



# Oxidative esterification of renewable furfural on gold-based catalysts: Which is the best support?



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## ABSTRACT

Gold-based catalysts over different supports were investigated in the oxidative esterification of furfural by employing an efficient and sustainable process. The catalytic performances follow the trend: Zirconia–Au > Ceria–Au ≫ Titania–Au. Zirconia came out to be the best support option to promote activity, selectivity and also stability. The chemical and morphological properties observed for zirconia-supported sample seem to fulfill a good compromise between high gold dispersion and the presence of suitable acid–base properties, for good selectivity. Moreover, stability and recycling of the catalysts were also investigated.

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## 1. Introduction

With diminishing fossil resources, developing new technologies to utilize versatile and renewable biomass as the alternative feedstock of energy and chemical sources has been attracting more attention than ever. In particular, the upgrading of lignocellulosic biomass wastes into fuels and higher added-value chemicals is one of the most researched topics in the forthcoming concept of biorefinery [1].

The sustainability of bio-refineries derives from their ability of exploiting every product. Furfural (2-FA), a C5 compound, is industrially manufactured for a long time through hydrolysis of pentose which comes from agricultural raw materials including corncobs, oat, wheat bran, sawdust, etc. These materials are yearly renewable and not competitive with the food sector. Thus, exploring the products derived from furfural as the replacements of fossil resources is greatly attractive. In fact, utilization of furfural as the starting material could synthesize a variety of chemicals including more than 1600 commercial products [2].

Actually furfural has many different uses: it is considered an excellent solvent for many organic materials, and it can also be used as a feedstock to make gasoline, diesel, or jet fuel [3]. It is also a precursor to other desired compounds such as furfuryl alcohol (via hydrogenation), furan (via decarbonylation) and tetrahydrofuran

(via hydrogenation of furan). However, additional transformations of furfural are highly desired [4]. There already have been efforts to modify furfural-based derivatives by gold catalysis [5–8]. The synthesis of alkyl furoates can open very interesting perspectives for the use of xylooses because they find applications as flavor and fragrance component in the fine chemical industry.

Up to now, only a few studies have investigated the heterogeneous catalysis in oxidation of 2-FA [9,10]. Traditionally, the ester is prepared by oxidizing furfural with potassium permanganate, preferably using acetone as solvent, and reacting the furoic acid so formed with methyl or ethyl alcohol, in the presence of sulfuric acid. The use of these substances has a substantial negative impact on the environment. It has been shown [9] that furfural can be converted to methyl furoate under mild conditions by an oxidative esterification with NaCH<sub>3</sub>O and CH<sub>3</sub>OH on the Au/TiO<sub>2</sub> reference catalyst purchased from the World Gold Council (WGC) [11]. In fact, gold supported on oxides or carbon, once considered catalytically inert, is now firmly established as an effective catalyst [12]. Very recently, we have observed [13] good catalytic performances during esterification of furfural over a gold-supported sulfated zirconia support, especially when compared with the Au/TiO<sub>2</sub> reference catalyst. Homogeneous oxidative esterifications by gold have also been reported, but most unfortunately, these depend on peroxides as oxidants [14]. Afterward, we have investigated a series of Au/ZrO<sub>2</sub> catalysts calcined at different temperatures (from 150 °C up to 650 °C) in order to modulate the size of the gold nanoparticles, demonstrating that in this reaction, the catalytic activity

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is strictly connected to the metal dispersion. In particular, the presence of highly dispersed gold clusters ability to activate atomic oxygen is required for good catalytic performances. Moreover, the stability of these new catalysts has been also studied [15]. We demonstrated that the catalytic activity can be completely recovered when the organic residue of the exhausted sample is removed from both gold and zirconia sites [15]. Such results suggested that the support also plays a role in the furfural esterification reaction.

Therefore, we decided to investigate different oxidic supports that are commonly used in catalysis. In particular, we examined plain titania ( $\text{TiO}_2$ ), ceria ( $\text{CeO}_2$ ), and zirconia ( $\text{ZrO}_2$ ).  $\text{TiO}_2$  is widely used for a variety of applications because of its high photocatalytic activity, non-toxicity, good availability, low cost, and stability. Its main characteristics strongly depend on its physicochemical properties, such as surface area, crystal structure (anatase, rutile, brookite), crystallite size, and surface hydroxyl groups [16]. Ceria is characterized by a high oxygen storage capacity and reducibility [17]: we can take advantage of these properties in furfural esterification reaction, in which atomic oxygen produced on gold species play a fundamental role. Moreover, gold on cerium oxide support has been shown by IR studies to stabilize gold(III) for heterogeneous catalytic applications [18]. Finally, the choice of zirconia as a support is due to its intrinsic chemical and physical characteristics that can be adjusted by choosing different precursors and synthesis conditions [19].

The aim of the present work is to verify the role of the nature of the support in the base free oxidative esterification of furfural catalyzed by gold-based systems. In particular, the goal is to investigate the above tested catalysts by employing the main characterization techniques typically used in surface science approach.

## 2. Materials and methods

### 2.1. Catalyst preparation

$\text{Zr}(\text{OH})_4$  was prepared by precipitation from  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  at constant pH = 8.6 and then aged for 20 h at 90 °C [20]. Then, zirconium hydroxide was calcined in air (30 mL/min STP) at 650 °C for 3 h.

