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Gold-iridium catalysts for the hydrogenation of biomass derived products

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ABSTRACT

Au-Ir and Au-Ru on TiO₂ catalysts prepared by sequential deposition-precipitation technique were compared with the corresponding monometallics in the hydrogenation of levulinic acid to γ -valerolactone. Interestingly the addition of Au to Ir/TiO₂ showed a detrimental effect on the activity of Ir monometallic catalyst whereas a positive synergistic effect was shown in the case of Ru. Both catalysts were reduced under H₂ to increase the M⁰-Au⁰ interaction. From previous DFT calculations and catalytic test, we addressed the lower activity of Au-Ir/TiO₂ than that of Ir/TiO₂ to the interference of Au into the redox mechanism of Ir atoms.

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1. Introduction

γ -Valerolactone (GVL) has been identified as a potentially sustainable platform molecule for the production of renewable fuels and fine chemicals [1–6], and its production is mainly based on the hydrogenation of levulinic acid (LA), which can be directly obtained from cellulosic materials by acidic hydrolysis [1]. A cascade reaction involving hydrogenation and dehydration steps takes place (Scheme 1) under acidic conditions in the presence of metallic catalysts. On this topic a lot of studies have been carried out [7,8] in particular on Ru [9] or Cu [10] supported on activated carbon (AC) or oxidic supports in different solvents, such as water or alcohols [4–6] and dioxane [11,12]. The addition of acidic co-catalyst, such as niobium phosphate or oxide, to Ru/AC [13] or the use of acidic carbons [14] has been shown to speed up the reaction rate under mild reaction conditions (70 °C, 0.3 MPa of H₂), keeping a selectivity >98%

towards the GVL product. This result has been attributed to the promotional effect of the acidic sites on the dehydration step (Scheme 1).

The major limitation of most of the heterogeneous catalysts applied in this reaction is the low stability and in this respect the addition of Au to Ru/AC with the formation of a bimetallic phase appeared essential from both activity and durability point of view [15]. The synergistic effect between Au and Ru has been addressed to an alloyed phase due to the Au atom diffusion within the Ru particles. However, it was not possible to disentangle any electronic effects or improved metal-support interaction could not be excluded.

Ir-based catalysts have been poorly investigated in this reaction and only a few reports deals with heterogeneous systems showing that Ir/SiO₂ is poorly active and also poorly selective to GVL [16]. It became active (but not selective) only when Mo is added as modifier. Soluble Ir complexes, however,

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Scheme 1. Hydrogenation and dehydration steps of levulinic acid.

have been reported to show a good activity in levulinic hydrogenation as reported for half-sandwich [17] or pincer complexes [18]. A computational study of this latter case evidenced two possible pathways: the first where the limiting rate step is the hydride transfer to give La-H- and LIrH_2^+ , the second where a trihydride iridium complex is formed [19].

Based on this finding we thought that a reducible oxide as TiO_2 would have helped the activity of supported Ir particles as in the case of MoO_x . Therefore herein we investigate in the reduction of levulinic acid to GVL, Ir/ TiO_2 catalyst and investigated the effect of Au addition through sequential deposition-precipitation technique. We have previously fully characterized these catalysts and DFT calculations are also available providing us useful information about the interaction with the support (TiO_2) [20].

2. Experimental

Titania Evonik P25 was used as a support (45 m²/g, nonporous 70% anatase, 30% rutile, purity 99.5%). Commercial $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\text{IrCl}_4 \cdot 4\text{H}_2\text{O}$ and RuCl_3 from Aldrich were used as gold, iridium and ruthenium precursors, respectively. Before preparation, TiO_2 was dried in air at 100 °C for at least 24 h. NaBH_4 of purity >96% from Fluka was used. Gaseous hydrogen from SIAD was 99.99% pure.

2.1. Preparation of monometallic samples

The preparation of the 1 wt% Au/ TiO_2 and Ir/ TiO_2 sample was performed by deposition-precipitation with urea (DPU) in the absence of light, following a previously reported procedure [21–24].

The gold precursor HAuCl_4 or the iridium precursor IrCl_4 (4.2 mmol), and urea (0.42 mol) were dissolved in 50 mL of distilled water. Then, 1 g of titania was added to this solution. The suspension temperature was then increased to 80 °C and kept constant for 16 h under stirring. The samples were then washed with water and centrifuged four times, and dried under vacuum at 80 °C for 2 h and then calcined at 400 °C under H_2 atmosphere for 1 h. The samples were stored at room temper-

ature away from light. The metal loading of 1 wt% was obtained.

Monometallic 1% Ru/ TiO_2 has been prepared by incipient wetness impregnation. Solid RuCl_3 (equivalent to Ru 10 mg) was dissolved in water (1.5 mL) and added to 1 g of support (final ruthenium loading of 1 wt%). The catalyst was then dried at 80 °C for 2 h and reduced in H_2 at 200 °C for 2 h.

