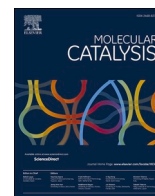




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# Study of the oxidative esterification of furfural catalyzed by Au<sub>25</sub>(glutathione)<sub>18</sub> nanocluster deposited on zirconia

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## ABSTRACT

Au/ZrO<sub>2</sub> catalyst prepared from Au<sub>25</sub>(SG)<sub>18</sub> nanoclusters (SG stands for glutathione) deposited on ZrO<sub>2</sub> has shown to be an efficient system for the oxidative esterification of furfural with methanol. The influence of the supported nanoclusters was studied and showed that partial calcination of the supported nanoclusters at 300 °C was sufficient for a quantitative formation of methyl-2-furoate even in the absence of a base. In the presence of 0.27 mol% of Au, initial activities up to 250 h<sup>-1</sup> were obtained at 100 °C under 6 bar of O<sub>2</sub>. The reactivity was extended to the oxidative esterification of furfuryl alcohol and the formation of various products and intermediates was discussed.

## 1. Introduction

Furfural is a chemical produced at industrial scale from biomass and of importance for the development of the biobased economy. Among promising valorizations of furfural, the oxidative esterification into alkyl-2-furoates is a route giving compounds finding applications in the fine chemical industry as flavors or fragrances. The last decade saw the development of environmentally friendly methods for oxidative esterification of aldehydes in the presence of heterogeneous catalysts using H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> as green oxidants. In the case of furfural, early works reported for example the use of V<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O<sub>2</sub> systems giving selective formation of methyl-2-furoate at mild temperature [1]. While examples with Co, Pd, Mn nanoparticles supported on carbon have been reported for the oxidative esterification of furfural and 5-hydromethylfurfural with O<sub>2</sub>, [2] Au nanoparticles have been mainly used for this reaction [3–6]. Following reports from Christensen and co. on alcohols [7] and aldehydes [8] esterification with Au/TiO<sub>2</sub>, Signoretto and Manzoli and co. have been very active in this subject [3,9–14]. They particularly noticed the superiority of ZrO<sub>2</sub> as support for Au nanoparticles over CeO<sub>2</sub> and TiO<sub>2</sub> in terms of activity, selectivity and stability, due to better Au dispersion and adequate acid-base properties [12].

We recently reported the efficiency for simple benzyl alcohol oxidation into benzaldehyde of a new composite material, Au<sub>25</sub>(SG)<sub>18</sub> gold thiolate nanocluster (SG standing for glutathione) supported on ZrO<sub>2</sub> [15]. The use of atomically well-defined Au nanoclusters as

catalysts has been recently introduced and the ligands around the cluster play definitively a role in the reactivity even for liquid phase catalysis [16–18]. For the synthesis of supported metal catalysts the use of such nanoclusters is a way to form metal nanoparticles of controlled size, the ligands limiting their sintering while keeping reactivity even after (partial) ligand removing [19–21]. For benzyl alcohol oxidation, we studied the importance of the calcination temperature clearly showing that the partial defunctionalization of the Au core is required to observe the highest activity while keeping a small and well-dispersed particle size distribution.

Based on this previous work we report here as new catalytic application of these materials the more sophisticated transformations that are the oxidative esterification of furfural and of furfuryl alcohol. We particularly investigated the catalytic and reaction parameters influencing the transformations, and discussed the evolution of possible intermediates.

## 2. Experimental section

### 2.1. Chemicals

All chemicals were used as received: HAuCl<sub>4</sub>·3H<sub>2</sub>O (purity 99.9 %), NaBH<sub>4</sub>, Zr(OH)<sub>4</sub>, and reactants from Sigma; glutathione (purity 98 %) from Alfa-Aesar; O<sub>2</sub> (B50 cylinder) from Air Liquide.

