

**Au/Al<sub>2</sub>O<sub>3</sub> – efficient catalyst for 5-hydroxymethylfurfural oxidation to  
2,5-furandicarboxylic acid**

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**Abstract**

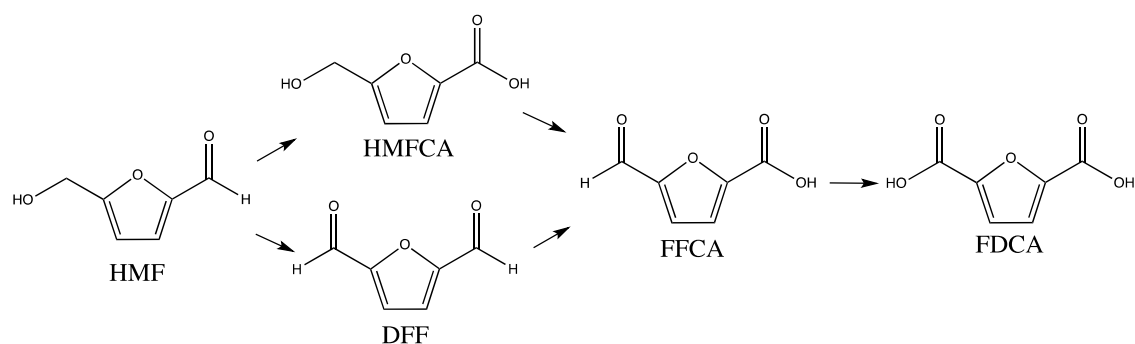
The catalytic activity of a simple Au/Al<sub>2</sub>O<sub>3</sub> catalytic system prepared by the direct anionic exchange (DAE) method was evaluated in the selective 5-hydroxymethylfurfural (HMF) oxidation under mild conditions, using molecular oxygen as the oxidant. The influence of the HMF/NaOH ratio and reaction time on product yield and distribution were studied and discussed in detail. Extremely high activity and selectivity were observed in mild conditions, with 99% of 2,5-furandicarboxylic acid (FDCA) production at full HMF conversion after 4 hours with the use of only 4 equivalents of NaOH at 70 °C. Catalyst viability and stability were verified by repeating the cycle up to five times. Changes in the nature of the support were also contemplated by introducing some ceria fraction, i.e. 20 wt%.

**Keywords:** biomass conversion, HMF oxidation, gold catalysts, 2,5-furandicarboxylic acid

## 1. Introduction

The start of the 21<sup>st</sup> century is considered to mark a turning point toward a more conscious society, one completely aware of the economic and environmental problems caused by the use of fossil fuels. The main issues connected with their depletion and non-renewability have led the scientific community to search for alternatives, with lignocellulosic biomass receiving much attention [1–3]. Its great usefulness mostly lies in its biomass chemical composition, based on molecules with multiple functional groups (carbohydrates/sugars) that can be transformed into highly functionalized useful molecules (Bio-Based Building Blocks), from which some valuable and important chemicals and fuels can be obtained.

Among the various lignocellulosic biomass fraction transformations into valuable chemicals, an important role is played by furfural derivatives with functional groups in position five [3–5]. Indeed, the 5-hydroxymethylfurfural (HMF) molecule is considered a versatile platform chemical [6,7], produced directly from six carbon sugars via isomerization-dehydration reactions [8–10]. It is a key precursor for the synthesis of numerous chemicals; among them, worthy of note are those for fuel applications and the polymer industry [11–13].



**Scheme 1.** General reaction network for HMF oxidation

The selective oxidation of the alcoholic and aldehydic functions of the HMF molecule (Scheme 1) leads to the formation of 2,5-furandicarboxylic acid (FDCA), which – according to the US Department of Energy – is one of the top 12 high-potential bio-based products [14,15]. FDCA is actually considered to be a possible replacement monomer for terephthalic acid, which is used to produce polyethylene terephthalate (PET) [16]. Gandini et al. reported that FDCA-based polymers, e.g. polyethylene furandicarboxylate (PEF), are structurally and physicochemically similar to PET [7,17–19].

The synthesis of 2,5-furandicarboxylic acid from HMF has been extensively studied in recent decades, using different catalysts and reaction conditions. Unlike in the homogeneous processes where  $\text{KMnO}_4$  is used as oxidant [20–22], the heterogeneously catalyzed transformation of HMF to FDCA uses molecular oxygen, which is highly desirable from the chemical and environmental standpoint [18]. Gold-supported catalysts were found to be active for HMF oxidation to FDCA, and many efforts have recently been focused on the search for the best supports and reaction conditions for improving FDCA yield [23,24]. The use of a base for this reaction is a general requirement for promoting the catalytic activity and assuring the solubility of the products formed [24–26]. Nevertheless, strong alkali conditions, in some cases up to 20 equivalents of NaOH [27], make the process highly corrosive. For this reason, the development of more efficient catalysts in a low base concentration is highly recommended.

It is generally accepted that support composition, metal particle size, and metal-support interaction play an important role in the oxidation processes over gold catalysts [28]. Some studies suggest that support composition and metal-support interaction affect the FDCA yield [17,24,29]. However, there are still no detailed studies correlating gold particle size and support nature to catalyst activity.

