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# Selective oxidation of 5-hydroxymethyl-2-furfural over TiO<sub>2</sub>-supported gold–copper catalysts prepared from preformed nanoparticles: Effect of Au/Cu ratio

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#### 1. Introduction

One of the most important sources of biomass is represented by sugars, which are widely available and easily transformed. Homogeneous dehydration of glucose and/or fructose leads to the formation of 5-hydroxymethyl-2-furfural (HMF) which is a key precursor for the synthesis of chemicals that have applications within the pharmaceutical and polymer industries [1,2]. Moreover, HMF can also be oxidized to 2,5-furandicarboxylic (FDCA) acid, which has been recently proposed as a possible surrogate for terephthalate acid [3,4]; the monomer used for the production of terephthalate plastic (PET).

The synthesis of FDCA from HMF has been widely studied in the last two decades using different catalysts and reaction conditions. In particular, supported Au nanoparticles have been found to be very active catalysts for FDCA synthesis and many researchers have focused their attention in searching for the best supports, reaction conditions and mechanistic studies to improve the yield of the FDCA

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#### ABSTRACT

5-Hydroxymethyl-2-furfural (HMF) oxidation to furandicarboxylic acid (FDCA) was performed under mild reaction conditions using TiO<sub>2</sub>-supported Au and Au–Cu catalysts synthesized from pre-formed nanoparticles of different composition. Catalysts were characterized by BET, XRD and XPS. The Au<sub>3</sub>Cu<sub>1</sub>/TiO<sub>2</sub> catalyst exhibited the best catalytic performance for FDCA yield. Moreover, after reaction, bimetallic Au–Cu catalysts with high gold content can be recovered by filtration and reused without significant loss of activity and selectivity; whereas, the monometallic gold materials are not stable.

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[5–10]. Nevertheless, despite this activity, process productivity and, in particular, catalyst stability remains very low.

Recently, we demonstrated that bimetallic gold-copper nanoparticles supported on titania were excellent catalysts for the oxidation of 5-hydroxymethyl-2-furfural to furandicarboxylic acid [11]. A strong synergistic effect was evident with the addition of Cu to Au, especially in terms of sample stability and resistance to poisoning. Moreover, obtained results emphasize the importance of the bimetallic catalyst synthesis procedure in order to achieve the desired Cu promotional effect on Au.

Herein, we report a detailed investigation of the selective oxidation of 5-hydroxymethyl-2-furfural over TiO<sub>2</sub>-supported gold–copper catalysts prepared from preformed nanoparticles. In particular, we investigate the effect of the copper–gold ratio on the structure and activity of the prepared catalysts.

#### 2. Experimental

#### 2.1. Catalyst preparation

Au/TiO<sub>2</sub>, Cu/TiO<sub>2</sub> and Au–Cu/TiO<sub>2</sub> catalysts were prepared by immobilization on the TiO<sub>2</sub> surface of the preformed monometallic and bimetallic colloids. Mono and bimetallic nanoparticles were prepared using the method previously developed [12–14]. In brief, to a solution of  $\beta$ -D-glucose in water was added the necessary



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#### Table 1

Structural parameters and chemical composition of the  $\rm Au/TiO_2$  and  $\rm Au-Cu/TiO_2$  prepared catalysts.

Catalyst	Total metal loading (%, wt/wt)	Surface area (m²/g)	Au crystallite size (nm)ª	
TiO <sub>2</sub>	0	83	-	
0.5Au-Ti	0.5	78	n.d.	
1.0Au-Ti	1.0	74	6.0	
2.0Au-Ti	2.0	73	6.5	
0.5Au1Cu1-Ti 1.0Au1Cu1-Ti 2.0Au1Cu1-Ti	0.5 1.0 2.0	74 73 58	n.d. 4.0 5.0	
1.5Au-Ti	1.5	74	6.5	
1.5Au₃Cu₁-Ti	1.5	72	5.0	
1.5Au <sub>1</sub> Cu <sub>1</sub> -Ti	1.5	64	5.0	
1.5Au1Cu3-Ti	1.5	60	5.0	

n.d. = not detectable.

