/reduced and Au/TiO<sub>2</sub>-DP

Au<sup>0</sup> (83.8 and 87.4 eV) and Au<sup>δ+</sup> (85.1 and 88.6 eV)<sup>33</sup>. Whereas for AuNPs/TiO<sub>2</sub>/dried, AuNPs/TiO<sub>2</sub>/reduced and Au/TiO<sub>2</sub>-DP, only the Au 4f peaks assigned to metallic Au were detected. Compared with the Au 4f binding energies (BEs) for AuNPs, the three TiO<sub>2</sub> supported gold catalysts showed lower BEs corresponding to Au<sup>0</sup>. It should be noted that the treatment of AuNPs/TiO<sub>2</sub>/dried sample in H<sub>2</sub> (*i.e.* AuNPs/TiO<sub>2</sub>/reduced) led to a significantly negative BEs shift of the Au 4f peaks. Au/TiO<sub>2</sub>-DP showed the most negative shift compared with AuNPs (1.0 eV for Au 4f<sub>7/2</sub> and 1.2 eV for Au 4f<sub>5/2</sub>). The negative shift of Au 4f is due to an electron transfer from the reduced support to gold, which lead to the increase in the electron density on gold and can create more electron-enriched gold particles<sup>5</sup>. Combined with the catalytic test results as shown in Table-1, it can be proposed that the high selectivity of AuNPs/TiO<sub>2</sub>/reduced and Au/TiO<sub>2</sub>-DP toward cinnamyl alcohol is mainly attributed to the electron transfer from the reduced support to gold. This is in agreement with the results reported by Milone *et al.*<sup>14,15</sup> in studying the hydrogenation of benzalacetone and cinnamaldehyde over iron oxides supported gold catalysts.

## Conclusion

Our data showed that the selectivity of gold catalysts is little dependent on the gold particle size, but is strongly affected by the nature of the support in the liquid phase selective hydrogenation of cinnamaldehyde. Unsupported and inert SiO<sub>2</sub> supported AuNPs as well as AuNPs/TiO<sub>2</sub>/dried selectively hydrogenated the C=C bond. Whereas AuNPs/TiO<sub>2</sub>/reduced and Au/TiO<sub>2</sub>-DP exhibited good selectivity toward C=O hydrogenation. Characterization results indicated an electron transfer from the reduced TiO<sub>2</sub> support to gold, which may be the major factor for the enhanced selectivity toward cinnamyl alcohol.

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