It is well known that both metal-support interaction and particle size are strongly influenced by the preparation method. To the best of our knowledge, there are no studies applying the direct anionic exchange (DAE) method for gold catalyst synthesis for HMF oxidation. In many cases, preformed colloidal particles are transferred to an oxidic carrier and then the solid is dried. The calcination step is often avoided to prevent nanoparticle sintering; nevertheless, the presence of surfactants in the final solid makes a proper metal-support interaction difficult, affecting the catalytic behavior [29,30].

In this work, the catalytic activity of simple Au/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by the DAE method is evaluated for selective HMF oxidation under mild conditions using molecular oxygen as oxidant. The influence of the HMF/NaOH ratio and the reaction time on product yield and distribution will be discussed in detail. The results obtained are compared to previous literature reports using homologous systems but prepared using the colloidal method. The catalyst stability is also assessed by repeated cycles of activity under the same operating conditions. Finally, details are also provided on the catalytic behavior of the Au/Al<sub>2</sub>O<sub>3</sub> catalyst modified by the addition of a small fraction of CeO<sub>2</sub>.

## **2. Materials and methods**

### ***Catalyst preparation***

Commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>(20 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (both from Sasol) were used as supports. Gold was deposited (2 wt. % nominal value) according to the direct anionic exchange (DAE) method assisted by ammonia, as previously proposed by Ivanova et al. [31]. 10<sup>-4</sup> M aqueous solutions of HAuCl<sub>4</sub> (Johnson Matthey) gold precursor and corresponding support were used in order to obtain a final Au loading of 2 wt.%. The precursor solution was heated to 70°C and aged 20 min before the addition of the support.

Then the suspension was cooled down and  $\text{NH}_3$  (Aldrich) was added and aged for another 20 min. The slurry was then filtered, washed with water, dried at  $100^\circ\text{C}$  overnight, and finally calcined in air at  $300^\circ\text{C}$  for 4 h.

Caution/safety note: The contact of ammonia with a gold solution may result in the formation of gold ammonia complexes (“fulminating gold”), which are explosive. This preparation procedure is not dangerous when the gold complexes are strongly attached to the support by the DAE.

### ***Characterization***

Gold loadings were determined by X Ray Fluorescence (XRF) using a Panalytical AXIOS spectrometer with Rh tube of radiation.

Transmission electron microscopy (TEM) observations were performed on a PHILIPS CM-200.

$\text{N}_2$  adsorption experiments were conducted on a Micromeritics ASAP 2010 instrument. Before the analysis, samples were degassed for 2 h at  $150^\circ\text{C}$  in vacuum. The single-point BET analysis method was used for determining the specific surface area and pore size.

### ***Catalytic tests***

The oxidation of HMF was carried out in a 100 mL volume autoclave reactor, provided with mechanical stirrer and temperature/pressure controllers. In a typical experiment, the reactor was charged with an aqueous solution of HMF (approx. 25 mL, 0.08 M), the necessary amount of NaOH, and the catalyst in the HMF: Au: NaOH ratio of 1:0.01:2.

Before the test, the reactor was purged twice with pure  $\text{O}_2$  (10 bar) and finally pressurized to 10 bar. Temperature was raised to  $70^\circ\text{C}$  and the reaction mixture was stirred at approximately 400 rpm for 4 hours. Then the reactor was introduced into an ice bath and

the reaction mixture was centrifuged and filtered. Afterwards, a sample was taken and diluted before the test in an Agilent Infinity 1260 liquid chromatograph equipped with a DAD detector and an Aminex HPX-87H 300 mm × 7.8 mm column using 0.005 M H<sub>2</sub>SO<sub>4</sub> as eluent.

The stability was studied in the spent samples recovered from the post-reaction mixture and dried at 120°C overnight. HMF: Au: NaOH molar ratios were always kept constant. The conversion, selectivity, yield, and carbon balance were calculated from peak areas, after calibration using some reference commercial samples, according to the following equations (using *FDCA* as the example):

$$\text{Conversion (\%)} = \frac{\text{HMF moles}_I - \text{HMF moles}_F}{\text{HMF moles}_I} \times 100 \quad \text{Eq. 1.}$$

$$\text{FDCA Selectivity (\%)} = \frac{\text{FDCA moles}}{\text{HMF moles}_I - \text{HMF moles}_F} \times 100 \quad \text{Eq. 2.}$$

$$\text{FDCA Yield (\%)} = \frac{\text{Conversion}}{100} \times \text{Selectivity} \quad \text{Eq. 3.}$$

$$\text{C balance (\%)} = \frac{\text{Final carbon moles}}{\text{Initial carbon moles}} \times 100 \quad \text{Eq. 4.}$$

The carbon balance obtained in every reaction was always in the range 98-102%. If not indicated, byproducts were not formed during catalytic tests.

### 3. Results and discussion

Table 1 summarizes the most significant characterization results for both samples.