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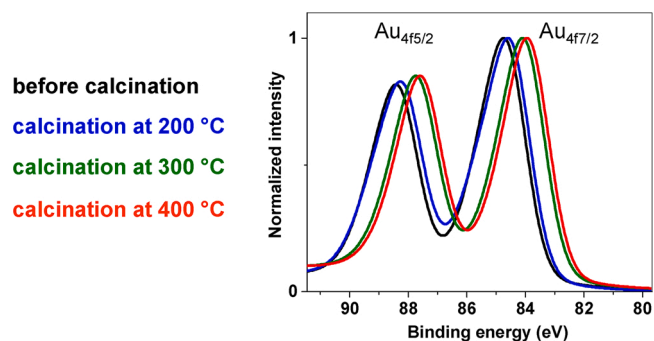


Fig. 1.  $Au_{4f}$  XPS spectra of  $Au_{25}(SG)_{18}/ZrO_2$  before and after calcination.

## 2.2. Preparation of $Au_{25}(SG)_{18}/ZrO_2$

The material was prepared as previously reported [15].  $ZrO_2$  obtained from calcination of  $Zr(OH)_4$  (550 °C, 12 h) was wet-impregnated with a water solution of  $Au_{25}(SG)_{18}$  clusters to give a material with a theoretical loading of 1 wt% of Au. Calcination was performed at 200, 300 or 400 °C under air flow for 12 h.

## 2.3. Characterizations

XPS studies were performed on a AXIS Ultra DLD KRATOS apparatus using monochromatized  $AlK\alpha$  source ( $h\nu = 148606$  eV).

## 2.4. Oxidative esterification of furfural

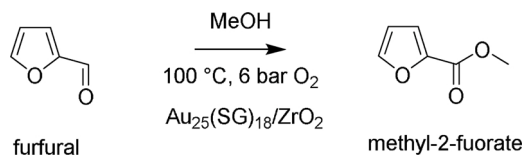
In a typical experiment, furfural (35 mg, 0.36 mmol), catalyst (40 mg, corresponding to 0.2 mg of Au, 1  $\mu$ mol of Au),  $Na_2CO_3$  (75 mg, 0.33 equiv./furfural) were added to methanol (35 g, 44 mL) in a 50 mL autoclave. After pressurization with  $O_2$  (6 bar), the mixture was heated to 100 °C (5 °C.min<sup>-1</sup>) and let for the desired time. The reaction was monitored by regular samplings (0.5 mL) that were diluted in methanol in the presence of butyric acid as standard for gas chromatography analysis (Shimadzu GC-2010, FID detector, CP-WAX 52 CB 30 column,  $N_2$  carrier). After reaction, the catalyst was separated by filtration over Teflon filter, washed with methanol and dried before reuse in other experiments.

TOFs are related to substrate consumption and were calculated as follows:  $(n_0 - n_t)/(n_{Au} \times t)$  with  $t$  arbitrarily fixed at 0.5 h for all experiments.

## 3. Results and discussion

### 3.1. Catalyst preparation and characterization

$Au_{25}(SG)_{18}/ZrO_2$  catalysts were prepared as described in the Experimental section following previous report [15], and contain 1 wt% of Au before calcination steps. Thermogravimetric analyses on the  $Au_{25}(SG)_{18}$  clusters indicate that calcination at 200, 300 and 400 °C led to 36, 75 and 100 % loss of ligand, respectively [15]. As an additional characterization for the present work, XPS studies of Au indicate here that the oxidation state of Au changed upon calcination (Fig. 1) [22]. For initial  $Au_{25}(SG)_{18}/ZrO_2$ , the  $Au_{4f5/2}$  and  $Au_{4f7/2}$  bonding energies (signals at 88.4 and 84.7 eV, respectively) are similar to those after calcination at 200 °C (signals at 88.2 and 84.7 eV), all corresponding to Au ( $\delta^+$ ) species as in  $Au_{25}(SG)_{18}$  [23]. After calcination at 300 then 400 °C the signals shifted to 87.8 (then 87.6) and 84.0 (then 83.9) eV respectively, indicating the reduction to metallic Au(0) species, in accordance with ligand departure [22]. In addition, XPS of N1s and S2p (Fig. S1 in Supplementary information) shows that the amino and thiolate functions from the SG ligands are present on the clusters calcined at 200 °C, and are absent after calcination at 300 and 400 °C, confirming their



Scheme 1. Oxidative esterification of furfural into methyl-2-furoate.

