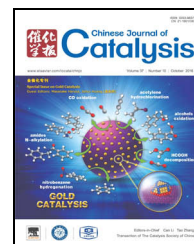


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Article (Special Issue on Gold Catalysis)

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

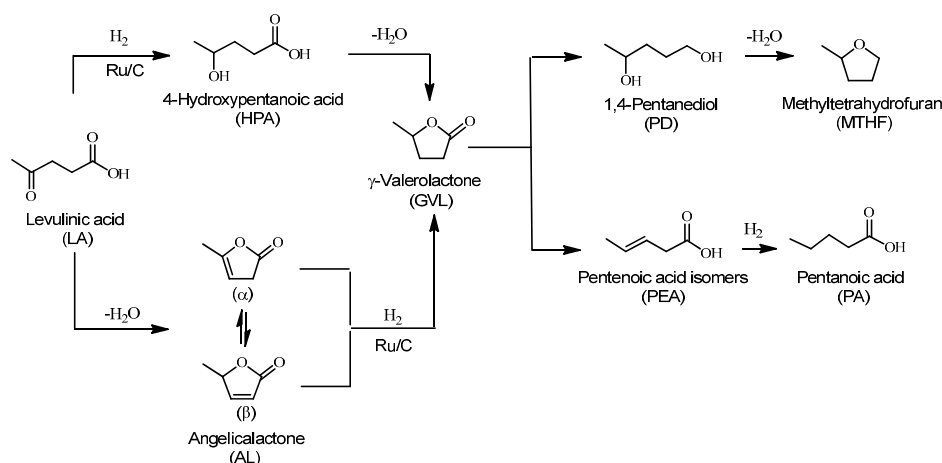
γ -Valerolactone (GVL) has been identified as a potentially sustainable platform molecule for the production of renewable fuels and fine chemicals [1–6], and its production is mainly based on the hydrogenation of levulinic acid (LA), which can be directly obtained from cellulosic materials by acidic 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 acid 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 LlrH_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 m^2/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

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