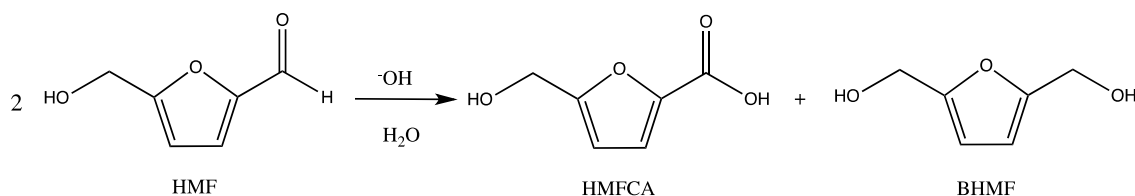
**Table 1.** Summary of characterization data for AuAl and AuCeAl samples

Sample	% Au	Average particle size, nm	Dispersion, %	S <sub>BET</sub> (m <sup>2</sup> /g)	Average pore size (nm)	Pore volume (cm <sup>3</sup> /g)
AuAl	1.64	5.1±1.5	26	187	8.7	0.47
AuCeAl	2.36	3.4±0.8	38	158	7.6	0.39

For the AuAl catalyst, a metal loss of around 18% was detected in relation to the nominal value, which indicates an incomplete gold deposition. The presence of ceria, however, prevents gold loss, thus leading to an even higher value than that targeted. This result could be attributable to an increase in gold preferential nucleation sites due to oxygen vacancy formations in the ceria lattice [32], and also to some support loss during the preparation stage. Average gold particle sizes were determined by TEM microscopy, as previously reported [33]. The AuAl catalyst shows a slightly wider size distribution resulting in a higher average size (5.1±1.5 nm) than the AuCeAl sample (3.4±0.8 nm). Gold metal dispersion was estimated on the basis of the particle sizes calculated for fresh catalysts, using the particle modeling system proposed by Polisset [34]. The calculated dispersions are listed in Table 1 and reflect the dispersion increase and particle size diminution with the addition of ceria. As for the textural properties, both solids are mesoporous materials with average pore sizes of around 8 nm and high specific surface areas, which are slightly lower in the presence of ceria.

The most important reaction parameter to be considered is probably the presence of a base. The activity of the catalyst in HMF oxidation is strongly dependent on base equivalents; the basic media, however, also provides the perfect conditions for different secondary reactions. HMF has different functionalities among which the presence of alcohol and aldehyde groups are the most important. In the presence of a strong base, aldehydes without  $\alpha$ -hydrogen(s) (non-aldolizing aldehydes), as in our case, undergo a

disproportionation (self-oxidation and reduction), also called the Cannizzaro reaction. Scheme 2 shows the Cannizzaro reaction of HMF to 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) and 2,5-Bis(hydroxymethyl)furan (BHMF).



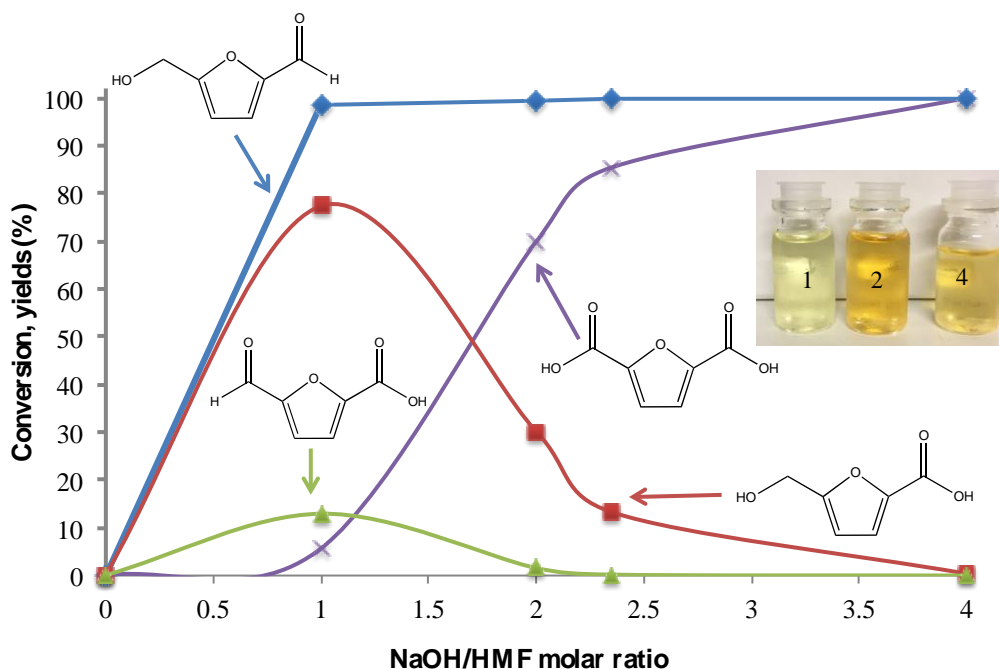
**Scheme 2.** Cannizzaro reaction of HMF in presence of base

In the typical reaction conditions described above, the degradation of pure HMF to HMFCFA and BHMF cannot be ignored. Indeed, the blank experiments conducted in these conditions by Albonetti et al. [29] showed that a significant amount of HMF degrades in base conditions and a 40% conversion of HMF is reached after 10 min at 70°C, with no formation of oxidation products. The reaction mixture turns from colorless to yellow, and then to red, with time on reaction. After 30 min, total HMF conversion is observed. This indicates the formation of high molecular weight compounds, commonly called humins, as a result of multiple aldol condensations. The HMF molecule and its derivatives do not present  $\alpha$ -hydrogen(s), and the mechanism of humin formation in basic conditions is different from that in acidic media, going through furan ring hydrolysis and opening [35]. In a recent study, Ait Rass et al. [24] suggested that the formation of humins in basic media occurs via the Cannizzaro reaction, with the products binding further to form polymeric products at high temperatures, while the only products at low temperatures are those of disproportionation.