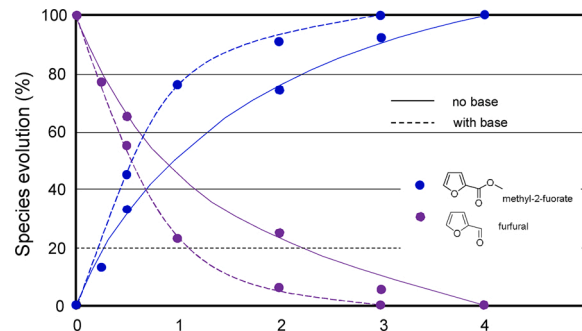


Fig. 2. Furfural oxidative esterification into methyl-2-furoate with 0.1 wt% of furfural in methanol: comparison of reaction profiles in the absence or presence of a base. Furfural 35 mg (0.36 mmol); methanol 44 mL; base  $Na_2CO_3$  75 mg (0.33 mol equiv./furfural); catalyst 40 mg (0.2 mg of Au, 1  $\mu$ mol);  $O_2$  6 bar, 100 °C.

defunctionalization at this level of calcination.

Note that despite the fact that TGA indicated that some organic component remained after calcination at 300 °C, XPS showed the absence of N- and S- species. Probably at this stage only carbonaceous species formed from ligand decomposition at 300 °C were still present however not detectable at the surface.

### 3.2. Initial experiments

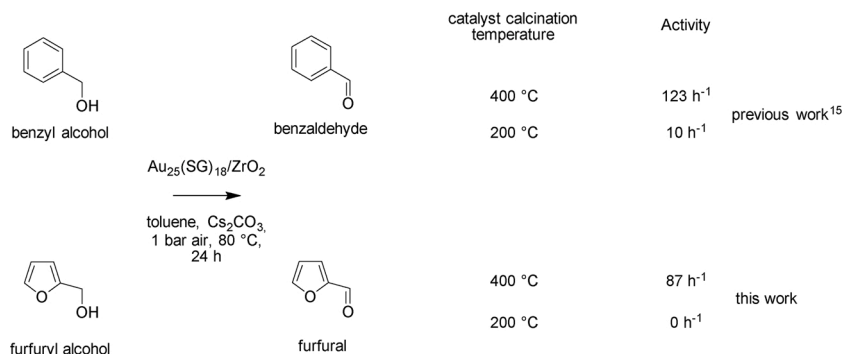
Initial set of experiments was conducted in the condition depicted in Scheme 1 and Fig. 2. The reactions were performed with the catalyst obtained after calcination at 400 °C, a temperature allowing complete removal of SG ligands. The amount of introduced catalyst was 1  $\mu$ mol of Au corresponding to a ratio Au/furfural of 0.57 wt% (0.27 mol%).

Fig. 2 indicates that in these conditions and in the absence of a base, the conversion was complete after 4 h with a yield of 100 % into methyl-2-furoate. Interestingly the presence of a base did not have significant impact, slightly faster reaction and complete product formation was achieved after 3 h (Fig. 2) (TOF at 0.5 h were 250 h<sup>-1</sup> and 320 h<sup>-1</sup>, respectively). Clearly, the use of a base supposed to help methanol deprotonation is not of definitive interest in these conditions. Besides, the influence of the amount on Au was assessed by performing the reaction in the presence of 0.5  $\mu$ mol of Au still in the absence of a base (Fig. S2). Here the transformation was overall slower and 5 h were necessary for complete transformation despite close initial rate (TOF of 245 h<sup>-1</sup>). Note that in the absence of oxygen pressure (reaction performed under ambient air, Fig. S3), the conversion was limited to 55 %, even after running a 24 h reaction (TOF of 85 h<sup>-1</sup>), while still being fully selective.

