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### Ir Promotion of TiO<sub>2</sub> Supported Au Catalysts for Selective

### Hydrogenation of Cinnamaldehyde

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**Abstract**: We synthesized Ir-on-Au (Au-Ir) nanoparticles (NPs) using 8-9 nm Au NPs, which had a partial coverage of Ir. Both the studied systems allowed to obtain cinnamyl alcohol with high selectivities (>83%). However, Au-Ir/TiO<sub>2</sub> delivered a hydrogenation rate 5 times higher than that of Au/TiO<sub>2</sub>. The deposition of Ir onto the surface of Au and the presence of surface Au-Ir alloy was confirmed by UV-vis and HRTEM respectively. Moreover, XPS binding energy shifted strongly implying the fact of that the electron transfer from Ir to Au, which was believed to be responsible for the enhanced H<sub>2</sub> activation capacity of Au.

Keywords: bimetallic catalysts, Ir, Au, Surface alloy, Selective hydrogenation.

#### 1. Introduction:

Selective hydrogenation of α,β-unsaturated aldehydes into their corresponding unsaturated alcohols (UA) is not only of commercial interest in the production of fine chemicals, but also of special scientific interest [1]. Thermodynamics and kinetics both favor the hydrogenation of the C=C bond over the C=O bond on conventional hydrogenation catalysts that are based on Pt, Ru, Pd or Ni [2]. Catalysis by Au supported catalysts has shown a remarkable higher selectivity towards the hydrogenation of the conjugated C=O groups in unsaturated aldehydes hydrogenation compared with the conventional catalysts mentioned above [3]. However, Au is usually much less practical in catalytic applications than platinum-group metals due to the "intrinsic" nobleness of Au for H<sub>2</sub> activation [4].

Great efforts have been made to elevate the catalytic activity of Au, such as carrying a more active metal on Au-based catalysts. Such modified catalysts may show unexpected catalytic features [5]. For example, Xu showed that the activity of Au/SiO<sub>2</sub> was enhanced remarkably (1-2 orders of magnitude higher) after it was impregnated with a small amount of Pt [6]. However, the selective propensity of Au NPs favors the hydrogenation of the C=C with respect to the C=O bond (21% selectivity towards the hydrogenation of the C=O bond for cinnamaldehyde). Catalytic activity may also be enhanced by reducing the particle size of Au NPs. It was found that the hydrogenation turnover frequency (TOF) over Au/TiO<sub>2</sub> was significantly increased when Au particle size decreased from 8.7 to 1.7 nm [7]. The higher TOF exhibited by smaller Au particles may be associated with an increased capacity to activate or dissociate hydrogen [8]. However, the selectivity towards UA may increase as the Au particle size increases. This effect was demonstrated by the calcination of 5 wt% Au/ZnO between 250-400 °C in which the crotyl alcohol selectivity increased dramatically (from 54% to 81%) with an increase in Au particle size [9].

Therefore, carrying a more active metal on Au-base catalyst is more desired to improve the total activity of the catalyst, while keeping the high selectivity unchanged.

With the goal to enhance the catalytic activity of Au, we proposed Ir as a promoter, as the formed Au-Ir surface alloy can dissociate molecular hydrogen more readily than noble metals [10]. In the present work, TiO<sub>2</sub>-supported Au-Ir catalysts were prepared by the deposition-precipitation (DP) method with the loading of Au and Ir to be 1.75 wt% and 0.25 wt% respectively. We examined the catalytic performance of Ir promoted Au/TiO<sub>2</sub> in the selective reduction of cinnamaldehyde (CALD) to cinnamyl alcohol (COL). In-depth characterization of their structural and electronic properties by TEM, XPS and UV-vis techniques aimed at disclosing the nature of the active sites controlling the hydrogenation rate of CALD.