Scientific literature extensively reports the positive effects of homogeneous base addition during HMF oxidation [23,24,36,37]. The HMF oxidation rate most certainly depends



significantly on the presence of NaOH, and seems to promote the formation of 5-hydroxymethyl-2-furancarboxylic acid (HMFCAs), which is further oxidized to 5-formyl-2-furancarboxylic acid (FFCA) and 2,5-furandicarboxylic acid (FDCA) (Scheme 1) [38]. However, in the absence of an active catalyst, the basic environment leads to the formation of byproducts. Therefore, it is important to design an active catalyst able to rapidly oxidize HMF to HMFCAs, thus avoiding fast degradation via disproportionation. So the first catalytic study was carried out over a AuAl sample and the effect of NaOH/HMF molar ratio (Figure 1) was studied.



**Figure 1.** Conversion and product yields over AuAl catalyst at different NaOH/HMF molar ratio. Reaction conditions: HMF: Au molar ratio 100:1, 10 bar O<sub>2</sub>, 70 °C, 400 rpm, 4h.

In the absence of a base (NaOH/HMF molar ratio = 0), no HMF is converted. In the presence of NaOH, the HMF conversion reaches 100% in a 4-hour reaction, regardless of the quantity of added base. Unlike the conversion, however, product yields dramatically changed when the NaOH amounts were changed: an effect also reported in

literature [16,18,29,39]. HMF transforms immediately into oxidation products. The disproportionation reaction does not occur, as confirmed by the color of the solutions obtained (clearly yellow in Figure 1), testifying to the efficiency of the catalyst.

As the NaOH to HMF ratio increases, the first oxidation step toward HMFCa is promoted and the final FDCA yield appears higher. The intermediate oxidation product 2,5-formylfurancarboxylic acid (FFCA) is practically undetectable due to its fast oxidation to the final FDCA.

Two oxidation routes are possible for HMF oxidation (see Scheme 1). In the first route, the HMF is rapidly oxidized to HMFCa, while the subsequent transformation of the hydroxyl to an aldehyde group is a very slow reaction [17]. Therefore, the rate-limiting step will be the oxidation from HMFCa to FFCA, which undergoes a rapid oxidation to FDCA. Thus, the products usually detected are HMFCa and FDCA. The second oxidation route refers to the DFF formed by the oxidation of HMF alcohol to the aldehyde group. Over Au/Al<sub>2</sub>O<sub>3</sub> catalyst, diformylfuran (DFF) was not observed, thus suggesting that the reaction occurs via HMFCa formation. The latter is also consistent with previous studies with gold catalysts [16,39]. In fact, the formation of DFF is reported for Pd- and Ru-based catalysts used without a base [40–42].

It is worth mentioning that a total HMF conversion toward a FDCA yield of >99% is achieved by using 4 equivalents of NaOH in just 4 hours' time at 70°C. Similar results can be obtained over bimetallic Au-Pt catalysts [16]. In the reaction conditions applied, however, a changing FDCA yield (19-47%) was reported on bare gold catalysts (Au/TiO<sub>2</sub> and Au/CeO<sub>2</sub>, respectively) [16,29]. The improved FDCA yield with the presence of ceria was observed and directly attributed to oxide intrinsic properties related to Ce<sup>4+</sup>/Ce<sup>3+</sup> fast redox cycles, and as a consequence of increased oxygen mobility and oxidation abilities [17,36,38]. This effect, which was observed on the support, is metal-induced, and is

strongly affected by the major Au-support interaction [43]. Those catalysts were prepared via gold colloid immobilization technique, in which preformed nanoparticles are transferred to the oxide support. This technique requires the presence of a protecting agent such as polyvinylpyrrolidone (PVP) to avoid particle sintering; however, its presence strongly affects Au-support interaction and the final FDCA yield [29].