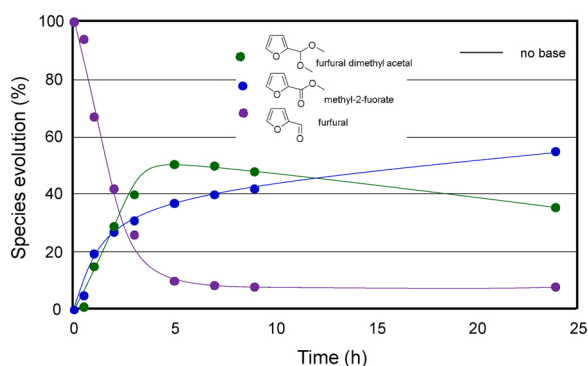
The results obtained here are completely in line with those reported in the literature with other Au/ $ZrO_2$  catalysts [9,11,13,24]. More recently Au/UiO-66 [6] and Au/CMK-3 [4] catalysts, also showed comparable activity in similar conditions, particularly involving less than 1 wt% Au/furfural and most of the time in the absence of base.

### 3.3. Influence of calcination temperature

The above initial experiments were realized after calcination of the catalyst at 400 °C, allowing complete SG ligands removing and while

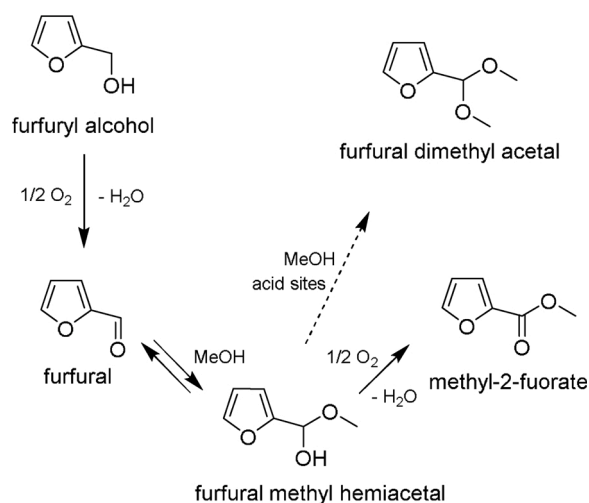


**Scheme 2.** Comparison of benzyl alcohol and furfuryl alcohol oxidation in the presence of Au<sub>25</sub>(SG)<sub>18</sub>/ZrO<sub>2</sub> catalyst.



**Fig. 3.** Furfural oxidative esterification into methyl-2-furoate with 1 wt% of furfural in methanol: comparison of reaction profiles in the absence of a base. Furfural 350 mg (3.6 mmol); methanol 44 mL; catalyst 40 mg (0.2 mg of Au, 1 μmol); O<sub>2</sub> 6 bar, 100 °C.