Ceria support was synthesized by precipitation from  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  by urea at 100 °C in aqueous solution [21,22]. The solution was mixed and boiled for 6 h at 100 °C, and the precipitate was washed twice in boiling deionized water and dried at 110 °C overnight. The material was then calcined in flowing air (50 mL/min) at 650 °C for 3 h.

Titanium hydroxide was precipitated at pH = 8.0 from 0.5 M titanyl sulfate aqueous solution [6]. In particular, 40 g of  $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot y\text{H}_2\text{O}$  (Aldrich) was dissolved in 300 mL of distilled water at room temperature under vigorous stirring. The  $\text{Ti}(\text{OH})_4$  precipitation was obtained by the drop wise addition of 9 M ammonia solution under vigorous stirring. The suspension was magnetically stirred at 60 °C for 20 h. Then, the precipitate was filtered, washed with distilled water in order to remove  $\text{SO}_4^{2-}$  ions, and dried at 110 °C for 18 h. The absence of sulfates in the material was verified by IEC analysis. Finally, the hydroxide was calcined in air flow at 300 °C for 4 h.

In all cases, gold was added by deposition–precipitation (DP) method at pH = 8.6. The oxide supports were suspended in an aqueous solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  for 3 h, and the pH was controlled by the addition of NaOH (0.5 M). After filtration, the samples were dried at 35 °C overnight and finally calcined in air for 1 h at 300 °C. Samples were denoted as Z–Au, C–Au, and T–Au.

Oxidative treatments of the exhausted catalysts were carried out with a temperature rate of 2 °C/min from 25 °C to 300 °C in a 5% $\text{O}_2$ /He flow (40 mL/min).

### 2.2. Catalyst characterization method

The sulfate content was determined by ion chromatography (IC). Sulfate concentration was calculated as the average of two independent analyses, each including two chromatographic determinations.

The gold amount for both fresh and exhausted catalysts was determined by atomic absorption spectroscopy (AAS) after microwave disaggregation of the samples (100 mg) using a Perkin–Elmer Analyst 100.

Surface areas and pore size distributions were obtained from  $\text{N}_2$  adsorption/desorption isotherms at –196 °C (using a Micromeritics ASAP 2000 analyzer). Surface area was calculated from the  $\text{N}_2$  adsorption isotherm by the BET equation, and pore size distribution was determined by the BJH method [23]. Total pore volume was taken at  $p/p_0 = 0.99$ .

High-resolution transmission microscopy (HRTEM) analysis was performed on all catalysts using a side entry Jeol JEM 3010 (300 kV) microscope equipped with a LaB6 filament and fitted with X-ray EDS analysis by a Link ISIS 200 detector. For analyses, the powdered samples were deposited on a copper grid, coated with a porous carbon film. All digital micrographs were acquired by an Ultrascan 1000 camera, and the images were processed by Gatan digital micrograph. A statistically representative number of particles were counted in order to obtain the particle size distribution.

CO pulse chemisorption measurements were performed at –116 °C in a lab-made equipment. Before the analysis, the following pretreatment was applied: the sample (200 mg) was reduced in a  $\text{H}_2$  flow (40 mL/min) at 150 °C for 60 min, cooled in  $\text{H}_2$  to room temperature, purged in He flow, and finally hydrated at room temperature. The hydration treatment was performed by contacting the sample with a He flow (10 mL/min) saturated with a proper amount of water. The sample was then cooled in He flow to the temperature chosen for CO chemisorption (–116 °C) [24].

FTIR spectra were obtained on a BRUKER IFS28 spectrophotometer (resolution: 2  $\text{cm}^{-1}$ , MCT detector). All materials were inspected in the form of self-supporting pellets (about 10  $\text{mg cm}^{-2}$ ). All samples were activated in a controlled atmosphere at 300 °C for ~1 h in a controlled atmosphere ( $\text{O}_2$ , ~60 Torr) in quartz cells that were connected to a gas vacuum line and equipped with mechanical and turbo molecular pumps (residual pressure  $p < 10^{-5}$  Torr). BT (IR beam temperature, ~50 °C)  $\text{CO}_2$  adsorption (~20 Torr) and desorption (up to 30 min of direct pumping off in vacuo) measurements were carried out in a strictly in situ configuration that allowed background subtraction and spectra ratiomings.

TPO measurements were carried out in a lab-made equipment: samples (100 mg) were heated with a temperature rate of 10 °C/min from 25 °C to 600 °C in a 5% $\text{O}_2$ /He flow (40 mL/min). The effluent gases were analyzed by a TCD detector and by a Genesys 422 quadrupole mass analyzer (QMS).

### 2.3. Catalytic activity measurements

2-FA oxidative esterification with oxygen and methanol was investigated at 120 °C, without  $\text{NaCH}_3\text{O}$  addition, using a mechanical stirred autoclave fitted with an external jacket [15]. Catalyst (100 mg), 2-FA (Sigma Aldrich, >99%; 300  $\mu\text{L}$ ) and *n*-octane (Sigma Aldrich, >99%; 150  $\mu\text{L}$ ), used as internal standard, were added to the solvent (150 mL of methanol). The reactor was charged with oxygen (6 bar) and stirred at 1000 rpm. The progress of the reaction was determined after 90 min by gas-chromatographic

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