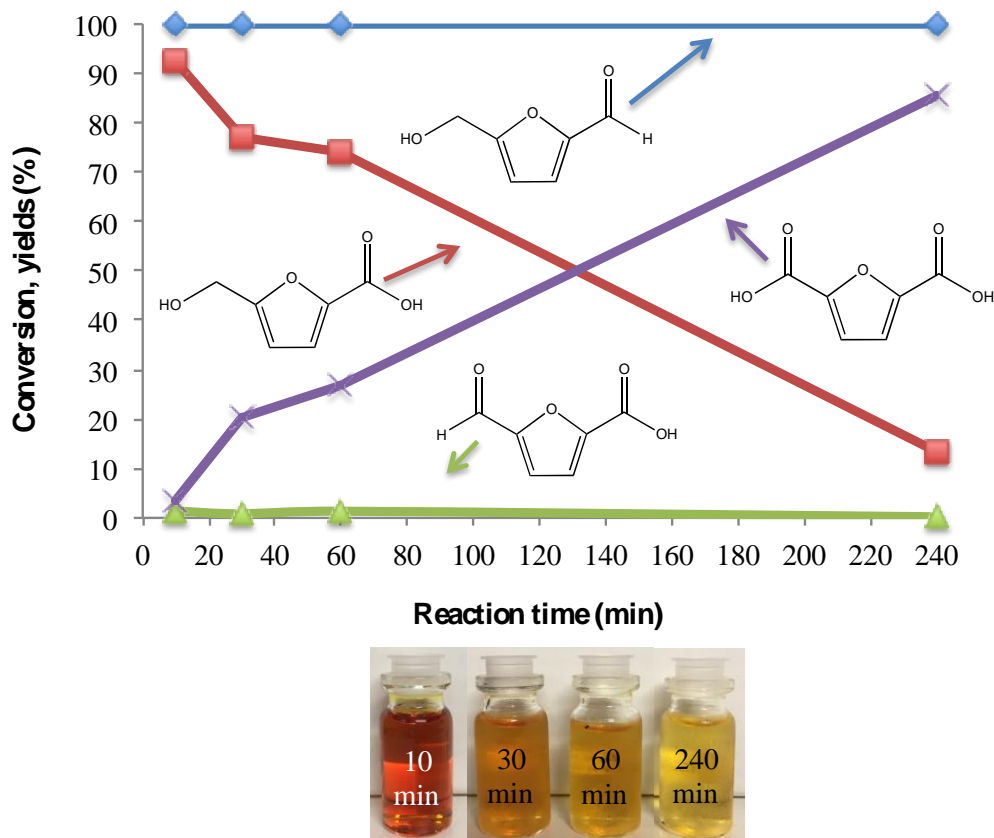
Contrary to the colloidal route, the synthesis method used in this work is based on the direct anionic exchange method of gold species in a solution with the hydroxyl groups of the support, thus establishing a direct interaction between them. The interaction occurs via an exchange after alumina OH group protonation ( $\text{Al}_2\text{O}_3$  IEP = 7.6), the subsequent release of water with vacancy formation, and interaction with the hydrolyzed groups of the gold complex. Belevantsev and coworkers [44,45] reported on gold precursor ( $\text{HAuCl}_4$ ) hydrolysis and speciation, leading to the speciation of different gold complexes upon heating and pH changes. When, as in our case, much-diluted gold precursor solutions were used, the pH of the solution approached that of the distilled water (6-6.5) and 70% of Au species were detected as  $[\text{Au}(\text{OH})_2\text{Cl}_2]^-$  and  $[\text{Au}(\text{OH})_3\text{Cl}]^-$ , which were interacting very rapidly with the support [46]. Therefore, the Au-support interaction depends on the degree of the gold precursor hydrolysis, being very strong between both  $[\text{Au}(\text{OH})_2\text{Cl}_2]^-$  and  $[\text{Au}(\text{OH})_3\text{Cl}]^-$  complexes and alumina [46]. The use of ammonia during this synthesis also provides an additional charge on the gold particle surface, stabilizing the particles against sintering (very narrow particle size distribution with average size around 4 nm) and providing a clear surface for any reaction [47]. The important gain in activity of the catalysts prepared by DAE in comparison to the immobilized colloid route suggests that the intrinsic activity of gold particles depends firstly on the available clear metal surface, and secondly on the good metal dispersion.

Consequently, and in view of all what is described above, a clear superiority of the AuAl catalyst in comparison to the majority of the reported catalysts may be related to a better active phase/carrier interaction resulting in >99% FDCA yield in the presence of only 4 equivalents of base at 70°C. To the best of our knowledge, this is the best result reported over monometallic gold/alumina catalysts.

Due to the high conversion and activity, all the following reaction parameters were studied at the low base conditions of 2 NaOH equivalents. Thereafter, all experiments were performed at a HMF: Au: NaOH molar ratio of 1:0.01:2.

The decreased base leads again to the full HMF conversion with 70% FDCA yield, a result comparable to or even better than other reported systems using larger amounts of base. The latter demonstrates an excellent viability of the Au/Al catalyst at this stage, and in terms of FDCA yield in low-corrosive conditions.

The reaction time considerably affects the FDCA selectivity, as shown in Figure 2, where HMF conversion and product yields are plotted as dependent on the reaction time over the AuAl catalyst at 70°C. In these conditions, a 100% conversion is achieved after 10 min of reaction, with the HMFCFA being the prevalent product at this time (yield 94%), thus suggesting that the HMF conversion is completed in less than 10 minutes and that a part of the HMFCFA undergoes further oxidation. This observation is consistent with all the results described above, confirming that HMF oxidation to HMFCFA is a rapid process which is completed within a few minutes. Moreover, no byproducts are formed.