forming Au particle size of  $2.0 \pm 0.7$  nm, as shown in our previous report [15]. What is more surprising is that when the reaction was performed with a material calcined at 300 °C in which 25 % of thiolate ligands remained (with Au particle size of  $1.7 \pm 0.5$  nm) [15], similar results were obtained (TOF of  $260 \text{ h}^{-1}$ , Fig. S4). Total calcination is therefore not a prerequisite for this reaction and the particle size has low influence in this range, as long as the clusters are able to activate the substrates [3, 11] despite the presence of ligands. A recent study, involving Au/Nb<sub>2</sub>O<sub>5</sub> catalysts prepared from Au<sub>n</sub>(SC<sub>12</sub>H<sub>25</sub>)<sub>m</sub> clusters, showed that for CO oxidation, an optimized calcination temperature (300 °C) has to be performed to balance the effect of remaining ligand and nanoparticle size [25]. The latter study is in line with what we observed previously for benzyl alcohol oxidation: the activity was twice with catalyst calcined at 300 °C compared to 400 °C [15]. However a difference was obtained with catalyst partially calcined at 200 °C: while benzyl oxidation was observed despite the presence of 64 % of ligand on the Au clusters, for the present reductive oxidation this low level of calcination totally prevented the reaction (data not presented). For more pertinent comparison, we present here furfural oxidation under the same conditions as for benzyl alcohol (Scheme 2) [15]. We observed here an influence with catalyst calcined at 200 °C giving no reactivity of furfuryl alcohol, while lower activity was obtained with catalysts calcined at 400 °C. Benzyl of furfuryl ring has an influence, and the reaction seems more difficult with furan derivatives. This is why the calcination temperature and therefore the presence or not of thiolate ligands appears more important in this case. A very recent study showed that for Au<sub>38</sub>(SR)<sub>24</sub> clusters deposited on CeO<sub>2</sub>, ligand migration onto the surface occurred forming sulfur species on the support, having an importance on catalytic properties especially for oxidation [26]. In our case, as indicated above XPS analysis discarded the presence of sulfur species at the surface of zirconia for catalyst calcined at 300 and 400 °C. Therefore these aspects appeared



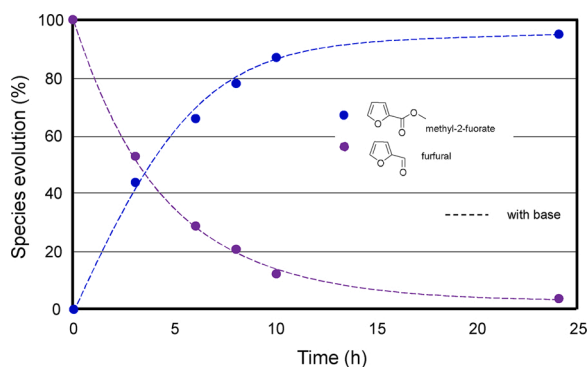
**Scheme 3.** Reaction pathway from furfuryl alcohol to methyl-2-furoate.

difficult to rationalize and other parameters like adsorption/desorption of species at the surface may play a definitive role.

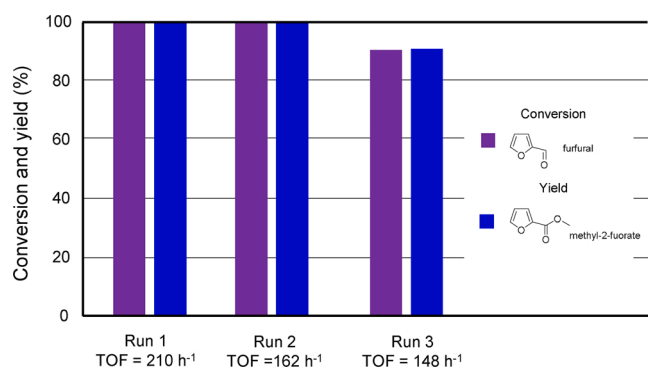
### 3.4. Influence of initial furfural concentration

For the next set of experiments, we performed the reaction with the catalyst calcined at 400 °C by increasing the initial concentration of furfural by a factor 10 without changing the amount of catalyst (Fig. 3). In the absence of base, incomplete conversion was obtained even after 24 h (TOF of  $60 \text{ h}^{-1}$ ). Here we observed the presence of furfural dimethyl acetal besides methyl-2-furoate (Scheme 3). Some literature studies propose that this dimethyl acetal is not an intermediate towards methyl-2-furoate, in contrast to the methyl hemiacetal (Scheme 3), but is formed as a side product stable under reaction conditions [3,27]. However in our case performing the reaction over a longer time allows a consumption of this compound after 5 h with concomitant formation of target methyl-2-furoate (while furfural conversion remained stable). This observation can suggest that furfural dimethyl acetal could also be regarded at some point as an intermediate to methyl-2-furoate (see Section 3.6 for further discussion) [28]. As an hypothesis, the presence of water formed during the oxidation step of furfural may have an importance here implying furfural dimethyl acetal reactivity on some catalytic sites of the materials.