2.2. Preparation of bimetallic samples

A sequential deposition method was used to prepare the bimetallic catalyst. Iridium was first deposited on TiO_2 by deposition-precipitation with urea as described above. After drying at 80 °C for 2 h, the Ir/ TiO_2 sample was calcined in air at 500 °C for 2 h at a heating rate of 2 °C/min, before gold was deposited by deposition-precipitation. The same procedure of washing, drying and calcination as above was applied. The total loading of the metals was 1 wt% and the molar ratio Au/Ir = 1/1. Chemical analysis of Au and Ir in the samples to determine the actual loadings was performed by X-ray fluorescence (XRF) using a spectrometer XEPOS HE (AMETEK). The Au and Ir mass loadings were expressed in grams of each metal per gram of the sample (Table 1).

The Au-Ru was prepared following a sequential impregnation. A solution of NaAuCl_4 was added to 0.27 wt% Ru/ TiO_2 prepared as above reported. After 3 h the catalyst was filtered, dried and then calcined as for the monometallic sample. The total metal loading was 1 wt% and the molar ratio Au/Ru = 8/2. The metal content was checked by ICP analysis of the filtrate using a Jobin Yvon JY24 instrument. Morphology of the catalysts was characterized in a Philips CM200 FEG electron

Table 1
Theoretical and actual Au and Ir loadings in the studied catalysts.

Sample	Metal loading (wt%)			
	Nominal Au	Actual Au	Nominal Ir	Actual Ir
Au/ TiO_2	1	1.1	0	0
Ir/ TiO_2	0	0	1.0	0.96
Au-Ir/ TiO_2	0.5	0.57	0.5	0.5

microscope, operating at 200 kV and equipped with a Gatan imaging filter, GIF Tridiem.

2.3. Catalytic test

Levulinic acid (LA) hydrogenation was performed at 70 °C, using a stainless steel reactor (50 mL capacity), equipped with heater, mechanical stirrer, gas supply system and thermometer. The LA solution (30 mL; 0.3 mol/L) was added into the reactor and the desired amount of catalyst (LA/metal molar ratio = 1000) was suspended in the solution. The autoclave was then purged three times with nitrogen before charging 0.7 MPa of H₂. The mixture was heated to the reaction temperature, 70 °C, and mechanically stirred (1250 r/min).

For product analysis, the reaction mixture, after separation from the catalysts by filtration, was analyzed using high performance liquid chromatography (HPLC). Samples were removed periodically (0.5 mL) under stirring and analyzed by HPLC using a column (Alltech OA-10308, 300 mm × 7.8 mm) with UV and refractive index (RI) detection in order to analyze the product mixtures. H₃PO₄ solution (0.1 wt%) was used as the eluent. The identification of the possible products was done by comparison with the original samples.

In some cases an activation step was performed prior to the reaction and the catalyst was pre-reduced in the autoclave for 1 h at 150 °C under 0.3 MPa of H₂.

3. Results and discussion

The catalytic results of the monometallic sample are reported in Table 2. Monometallic Ir appeared very active, more than Ru. However, it presented a slight lower selectivity to GVL. The reductive pretreatment carried out in situ seems to have a beneficial effect restoring an almost full selectivity to GVL. The same pretreatment on Ru/TiO₂ showed a negligible effect, maintaining very similar activity and selectivity as without the pretreatment. Monometallic gold did not show any activity.

We already demonstrated that when depositing Au on Ru catalyst, a migration of Ru on Au occurred forming Au-core particles with enriched Ru-surface [15]. On the contrary, when depositing Au on Ir catalysts, a segregation of Ir atoms toward

the TiO₂ surface occurred. Au-Ir bimetallic particles are formed on top of Ir slags [20]. The two catalysts showed a very different catalytic behavior (Table 2). In particular the addition of Au to Ir/TiO₂ led to a drastic drop of the activity despite the small size of the metal particles (2.65 ± 1.07 nm [20]) and only 12% of levulinic acid conversion could be obtained after 6 h reaction. Pretreating the catalyst with H₂ a slight increase of the conversion was observed (38%) but still lower than the activity of Ir/TiO₂ (>99%; Table 2). The presence of bimetallic Au-Ir species, however, promoted the selective formation of GVL as shown by the increasing of selectivity (>99). On the contrary, Au-Ru/TiO₂ showed an enhancement of the activity (conversion after 3 h = 86%; Table 2) with respect to monometallic, also maintaining the full selectivity to GVL. A representative TEM image with particle distribution is reported in Figure 1.

The real presence of bimetallic particles and the presence of synergism between Au and Ir (negative effect) or Ru (positive effect) was also studied by carrying out catalytic tests in the presence of physical mixture of the two catalysts: Au/TiO₂+Ir/TiO₂ or, alternatively, Au/TiO₂+Ru/TiO₂. In the first case the conversion reflected the composition of the mixture, i.e., consistent with the reduced amount of the active metal Ir. Moreover, the selectivity is basically the same as for monometallic iridium thus supporting the idea that no bimetallic species are formed within the reaction medium. On the contrary, in the case of Au/TiO₂+Ru/TiO₂ systems the conversion appeared higher than expected on the basis of the amount of the actually present Ru metal (i.e., calculated around 50% instead of 73%, Table 2). This finding can be explained by the in situ formation of alloyed species due probably, to the detachment of Ru particles from the TiO₂ surface and the migration onto Au ones. This sort of migration, in the case of Ir, is probably neglected by the strong metal-support interaction of Ir with TiO₂ established also by DFT calculations [20].