**Figure 2.** Conversion and product yields over AuAl catalysts as function of the reaction time (samples imaged at 0, 30, 60 and 240 min.) Reaction conditions: HMF: Au: NaOH molar ratio 1:0.01:2, 10 bar O<sub>2</sub>, 70 °C, 400 rpm.

From this moment, up to the end of the reaction (240 min), the progressive oxidation of the HMFCFA hydroxyl group is taking place. Once oxidized to aldehyde, it is rapidly converted into dicarboxylic acid, as can be deduced from the absence of FFCA (FFCA yield lower than 1%). As shown in Figure 2, the solution color also testifies to the progress of the reaction, since the final solution is less colored with the increased FDCA yield. Again, no byproducts are formed, suggesting that the rapidly produced (in 10 min) HMFCFA is stable in basic conditions and does not undergo any degradation. It is also a fact that only aldehydes can undergo the Cannizzaro reaction, with HMF and FFCA involved in the self-oxidation reduction process. Nevertheless, the fast oxidation of FFCA

to FDCA prevents FFCA degradation, which is the only process of byproduct formation attributed to the HMF molecule. Therefore, once HMF disappears from the media, the probability of Cannizzaro reaction and further polymerization decreases exponentially.

At this point, it is also interesting to evaluate the possible contribution of the bare support to the reaction. Table 2 compares HMF conversion and product selectivity over AuAl, bare Al, and in a blank reaction (absence of support with the same reaction conditions). The comparison between AuAl and Al (Table 2, entries 1 and 2) clearly shows that without gold the oxidation reaction is virtually inexistent, leading to a very low HMFCa selectivity (8%) and high byproduct selectivity (92%) for 57% HMF conversion. These results are very similar to those obtained without a catalyst for the blank experiment under the same reaction conditions (Table 2, entry 3). Therefore, it is possible to state that the support is not contributing to the overall oxidation process in a separate manner when gold is absent, but is only useful for nanoparticle stabilization.

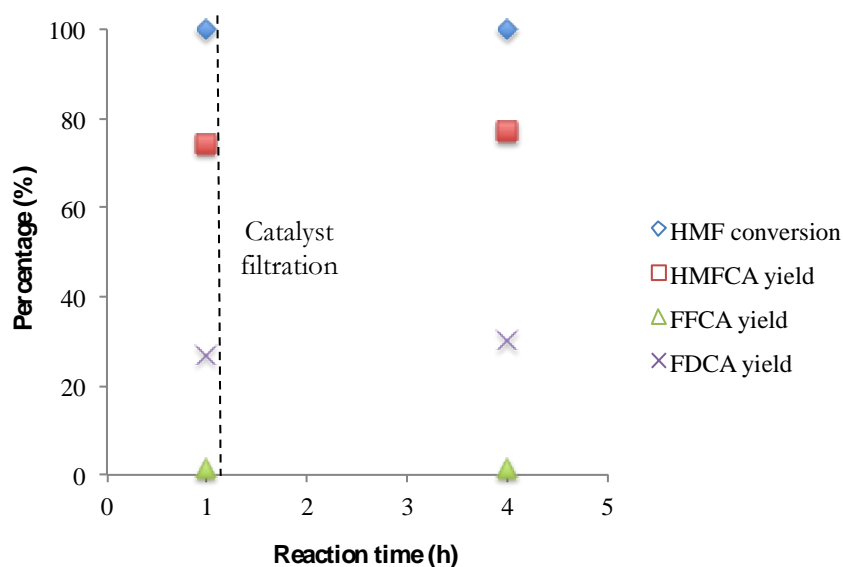
**Table 2.** Comparison of the selectivity to different products over AuAl, bare Al and in absence of catalyst

Entry	Catalyst	HMF conversion (%)	HMFCa selectivity (%)	FFCA selectivity (%)	FDCA selectivity (%)	Byproducts selectivity (%)
1	AuAl	100	29	1	70	0
2	Al	57	8	0	0	92
3	None	67	8	0	0	92

Reaction conditions: HMF:NaOH 1:2, 70 °C, 10 bar O<sub>2</sub>, 240 min, 400 rpm

It is known that some gold leaching can occur in a liquid phase reaction, while the lixiviated gold may catalyze HMF (or intermediate) transformation [33]. In order to verify the occurrence of these events, a leaching test was conducted under the standard reaction conditions explained above (Figure 3). In this experiment, the reaction was stopped after the first hour of reaction, and the mixture was centrifuged and microfiltered to remove