#### 2. Experimental Section:

#### 2.1 Catalyst preparation

All chemicals used in this experiment were analytical grade and were used without further purification. Au/TiO<sub>2</sub> (2 wt.% Au) catalysts were prepared by the DP method using ammonia. The advantage of using ammonia was to control the pH more easily and to avoid the formation of residues produced from other bases [11] and it has been successfully applied in obtaining Au supported catalysts with small particle size in a recent study [12]. TiO<sub>2</sub> (Degussa, P25, specific surface area of 50 m<sup>2</sup> g<sup>-1</sup>, 80% anatase and 20% rutile) was added to the aqueous solution of HAuCl<sub>4</sub> (0.05 g<sub>metal</sub>/mL) at a fixed pH (8.0) adjusted by ammonia (4.98 N solution). Subsequently, the samples were filtered, washed by distilled water, then dried and calcined at 400 °C for 4 h. Finally, they were reduced in H<sub>2</sub> stream at 400 °C for 4 h.

The Ir promoted Au/TiO<sub>2</sub> catalysts (0.25 wt.% Ir) were also prepared by DP with ammonia. The calcined Au/TiO<sub>2</sub> (1.75 wt.% Au) was added to the aqueous solution containing HIrCl<sub>4</sub> (0.035  $g_{metal}$ /mL)

and ammonia. The suspension was maintained at 80 °C and vigorously stirred for 12 h. Subsequently, the samples were filtered, washed and dried before being calcined at 400 °C for 4 h. Au-Ir/TiO<sub>2</sub> catalysts were finally produced by being reduced in  $H_2$  stream at 400 °C for 4 h. The same procedures were used to prepare Ir/TiO<sub>2</sub> (2 wt.% Ir) catalysts.

#### 2.2 Catalyst characterization

The microstructure and components of the NPs were examined by TEM (Philips-FEI Tecnai G2 F30 S-Twin). XPS analysis was performed by Kratos AXIS Ultra DLD spectrometer with monochromatized aluminum X-ray source (1486.6 eV) and the pass energy of 40 eV. The pressure in the sample analysis chamber was lower than  $6 \times 10^{-9}$  Torr during data acquisition. The C1s peak at 284.8 eV arising from adventitious carbon was taken as references for correcting surface-charging effects. This reference gives binding energy values with a precision of  $\pm 0.02$  eV. The Au and Ir loading of the catalysts were measured by ICP-MS (Thermo Electron IRIS Intrepid II XSP spectrometer). Diffuse reflectance UV-vis spectra of the solids diluted in BaSO<sub>4</sub> were recorded on a Shimadzu UV 2450 Spectrometer equipped with an integrating sphere and BaSO<sub>4</sub> was used as the reference.

#### 2.3 Typical procedure for the hydrogenation of CALD

Hydrogenation reactions were performed in a high-pressure batch reactor equipped with a Parr 4871 controller and a 50-mL Hastelloy autoclave. Unless otherwise specified, the autoclave was loaded with 20 mL of 2-propanol/H<sub>2</sub>O (4/1 volume ratio), 0.3 g of CALD, and 0.15 g of catalyst. The reactions proceeded at the required experimental conditions (see Table 1) after the autoclaves were purged by hydrogen to remove the air. Only CALD, hydrocinnamaldehyde (HCAL), hydrocinnamyl alcohol (HCOL) and COL were detected as the reaction products and were quantified by using n-heptane as the internal

#### standard substance, and the carbon balance values of 100%. The conversion and selectivities were

calculated using the following formulas:

$$Conversion_{CALD} = \left(1 - \frac{m_{CALD}\%}{m_{CALD}\% + m_{HCAL}\% + m_{COL}\% + m_{HCOL}\%}\right) \times 100\%$$
(1)  
Selectivity\_{COL} = 
$$\frac{m_{COL}\%}{m_{COL}\% + m_{HCAL}\% + m_{HCOL}\%} \times 100\%$$
(2)

Selectivity<sub>HCAL</sub> = 
$$\frac{m_{HCAL}\%}{m_{COL}\% + m_{HCAL}\% + m_{HCOL}\%} \times 100\%$$
 (3)

Selectivity<sub>HCOL</sub> = 
$$\frac{m_{HCOL}\%}{m_{COL}\% + m_{HCAL}\% + m_{HCOL}\%} \times 100\%$$
 (4)

Reaction rate 
$$(h^{-1}) = \frac{m_{CALD}}{m_{Au+Ir}} \times \text{conversion/time (h)}$$
(5)

Where  $m_{CALD}$ ,  $m_{HCAL}$ ,  $m_{HCOL}$ , and  $m_{COL}$  represent the moles of cinnamaldehyde, hydrocinnamaldehyde, hydrocinnamyl alcohol, and cinnamyl alcohol in the mixture.  $m_{Au+Ir}$  is the moles of Au and Ir used in the reaction.