More to this point, it has been postulated in the literature that the formation of furfural dimethyl acetal was due to large Au particle sizes (over 4 nm) [11]. In our case, the Au particle size is of  $2.0 \pm 0.7$  nm ruling out the first hypothesis. Other studies indicate that its formation is due to the absence of basic sites in the reaction medium [27], preventing selective ester formation. Another report claims that the formation of



**Fig. 4.** Furfural oxidative esterification into methyl-2-furoate with 1 wt% of furfural in methanol in the presence of base. Furfural 350 mg (3.6 mmol); methanol 44 mL; base  $\text{Na}_2\text{CO}_3$  75 mg (0.33 equiv./furfural); catalyst 40 mg (0.2 mg of Au, 1  $\mu\text{mol}$ );  $\text{O}_2$  6 bar; 100 °C.



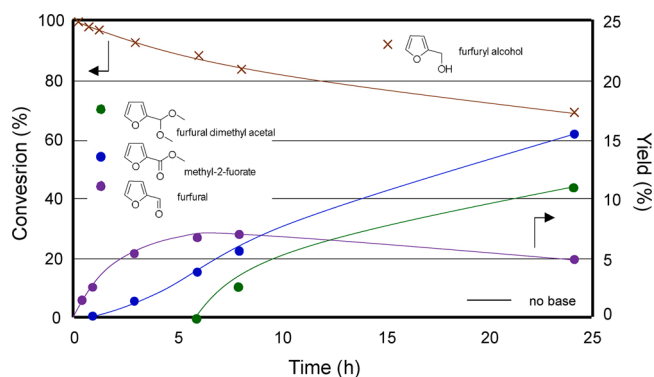
**Fig. 5.** Catalyst recycling of furfural oxidative esterification into methyl-2-furoate with 0.11 wt% of furfural in methanol in the absence of base. Furfural 35 mg (0.36 mmol); methanol 44 mL; catalyst 40 mg (0.2 mg of Au, 1  $\mu\text{mol}$ );  $\text{O}_2$  6 bar; 100 °C, 4 h.

this dimethyl acetal can be due to the Lewis acid sites of zirconia [13]. Indeed, generally acetal formation is an acid catalyzed reaction, in this particular case a recent work showed the synthesis of various dimethyl acetal of furfural in the catalytic presence of Lewis acids [29]. In our case this is feasible. Involving a large excess of furfural with respect to Au sites leaves the chance to furfural to adsorb and react at other catalytic sites, i.e. of zirconia phase, allowing furfural dimethyl acetal formation as side reaction. This possibility of acid catalyzed formation of furfural dimethyl acetal was confirmed by performing the reaction in the presence of the base, suppressing the low amount of acid sites of the support [30], and consequently only the formation of methyl-2-furoate was observed (Fig. 4), despite a longer reaction time due to a lower Au/furfural ratio (TOF of 230  $\text{h}^{-1}$ ).

Nevertheless, the fact that we observed this compound only at a higher furfural concentration indicates that these conditions were not adapted to fully convert furfural into methyl-2-furoate with such reactant amount and put the light on other phenomena that may play a role in this transformation. Note that increasing the reaction temperature to 120 °C increased significantly the initial conversion rate (TOF = 490  $\text{h}^{-1}$  vs 60  $\text{h}^{-1}$ ) and the yield into target methyl-2-furoate the formation of furfural dimethyl acetal was not totally suppressed (Fig. S5).