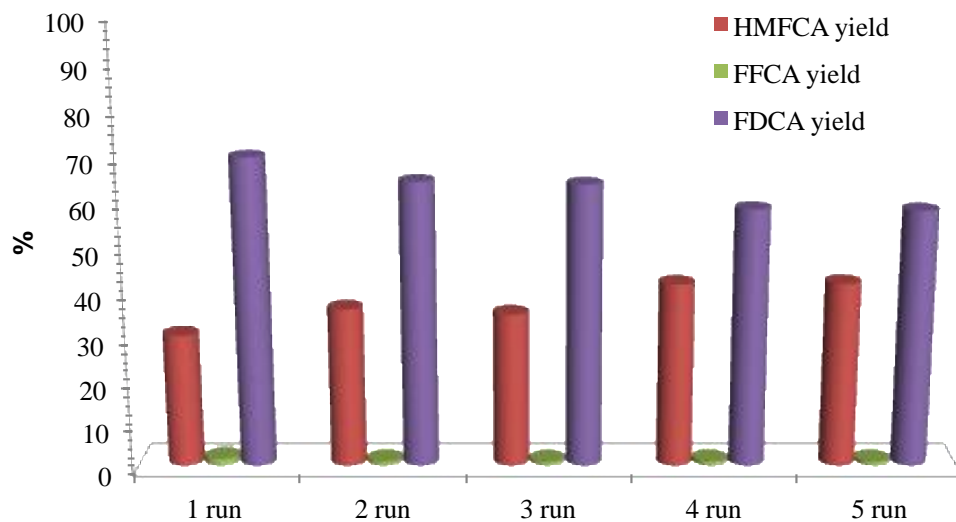
the catalyst. After analyzing the products by HPLC, the reaction mixture was charged again and oxygen was re-introduced following the usual protocol. The mixture was reacted 3 hours more to reach a total reaction time of 4 hours. As can be seen in Figure 3, the conversion and product yields remain unchanged after the first hour, thereby confirming the absence of an activity only due to the leached gold. XRF analysis of post-reaction mixtures also shows the absence of gold in the solution. However, traces of  $\text{Al}_2\text{O}_3$  were detected, indicating some support dissolution.



**Figure 3.** Leaching test. Reaction conditions: HMF: Au: NaOH molar ratio 1:0.01:2, 10 bar  $\text{O}_2$ , 70 °C, 400 rpm. After 1 h, the catalyst is removed,  $\text{O}_2$  re-introduced and the mixture re-reacted.

Several studies have reported the loss of activity for the gold-based catalysts during HMF oxidation, due to Au leaching/sintering and/or active phase blocking by a competitive absorption [17,48]. The stability of our Au/ $\text{Al}_2\text{O}_3$  catalyst was studied by reusing the solid under repeated cycles in the same HMF: Au: NaOH molar ratios. Figure 4 shows the results obtained after 5 cycles. The conversion appears to be complete in all cases (not plotted) and only product yields are presented. After 5 runs, the FDCA yield decreases

from 70 to 58% in favor of HMFCFA, indicating catalyst deactivation. As carbon balances, close to 100%, do not reflect an important carbon loss, the activity reduction should be attributed to some changes originating over the catalyst.

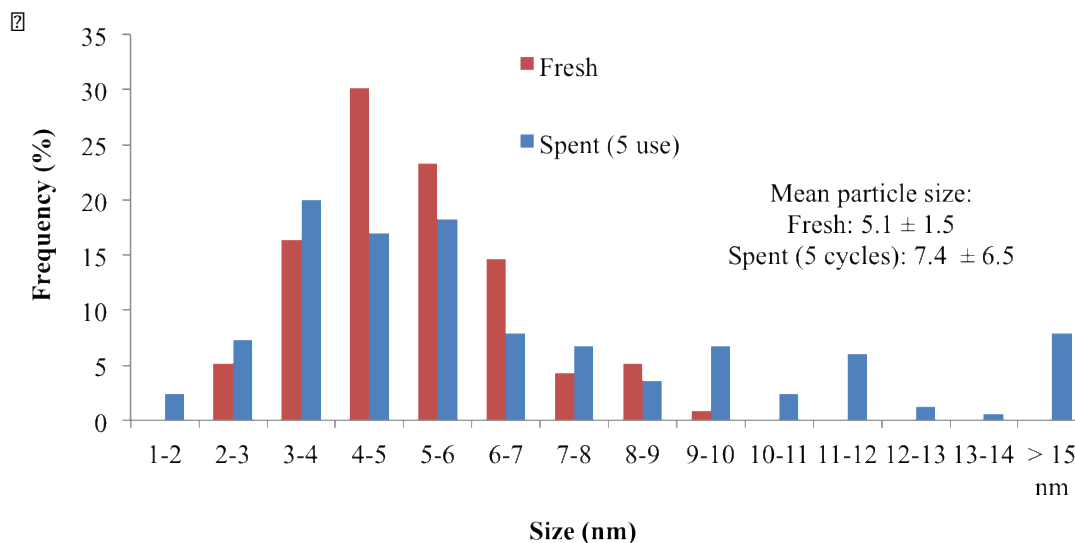


**Figure 4.** Reusability study over AuAl catalyst. Reaction conditions: HMF: Au: NaOH molar ratio 1:0.01:2, 10 bar O<sub>2</sub>, 70 °C, 400 rpm.

XRF analysis of post-reaction mixtures and solids confirm the absence of gold leaching. The post-reaction gold load is the same as it was initially. The spent sample shows an increased gold particle size as analyzed by TEM (Figure 5). The average gold particle size increases from 5.1 to 7.4 nm and is accompanied by a wider size distribution.



Although the size increase is not alarming, it appears to be the reason for the drop in FDCA yield.