#### 3. Results and discussion

TEM images in Fig. 1a and 1d show that Au nanoparticles (NPs) for Au/TiO<sub>2</sub> and Au-Ir/TiO<sub>2</sub> were both well dispersed on the support of TiO<sub>2</sub> with an average size of about 8.7 nm (Fig. 1c) and 9.7 nm (Fig. 1f) respectively. The HRTEM images show that the lattice spacing of the Au/TiO<sub>2</sub> sample is 0.235 nm, which is the indicative of Au (111) plane (Fig. 1b). However, for the Au-Ir sample (Fig. 1e), the lattice spacing is 0.231 nm, which is between that of the Ir (111) plane (0.219 nm) and the Au (111) plane (0.235 nm), indicating the formation of the surface Au-Ir alloy. However, Ir particles were not found in the TEM image

possibly due to the low loading, or the existence of them in Au-Ir alloy species. UV-vis spectra (Fig. 2) of the Au-Ir sample confirmed the Ir deposition on Au NPs, as evidenced by the decreased Au NP surface plasmon resonances (SPR) peak intensity compared with pure Au NPs [13]. Ir content of the samples detected via ICP-MS were close to the nominal value (0.25 wt.%). Fig. 3A shows the XPS spectra of Au 4f core level of Au/TiO<sub>2</sub> and Au-Ir/TiO<sub>2</sub>. The metallic Au  $4f_{7/2}$  peak of the Au/TiO<sub>2</sub> sample appeared at the binding energy (BE) of 83.8 eV similar to the reported value [14]. For Au-Ir/TiO<sub>2</sub>, the Au 4f<sub>7/2</sub> peak was detected at a lower BE value of 83.4 eV. The Ir 4f spectra of the Au-Ir/TiO<sub>2</sub> are shown in Fig. 3B. Because the Ir 4f peak was overlapped with the Ti 3s peak, and the fact that in the signal of Ir 4f for the catalyst with low Ir loading (0.25 wt.%) is quite weak even through the prolonged accumulating time, a precise deconvolution of the Ir 4f orbit from those spectra is difficult. Therefore, the Ir  $4f_{7/2}$  signal is not deconvoluted into the two spin orbit components doublet, but is deconvoluted into  $Ir^0$  and  $Ir^{\delta^+}$  peaks. This deconvoluted method has been adopted by W. Lin et al. in 2013 [15]. It was found that the peak corresponds to Ir<sup>0</sup> 4f<sub>7/2</sub> was at 61.4 eV, 0.5 eV higher than the standard BE of 60.9 eV [16]. This suggests the electron transfer from Ir to Au atoms, confirming that the electronic structure of the surface Au atoms was modified upon the addition of Ir. Likewise, a few of previous reports on Au-Pd systems with a "crown-jewel" structure had claimed that electron transfer from Pd to Au clusters and confirmed the electronegativity of the above-mentioned Au atoms [17-18]. The full-width-half-maximum (FWHM) of the Au  $4f_{7/2}$  peak was also given in Fig. 3A. The narrow FWHM (1.05 eV) obtained for Au/TiO<sub>2</sub> catalysts revealed that there was only metallic Au existed in this sample. Nevertheless, the FWHM obtained for Au-Ir bimetallic catalyst is about 1.50 eV. Since full width at half maximum of the Au peak is large, the

presence of more than one Au species is expected, indicating that Au-Ir alloy are probably formed on the surface of bulk Au NPs.

The experimental results for the hydrogenation of CALD over each catalyst were summarized in Table 1. We can see that the major product over both Au/TiO<sub>2</sub> and Au-Ir/TiO<sub>2</sub> catalysts was COL, produced via C=O bond hydrogenation with > 83% selectivity. For the Ir/TiO<sub>2</sub> catalyst, however, the selectivity of COL was only 55.68%. Although Au/TiO<sub>2</sub> showed a quite high selectivity (83.81%) towards the COL, only 8.6% conversion was obtained after reacting for 4 h, implying low activity of Au in the hydrogenation process. In comparison, the conversion of CALD reached 12% over Au-Ir/TiO<sub>2</sub> catalyst after reacting for 1 h, and the reaction rate of Au-Ir/TiO<sub>2</sub> catalyst (17.7 h<sup>-1</sup>) was 5-fold higher than that of Au/TiO<sub>2</sub> catalyst (3.2 h<sup>-1</sup>). Thus, a small amount of Ir (0.25 wt.%) could enhance the activity of Au/TiO<sub>2</sub> catalyst remarkably.