<sup>a</sup> Estimated from XRD.

quantity of PVP used as nanoparticle stabilizer. The solution was then heated to 95 °C. At this temperature NaOH and an aqueous solution containing the metal precursors (HAuCl<sub>4</sub> and CuSO<sub>4</sub>·5H<sub>2</sub>O) in the desired ratio were added and stirred for 2.5 min. The ratio among PVP,  $\beta$ -D-glucose, NaOH and metals was optimized for each gold and copper content [11,15].

Before use, the as-prepared sols were concentrated and washed with distilled water using 50 kDa Amicon Ultra filters (Millipore) to eliminate the excess PVP and other reagents dissolved in the aqueous media. The Au and Au-Cu colloids were then impregnated into TiO<sub>2</sub>. Two series of bimetallic samples were prepared. In one of them the nominal ratio Au:Cu was maintained at 1:1 and the total metal loading was varied from 0.5 to 2.0 wt%. In the other series, the total metal loading was maintained at 1.5 wt% while the ratio Au:Cu was varied from 3:1 to 1:6 on a molar basis. For all samples the solvent was evaporated by thermal treatment at 120 °C. The catalyst samples are denoted as zAu-Ti, zCu-Ti and  $zAu_xCu_y$ -Ti, where z refers to the total metal content in the material and x and y refer to the Au:Cu molar ratio (i.e., 1.5Au<sub>1</sub>Cu<sub>1</sub>-Ti indicates a TiO<sub>2</sub> supported sample synthesized with 1.5 wt% total metal with a Au:Cu molar ratio of 1). The catalysts were characterized in detail by XRD, TGA, BET and XPS analysis. The corresponding precursor nanoparticles were also studied. Table 1 reports the composition and characteristic of catalysts investigated in this work.

#### 2.2. Oxidation reactions

The oxidation of 5-hydroxymethyl-2-furfural (HMF) was carried out using an autoclave (Parr Instruments) reactor of 300 mL capacity and equipped with a mechanical stirrer (0-1200 rpm) and provision for measurement of temperature and pressure. The reactor was charged with an aqueous solution (25 mL distilled water) containing the appropriate amount of 5-hydroxymethyl-2-furfural, base (NaOH) and catalyst (HMF/metal molar ratio = 100). The autoclave was purged 3 times with  $O_2$  (5 bar) and then pressurized at 10 bar. If not differently indicated, the temperature was increased to 60 °C and the reaction mixture was stirred at ca. 1000 rpm for 4 h. At the end of the reaction, the reactor was cooled to room temperature and the solution was filtered. Then, 4 mL of water was added to an aliquot of the reaction solution (1 mL) before analysis with an Agilent Infinity 1200 liquid chromatograph equipped with a Aminex HPX 87-H  $300 \text{ mm} \times 7.8 \text{ mm}$  column using a 0.005 M H<sub>2</sub>SO<sub>4</sub> solution as the mobile phase. Identification of compounds was achieved by calibration using reference commercial samples.

#### 2.3. Analytical methods

XRD measurements were carried out at room temperature with a Bragg/Brentano diffractometer (X'pertPro PANalytical) equipped with a fast X'Celerator detector, using a Cu anode as the X-ray source (K $\alpha$ ,  $\lambda$  = 1.5418 Å). For all sols and catalysts, the complete diffractogram was collected over the 10–80° 2 $\theta$  range, counting for 20 s at each 0.05° step. However, for evaluation of the metal crystallite size, a second acquisition was performed in the 2 $\theta$  range 34–47° 2 $\theta$  range, counting for 1500 s at each 0.08 step. In fact, the coherence length of the Au crystalline domains was evaluated through single line profile fitting of the reflection at 2 $\theta$  38.2° or 44.3°, since at this last angle no overlap with the anatase pattern of the support was observed. Crystallite size values were calculated using the Scherrer equation from the full width at half maximum intensity measurements.