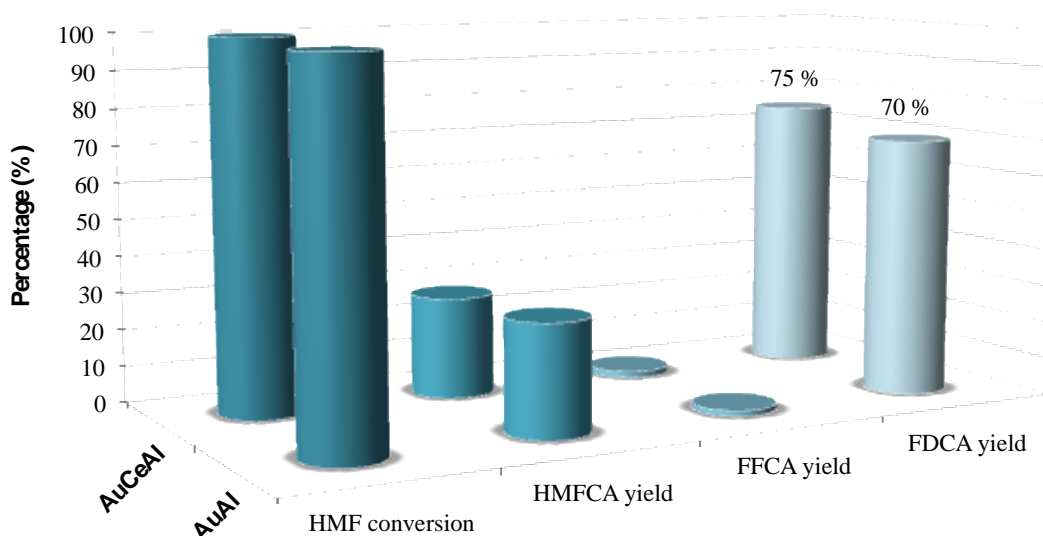
**Figure 5.** Particle size distributions of spent (after 5 cycles) and fresh AuAl.

Considering only the particle size change, one might suspect that the presence of smaller particles helps decrease the limiting step- i.e. hydroxyl group oxidation and accelerate the oxidation to FDCA. On the contrary, when Au particle size increases, the HMFCFA oxidation cannot progress and its yield increases, thus hindering FDCA formation. The latter suggests that HMFCFA oxidation is strictly size-sensitive, and the lower the gold particle size, the higher the FDCA yield.

Therefore, it is clear that metal sintering is the main problem that needs solving, and all future efforts must be focused on avoiding it.

The influence of the support modification was also investigated by using AuCeAl instead of AuAl (Figure 6). Both supports have similar structural properties but differ in gold loading and, especially, in particle size (Table 1). Gold supported on a CeAl support has

a smaller size due to the beneficial effect of the presence of ceria on gold nucleation and particle stabilization [49].



**Figure 6.** Influence of support modification in the HMF oxidation reaction. Reaction conditions: HMF: Au: NaOH molar ratio 1:0.01:2, 10 bar O<sub>2</sub>, 70 °C, 400 rpm.

HMF conversion is complete in both cases, suggesting that the support nature does not affect it. Conversely, product yield and distribution are affected. The presence of ceria (20 wt.%) seems to promote FDCA formation, leading to a 75% yield instead of 70% for the AuAl sample. This result seems logical, because the FDCA yield depends on the greater gold particle size for highly dispersed particles. Furthermore, it has been reported that CeO<sub>2</sub> is particularly effective for the oxidation of alcohols to the corresponding aldehyde [50]. In fact, the role of the CeO<sub>2</sub> support in gas phase reactions is normally correlated to oxide capacity for activating molecular oxygen and transferring it to the metal [51]. Although the exact role of ceria-containing solids remains unclear in liquid-phase reactions, an analogous behavior, as suggested by Corma et. al., is generally accepted [17]. Nevertheless, in aqueous media the collaborative effect of gold and ceria

might involve different oxygen species (hydroxyl or superoxide ions). This is an interesting starting point for some future research.

#### **4. Conclusions**

The Au/Al<sub>2</sub>O<sub>3</sub> catalyst was easily prepared by the direct anionic exchange (DAE) method and tested in a HMF oxidation reaction. High activity and selectivity are observed in mild conditions, highlighting the production of >99% FDCA yield after 4 hours by using only 4 equivalents of NaOH at 70°C. Au/Al<sub>2</sub>O<sub>3</sub> superiority after the comparison with similar gold-based systems might be related to the different catalyst preparation method and, more specifically, to the stronger Au-support interaction originated. Unlike the colloidal methods assisted by surfactants, the DAE method enables the fast and direct interaction between gold species while the support remains unchanged after the calcination step, thus leading to a very efficient and active catalyst for HMF oxidation. The stability/reusability study of the catalyst in 5 subsequent cycles shows both a slight deactivation in terms of FDCA yield (12% from 1<sup>st</sup> to 5<sup>th</sup> cycle) and an unaltered HMF conversion (always 100%). Particle sintering was confirmed as the main problem to be solved. Alumina modification with ceria (20 wt.%) leads to an increased FDCA yield, which is attributed to the particle size stabilization and to ceria's ability to undergo fast Ce<sup>4+</sup>/ Ce<sup>3+</sup> redox cycles, resulting in greater oxygen mobility.

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