The course of the hydrogenation of CALD over Au-Ir/TiO<sub>2</sub> is shown in Fig. 4a. The amount of COL increased with the reaction time during the hydrogenation of CALD over Au-Ir/TiO<sub>2</sub>, while the amount of HCAL increased to a maximum before decreasing. The completely reduced product of HCOL increased gradually. The conversion of CALD and the selectivities of products are shown in Fig. 4b. The selectivity of HCAL decreased whereas that of HCOL increased with the conversion. But the selectivity of COL was maintained at about 75% before the complete conversion of CALD. Evidently, Au-Ir/TiO<sub>2</sub> as a stable catalyst can deliver high selectivity at good conversion.

As mentioned previously, the activity of the Au-Ir/TiO<sub>2</sub> was 5 times higher than that of Au/TiO<sub>2</sub> catalyst. Therefore, an interpretation is needed to illustrate such catalytic behaviors. In fact, Au is not miscible with Ir; however, Au-Ir can form near-surface alloys and has shown promising results for

hydrogen-related applications [10]. Some near-surface alloys bind atomic hydrogen as weakly as the noble metals while retaining an ability to dissociate molecular hydrogen more readily than the noble metals [19]. Interestingly, the gold films on Ir (111) were able to dissociate molecular hydrogen [20]. The formed hydrogen atoms on Au/Ir (111) recombinatively can desorbe at low temperatures (< 400 K), suggesting that hydrogenation chemistry can be catalyzed by Au/Ir bimetallic nanoclusters/surfaces [20]. Moreover, the dissociative adsorption behavior of hydrogen on the surface of Au-Ir can be explained by changes in the surface electronic structure. The XPS results in the current work indicated that the electronic structure of the surface Au atoms was modified upon the addition of Ir. Therefore, it is evident that the significant improvement of the catalytic activity of Au-Ir/TiO<sub>2</sub> catalyst was highly related to the strong interaction between Au and Ir atoms which enhanced the electron density at the surface of Au. Indeed, the presence of Au<sup>6-</sup> species for Au catalysts may enable Au NPs to function as better hydrogenation catalysts than Au<sup>0</sup> has been reported before [21-23]. A more recent study using Au catalysts also claimed that the presence of charged negatively gold species formed at the surface of Au NPs improve the H<sub>2</sub> activation [24]. Thus, the formation of the charged negatively gold species might be one of the key factors for improving the catalytic activity of Au-Ir catalysts.

As for the high selectivity of Au-Ir/TiO<sub>2</sub> to COL, the key factor would be the electronic property of the Au<sup>0</sup> species, which might alter the interaction with carbonyl carbon. The XPS results clearly showed that the binding energy of the Au<sup>0</sup> and Ir<sup>0</sup> species shifted to lower and higher values respectively, suggesting a charge transfer from Ir to Au. This enhanced electron density over the Au<sup>0</sup> species is believed to be beneficial for the selectivity to COL, since it would lead to a lower binding energy of the C=O bond with respect to the C=C bond, favoring the hydrogenation of the C=O bond [25]. More specifically, it was found

