

# Oxidative esterification of renewable furfural on gold based catalysts: the role of the support

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## 1 Introduction

The upgrading of lignocellulosic biomass wastes into fuels and higher added-value chemicals is one the most researched topics in the forthcoming concept of bio refinery. The sustainability of bio refineries derives from their ability of exploiting every product, as actually occurs in the oil refineries. In particular, additional transformations of furfural are highly desired; the synthesis of alkyl furoates can open very interesting perspectives for the use of xyloses, because they find applications as flavour and fragrance component in the fine chemicals industry, and they also can be used either as solvent or extracting agents in many different industrial plants if produced in larger amounts and at low price. Traditionally, the furoate 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 sulphuric acid. Recently it has been shown [1] that furfural can be converted to methyl furoate by an oxidative esterification with NaCH<sub>3</sub>O and CH<sub>3</sub>OH under mild conditions on an Au/TiO<sub>2</sub> reference catalyst purchased by the World Gold Council. Lately, we have investigated Au/ZrO<sub>2</sub> catalysts for a base free esterification of furfural [2, 3].

In the present work we examine the role of different supports for gold based catalysts. In particular, we have studied zirconia (ZrO<sub>2</sub>), sulphated zirconia (ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>), titania (TiO<sub>2</sub>) and ceria (CeO<sub>2</sub>) oxides. The last support is characterized by both high oxygen storage capacity (OSC) and reducibility. It has been chosen in this work because of the leading role in the process of atomic oxygen produced by reaction with the oxygen molecule. TiO<sub>2</sub> 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 physico-chemical properties. The choice of zirconia as support is due to its intrinsic chemical and physical characteristics that can be adjusted by choosing different precursors and synthesis conditions. In particular, the addition of sulphates increases surface acidity, delays crystallization and enhances the surface area.

The goal of the present work is to verify the role of these interesting oxidic supports on gold based catalysts in the oxidative esterification of furfural, without the addition of NaCH<sub>3</sub>O, a base that would make the process less green and more expensive [4].

## 2 Experimental/methodology

Zr(OH)<sub>4</sub> was prepared by precipitation from ZrOCl<sub>2</sub>·8H<sub>2</sub>O at constant pH= 8.6. Half of the hydroxide was sulphated with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> by incipient wetness impregnation in order to obtain a 2 wt % amount of sulphates on the final support. Then both zirconium and sulphated zirconium hydroxides were calcined in air at 650 °C. Ceria support was synthesized by precipitation from (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> by urea at 100 °C and then calcined in air at 650 °C. Titanium hydroxide was precipitated at pH=8.0 from titanyl sulphate aqueous solution and then calcined in air at 300 °C. Catalysts were prepared by deposition-precipitation of HAuCl<sub>4</sub> and subsequent calcination at 300 °C. As for the catalysts supported on ZrO<sub>2</sub>, we considered a sample calcined at 500 °C as internal reference for its intrinsic properties [3]. As a general reference system, we considered the well-known Au-TiO<sub>2</sub> catalyst provided by the World Gold Council [2].

The oxidative esterification of furfural with methanol was investigated in the temperature range 60 – 120 °C; both molecular oxygen and air were charged in the 1-6 bar pressure range. Fresh and used samples were characterized by metal content analysis, ionic chromatography (IC), N<sub>2</sub> adsorption, HRTEM, FTIR spectroscopy, pulse-flow CO chemisorption, TPO.

## 3 Results and discussion

CO pulse chemisorption measurements were performed in order to have information on the amount of highly uncoordinated Au sites exposed at the surface of the different samples. Volumetric experiments show that the molar ratio between adsorbed CO and gold on both AZ and ASZ is quite high, indicating the presence of gold

clusters undetectable by HRTEM; such clusters are able to activate molecular oxygen producing atomic O species, that render the catalyst more active for furfural esterification reaction.