As reported in [24,25] Au-Ir/TiO₂ showed a higher activity than monometallic ones in the case of CO oxidation as well as in the total oxidation of propene [26]. The synergistic effect was addressed to a hindered reoxidation of Ir and the establishment of Au⁰-Ir⁰ interaction. Indeed XPS spectra in bimetallic sample showed the absence of the typical contribution of Ir⁴⁺ peak due to the reoxidation of Ir⁰ exposed to air [26]. In the monometal-

Table 2

Levulinic acid hydrogenation with monometallic and bimetallic catalysts after 3 h and 6 h reaction.

Catalyst	Conversion (%)		Selectivity to GVL (%)	
	3 h	6 h	3 h	6 h
1 wt% Ir/TiO ₂	91	>99	94	97
1 wt% Ir/TiO ₂ pretreated in situ	74	>99	>99	>99
1 wt% Ru/TiO ₂	62	90	>99	>99
1 wt% Ru/TiO ₂ pretreated in situ	52	95	>99	>99
1 wt% Au/TiO ₂	—	<1	—	—
1 wt% Au-Ir/TiO ₂	4	12	>99	>99
1 wt% Au-Ir/TiO ₂ pretreated in situ	26	38	>99	>99
1 wt% Au-Ru/TiO ₂	86	>99	>99	>99
1 wt% Au-Ru/TiO ₂ pretreated in situ	70	>99	>99	>99
1 wt% Au/TiO ₂ +1 wt% Ir/TiO ₂ (1:1) *	33	48	94	98
1 wt% Au/TiO ₂ +1 wt% Ru/TiO ₂ (4:1) *	73	98	>99	>99

Reaction conditions: LA = 0.3 mol; metal/LA = 1/1000 (mol/mol), *p*(H₂) = 0.5 MPa, 70 °C.

* Physical mixture.

Fig. 1. (a) Representative TEM image and (b) particle size distribution of Au-Ru/TiO₂.

lic sample this latter peak constitutes the main one of Ir. Under reducing conditions the Au⁰–Ir⁰ interactions are obviously still present, and therefore we have to address the negative synergistic effect to the Au interference into the redox mechanism of Ir atoms. Under reducing conditions the redox cycle of the metal could be even more influenced by the difficulty of the Ir to be oxidized representing the first elemental step of the reaction (Scheme 1). Previous study on CO chemisorption followed by DRIFT spectra supported the finding that alloying gold to iridium would result in the disappearance of contiguous Ir sites [26]. We thus might conclude that the interference in the redox cycle at the base of the catalytic activity is mostly due to this isolation of Ir sites.

4. Conclusions

We have tested and compared the activity of Ir/TiO₂, Ru/TiO₂ and bimetallic catalysts Au–Ir/TiO₂ and Au–Ru/TiO₂ in the levulinic acid hydrogenation. The bimetallic catalysts were prepared following a two steps procedure. Both catalysts pre-

sented a bimetallic structure but Ir provided a stronger metal-support interaction with TiO₂ compared to Ru. This will be beneficial for the stabilization of the metals onto the support. However, in the case of iridium, the addition of gold lowered the activity of the catalyst even if it enhanced the selectivity to GVL. A possible reason of the detrimental effect of Au on Ir catalyst is the electronic interaction between the two metals, which apparently affected the redox cycle of Ir. The possible presence of isolated Ir site could be at the origin of this effect.

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Graphical Abstract

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Gold-iridium catalysts for the hydrogenation of biomass derived products

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Gold as a modifier of Ir catalyst was studied in levulinic acid hydrogenation to γ -valerolactone. Differently from the case of Ru, the bimetallic Au–Ir catalyst showed a lower activity with respect to monometallic despite a higher selectivity.

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Au-Ir催化剂用于生物质衍生物加氢

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摘要: 采用沉积-沉淀法制备了TiO₂负载的Au-Ir和Au-Ru催化剂, 用于乙酰丙酸加氢制γ-戊内酯反应, 并与相应的单金属催化剂性能进行了比较. 有趣的是, Ir/TiO₂中添加Au抑制了催化剂活性, 而添加Ru则表现出正效应的协同作用. 这两个催化剂均在H₂中还原, 使得M⁰-Au⁰间相互作用增强. 结合以前的密度泛函理论计算和催化反应结果, 我们认为, Au-Ir/TiO₂催化剂活性低于Ir/TiO₂催化剂是由于Au影响了Ir原子的氧化还原过程.

关键词: 乙酰丙酸加氢; 金-铱催化剂; 金-钌催化剂; γ-戊内酯; 协同效应

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