that the preferential binding between the labile electrophilic carbon in the carbonyl group and negatively charged gold species would favor a high selectivity to unsaturated alcohols [22]. Moreover, the electropositive Ir atoms may act as electrophilic or Lewis acid sites for the adsorption and activation of the C=O bond. This effect, referred to as the "electrophilic C=O activation", was the most frequently invoked to account for the promoting effect of electropositive species [26]. Based on the above results, we propose a hypothesis for the selective hydrogenation of cinnamaldehyde over Au-Ir/TiO<sub>2</sub> catalyst in Fig. 5. The charge-deficient carbonyl carbon is believed to be adsorbed on the negatively charged gold species, and meanwhile, the charge-rich carbonyl oxygen is adsorbed on the electropositive Ir atoms. In this way, the C=O bond will be preferentially hydrogenated over the C=C bond, leading to the high selectivity of Au-Ir/TiO<sub>2</sub> to COL. In addition, according to the adsorption model of CALD, the C=C bond and the C=O bond are more likely to be adsorbed simultaneously on the small Au particles compared to the large Au particles. On large metal particles, the adsorption of the C=C group is hindered by a steric repulsion thus favoring hydrogenation of the C=O group [27]. In our work, the size of Au NPs as estimated by TEM increased from 8.7 nm to 9.7 nm when a small amount of Ir was added, which is probably also a reason for the observed high selectivity to COL.

#### 4. Conclusions

Both Au/TiO<sub>2</sub> and Au-Ir/TiO<sub>2</sub> were found to be able to catalyze the hydrogenation of cinnamaldehyde to cinnamyl alcohol with highly selectivities (> 83%). However, the specific hydrogenation rate of Au-Ir/TiO<sub>2</sub> was 5 times higher than that of Au/TiO<sub>2</sub>. The high activity of Au-Ir/TiO<sub>2</sub> catalyst might be attributed to the promoted H2 activation capacity of Au as a result of the strong interaction between Au and Ir in surface Au-Ir alloy and the electron transfer from Ir to Au. The high

selectivity to UA could be mainly ascribed to the enhanced interaction between the charge-enriched Au sites and the charge-deficient carbonyl carbon and the interaction between electropositive Ir atoms and electrophilic carbonyl oxygen.

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#### List of Table captions

Table 1 Catalytic results of the hydrogenation of cinnamaldehyde.

#### List of Figure captions

Fig.1 TEM images of Au/TiO<sub>2</sub> (a) and Au-Ir/TiO<sub>2</sub> (d); HRTEM images of Au/TiO<sub>2</sub> (b) and Au-Ir/TiO<sub>2</sub> (e) and

particle size distributions of  $Au/TiO_2$  (c) and  $Au-Ir/TiO_2$  (f).

Fig. 2 UV-vis diffuse reflectance spectra of (a) Au/TiO<sub>2</sub> and (b) Au-Ir/TiO<sub>2</sub>.

Fig. 3 (A) Au 4f XPS spectra of (a) Au/TiO<sub>2</sub> and (b) Au-Ir/TiO<sub>2</sub> catalysts; (B) Ir 4f XPS spectra of Au-Ir/TiO<sub>2</sub>

catalysts.

Fig. 4 Courses of the hydrogenation of CALD over Au-Ir/TiO<sub>2</sub> (a) and selectivity of products (b).

Fig. 5 Proposed adsorption model of cinnamaldehyde on Au-Ir/TiO<sub>2</sub> catalysts.

Catalyst	Time (h)	Conv.(%)	COL	Sel. (%) HCAL	HCOL	Reaction rate (h <sup>-1</sup> ) <sup>b</sup>
Au/TiO <sub>2</sub>	4	8.6	83.8	12.4	3.8	3.2
Au-Ir/TiO <sub>2</sub>	1	12.0	83.4	11.2	5.4	17.7
Ir/TiO <sub>2</sub>	1	10.9	55.6	38.0	6.4	15.9

#### Table 1

Catalytic results of the hydrogenation of cinnamaldehyde <sup>a</sup>.

 $^{\rm a}$  Reaction conditions: 0.3 g CALD, 150 mg catalyst, 20 ml 2-propanol/H2O as solvent,

100 °C, 2 MPa P<sub>H2</sub>.

<sup>b</sup> Reaction rate was calculated by the moles of CALD converted per mol Au and Ir per hour with TiO<sub>2</sub>-supported Au, Ir, and Au-Ir catalysts.



Fig.1









Fig.5



Research Highlights:

- ► Au-Ir NPs were prepared on TiO<sub>2</sub> support;
- ► Catalysts with Au-Ir/TiO<sub>2</sub> gave excellent activity toward cinnamaldehyde selective

hydrogenation;

▶ The enhanced catalytic activity may attribute to the improved H<sub>2</sub> activation capacity by

surface Au-Ir alloy.

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