Both catalytic performances and physico-chemical properties of all materials are reported in Table 1. Zirconia supported catalysts, if compared to the other systems, exhibit very good and comparable catalytic performances both for activity and selectivity. The catalyst supported on ceria exhibits a slightly lower performance than the zirconia-based ones. On the contrary, conversion for the ATi catalyst is very low, even if selectivity is quite good and on a par with the values attained by AZ and ASZ samples. Moreover, if we consider the mol<sub>CO</sub>/mol<sub>Au</sub> ratio for all samples, it is evident (see Table 1) that the ASZ500 system exhibits a much better performance than both ACe and WGC catalysts, indicating that, if the Au amount is comparable, a crucial role of the support might be invoked.

**Table 1.** Physico-chemical properties and catalytic performances (120 °C; 6 bar O<sub>2</sub>; 90 min)

sample	label	Surface area (m <sup>2</sup> /g)	Chemisorption (mol <sub>CO</sub> /mol <sub>Au</sub> )	Conversion (%)	Selectivity (%)
Au/ZrO <sub>2</sub>	AZ	39	0.24	82	92
Au/ZrO <sub>2</sub> SO <sub>4</sub> <sup>2-</sup>	ASZ	77	0.25	83	94
Au/CeO <sub>2</sub>	ACe	105	0.06	66	69
Au/TiO <sub>2</sub>	ATi	166	0.004	20	91
Au/TiO <sub>2</sub> WGC	WGC	46	0.03	64	64
Au/ZrO <sub>2</sub> SO <sub>4</sub> <sup>2-</sup> calc 500°C	ASZ500	75	0.03	96	97

No difference between the N<sub>2</sub> physisorption analyses in the absence/presence of Au is evident. The samples exhibit type IV isotherms with hysteresis loops typical of mesoporous materials. Sulphate-doped material retains a higher surface area than plain zirconia, whereas both ceria and titania samples possess higher surface area than zirconia samples. The absence of sulphates in the ASZ sample has been verified by IC: this is due to the leaching of sulphate groups during the Au deposition-precipitation step at pH=8.6. Thus, sulphates act as structural promoters of the support, as they allow redoubling the surface area with respect to plain zirconia, but they possess almost no role during the catalytic test.

In order to shed some light on the acido-base properties of the various materials, we performed FTIR spectra relative to the adsorption of CO<sub>2</sub> at RT. Summarizing, in order to get the best performing catalyst, both gold dispersion (for good conversion) and acid/base properties of the support (for good selectivity) must be taken into account: these are achieved only for the zirconia-supported catalysts. In fact, the ATi sample exhibits a low conversion degree, that can be due to the worst Au dispersion, even if it is extremely selective due to the scarce presence of O<sup>2-</sup> sites: FTIR analyses revealed the poor formation of carbonates/hydrogeno-carbonates species, with a parallel presence of a high amount of Lewis acid sites.

As sample deactivation is a major challenge in catalytic syntheses, we have investigated also catalyst stability. ATi sample is affected by metal leaching in the reaction medium and is not recyclable. As far as AZ and ASZ samples are concerned, we have ruled out metal leaching and gold sintering problems throughout the reaction time. As revealed by both TPO and FTIR analyses, the reason for catalysts deactivation is due to their tendency to adsorb/accumulate organic species in the reaction ambient. The deactivation is reversible by heating in oxygen atmosphere at a proper temperature [3]. Also the ACe catalyst is recyclable, but its performances are lower than that of zirconia supported samples.

AZ and ASZ catalysts are therefore active, selective, recyclable and proper for a chemistry based on renewable resources.

#### 4 Conclusions

Au-based catalysts were investigated in the oxidative esterification of furfural by an efficient and sustainable process. A comparison among Au samples over different supports was performed under identical experimental conditions, showing that the catalytic performances follow the trend: ASZ > AZ > ACe > ATi.

The chemical and morphological properties observed for zirconia samples seem to fulfil the best compromise between high dispersion and the proper acid-base properties for good selectivity.

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