### 3.5. Catalyst recycling

Studies on catalyst reuse were performed in conditions described in Fig. 2 allowing selective transformation in the absence of a base. After a first run the solid was recovered by filtration, washed with methanol before drying. TGA analysis indicated the absence of adsorbed organic

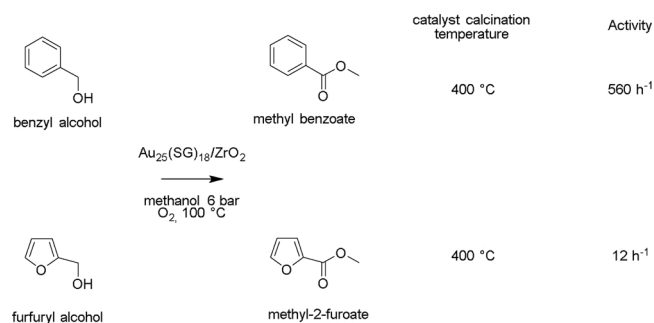


**Fig. 6.** Furfuryl alcohol reactivity in methanol in the absence of base. Furfuryl alcohol 36.5 mg (0.37 mmol); methanol 44 mL; catalyst 40 mg (0.2 mg of Au, 1  $\mu\text{mol}$ );  $\text{O}_2$  6 bar; 100 °C, 24 h.

materials (not presented). Therefore, the catalyst was reused without additional treatments. Fig. 5 shows a very low difference after the first recycling (Run 2) for the same reaction time, giving 100 % yield after 4 h. After the second recycling (Run 3), 90 % yield was obtained after 4 h (note that 100 % yield could be obtained after 5 h, data not presented). Analysis of reaction medium after Run 1 indicated that less than 0.05 % of initial supported Au leached during the reaction proving a high stability of the catalyst. On another side, analysis of the used catalyst average particle size increased from  $2.0 \pm 0.7$  nm to  $2.9 \pm 1.0$  nm. The increase in particle size may explain the observed lower initial activity of the reused catalyst.

### 3.6. Other reactants

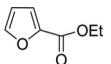
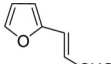
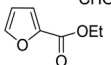
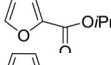
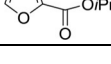
The oxidative properties of the catalyst were also assessed using furfuryl alcohol as reactant under the same conditions as above (Scheme 4). Concerning heterogeneous catalysis this reaction has been reported mainly with Co or Pd-based catalysts often in the presence of a base [31–37], while only few examples exist using Au. For instance AuPd/- $\text{Fe}_3\text{O}_4$  associated to  $\text{K}_2\text{CO}_3$  has been recently proposed. The authors showed that the presence of Pd was necessary to form methyl-2-furoate since furfuryl alcohol oxidation did not occur using Au/ $\text{Fe}_3\text{O}_4$  at room temperature [38]. Another study reported yields of 6–7 % with Au/ $\text{CeO}_2$  or Au/ $\text{ZrO}_2$  in the presence of  $\text{Cs}_2\text{O}_3$  at room temperature for 24 h [39], while almost quantitative transformation was possible with Au/ $\text{CeO}_2$  at 130 °C for 2 h [28]. In our case the results presented in Fig. 6 confirm a more difficult transformation than the oxidative esterification of furfural. A relatively slower transformation with only 30 % of conversion after 24 h occurred however in the absence of a base. Concerning product formation, furfural was formed as initial product from oxidation of furfuryl alcohol, and rapidly started to be consumed into methyl-2-furoate through oxidative esterification. This last step was fast enough to prevent furfural accumulation. Indeed, according to a study



**Scheme 4.** Comparison of benzyl alcohol and furfuryl alcohol oxidative esterification in the presence of  $\text{Au}_{25}(\text{SG})_{18}/\text{ZrO}_2$  catalyst.



**Table 1**  
Oxidative esterification of furfural in the presence of other alcohols.

Alcohol	Base	T (°C)	Time (h)	Conversion (%)	TOF (h <sup>-1</sup> )	Product	Yield (%)
ethanol	Na <sub>2</sub> CO <sub>3</sub>	100	24	71	33		17
							36
ethanol	none	120	24	70	17		70
iso-propanol	Na <sub>2</sub> CO <sub>3</sub>	100	24	78	80		35
iso-propanol	none	120	24	43	180		43

from Corma and co. involving 5-hydroxymethylfurfural, it seems that the global reactivity of the alcohol function is lower than that of the carbonyl function [28,40], and that the size of Au particles of catalysts plays also an effective role [41,42]. Furfural dimethyl acetal was also detected but later than methyl-2-furoate. Nevertheless this did not specifically prove that it was not an intermediate towards methyl-2-furoate. It could have been formed before but not detected due to fast transformation. The presence of this compound for same reaction has been evoked before [28,36]. Interestingly a recent study shows that this compound is the main product obtained by reacting furfuryl alcohol or furfural in methanol under O<sub>2</sub> pressure in the presence of Pd/ZrO<sub>2</sub>/PVA catalyst and methyl-2-furoate was even not formed [36]. Moreover based on the report of Manzoli et al. who studied the specific reactivity of furfural dimethyl acetal with Au/ZrO<sub>2</sub> catalysts under conditions similar to ours it was concluded that this compound was not reactive and not further converted [3]. Therefore furfural dimethyl acetal appears to be formed as a by-product.

Here also, and for comparison purposes, the same reaction applied to benzyl alcohol (Scheme 4) confirmed a higher reactivity of benzyl alcohol forming methyl benzoate with 100 % selectivity through the transformation (TOF of 560 h<sup>-1</sup>) (Fig. S6). Nor benzaldehyde neither acetals were observed during the course of the reaction. As it was for the simple oxidation, the overall reaction was faster with benzyl alcohol compare to furfuryl alcohol. A rare recent study reported the faster reactivity of benzaldehyde over furfural for the related acetalization reaction [29]. Obviously, benzyl derivatives are more reactive than furan ones for such kind of reactions. Due to the lack of literature data it appears difficult to give a reason. Nevertheless in our case one can speculate the possibility of different coordination modes between the two types of derivatives onto the surface leading to a different reactivity [43]. A more comprehensive and comparative adsorption study would be needed to definitively conclude.

Finally, the catalytic system was applied to other alcohols (Table 1). As previously observed, reaction becomes less efficient with the length of the alcohol chain. Interestingly, when the reaction was performed in ethanol and in the presence of base, we could mainly observe furan-2-acrolein, formed from oxidative condensation. Previous studies also reported the predominant formation of this product in the presence of Au or other metal supported catalysts with a base. Metal catalyst oxidizes ethanol to acetaldehyde and the base seems indeed necessary for coupling of the latter with furfural [6,44–49].

#### 4. Conclusion

This study demonstrates the activity of Au/ZrO<sub>2</sub> catalysts prepared from Au<sub>25</sub>(SG)<sub>18</sub> nanoclusters deposited on ZrO<sub>2</sub> for the oxidative esterification of furfural into methyl-2-furoate. We particularly showed that at least partial defunctionalization of the supported nanoclusters by

calcination at 300 °C has to be performed to observe a transformation. Full selectivity into methyl-2-furoate was observed through the transformation even in the absence of a base. The efficiency of reused catalyst was demonstrated for 3 consecutive runs despite a slight change in initial activity, probably due to the formation of larger Au nanoparticles during the reactions. When using higher initial furfural concentration, we noticed the formation of furfural dimethyl acetal as co-product that was suppressed in the presence of a base. This compound is supposed to form on acid sites of the surface. The reactivity was extended to the more demanding oxidative esterification of furfuryl alcohol into methyl-2-furoate.

#### CRediT authorship contribution statement

**Zahraa Shahin:** Investigation. **Franck Rataboul:** Investigation. **Aude Demessence:** Investigation.

#### Declaration of Competing Interest

The authors report no declarations of interest.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.mcat.2020.111265>.

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