Particle size distribution, based on hydrodynamic diameter, was evaluated at 25 °C by dynamic light scattering by using a Zetasizer Nano ZS (Malvern Instrument, UK) equipped with a He–Ne laser (wavelength 633 nm). Solution were filtered through nylon filters with a pore size of 0.45  $\mu$ m (Minisart NY). Hydrodynamic diameter includes both the coordination sphere and the species adsorbed on particle surface, such as stabilizers, surfactants and so forth. DLS analysis provides also a polydispersion index parameter (PDI), ranging from 0 to 1, quantifying of the colloidal dispersion degree.

Catalyst surface areas were measured by  $N_2$  physisorption apparatus (Sorpty 1750 CE instruments) and single point BET analysis methods, in which samples were pre-treated under vacuum at 100 °C.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD spectrometer. Data were acquired using a monochromatic Al source, operating at 120 W. All spectra were acquired using the Kratos immersion lens system for charge compensation, and the hybrid spectroscopy mode at pass energies of 40 and 160 eV for high resolution and survey scans respectively. Data were calibrated to the C 1s line at 284.8 eV, attributable to adventitious carbon and quantified using CasaXPS<sup>TM</sup> v2.3.15, using sensitivity factors supplied by the manufacturer.

To verify the behavior of different samples under thermogravimetric analysis TGA was obtained using a Rheometric Scientific STA1500 analyzer while heating the sample in air from 25°C to 600°C.

#### 3. Results and discussion

## 3.1. Colloidal characterization of preformed Au and Au/Cu nanoparticles

The preparation of gold and gold–copper materials by the reduction of HAuCl<sub>4</sub> and CuSO<sub>4</sub>·5H<sub>2</sub>O with  $\beta$ -D-glucose yielded nanoscale particles suspended in water. The resulting colloidal suspensions were stable for several weeks. Laser diffraction investigation (DLS) was applied to examine the particle diameter and the particle size distribution in suspension. These data can strongly differ from that obtained by XRD or TEM due to the different analytical techniques used, which provide information on the size of the diffracting nanocrystals (XRD) and on the hydrodynamic diameter of the scattering object, including the eventual amorphous surface layer and the solvation sphere (DLS) [16].

As an example of our results, Fig. 1 reports DLS analysis for Au/Cu samples at different Au:Cu atomic ratio. For gold and gold/copper suspensions, up to Au:Cu atomic ratio 1:1, a relatively monodispersed signal, with an averaged diameter of 17–20 nm, was detected. Increasing the copper content leads to polydispersed particles with larger dimensions. Table 2 summarizes DLS data on



synthesized samples and confirms that the average particle diameter of suspensions mainly depends on Cu content. Moreover, as indicated by the polydispersity index (PDI), the size distribution is closely related to the average particle diameter: the larger the particle diameter, the broader the particle size distribution. Actually these results seems to indicate that aqueous sols, up to Au:Cu atomic ratio 1:1, are predominantly constituted by homogeneous bimetallic nanoparticles with an unimodal particle size distribution while increasing the copper content in the sols causes the formation of aggregates or nanoclusters with inhomogeneous size and/or composition.

XRD patterns for Au/Cu dried nanoparticles with different Au:Cu atomic ratio (Fig. 2) show the characteristic peaks of gold as well as the peak broadening typical of nano-sized crystallites.

These patterns, enlarged to highlight the 1 1 1 reflections of gold at  $2\theta = 38.2^{\circ}$ , are consistent with single-phase fcc structure, with no observable impurities of CuO<sub>x</sub> of phase-segregated metals up to Au<sub>1</sub>Cu<sub>3</sub> sample. For the sample with the higher Cu content (Au<sub>1</sub>Cu<sub>6</sub> material) the presence of  $2\theta = 43.1^{\circ}$  reflection suggests the formation of segregated metallic copper.

Compared to the monometallic gold sample, bimetallic nanoparticles show a shift of the reflections toward higher  $2\theta$  values with increasing the Cu content. This shift is consistent with the alloying of gold and copper. Moreover, the bimetallic materials give broader XRD peaks, suggesting that the Au/Cu system has a smaller crystallite size than the monometallic one. In effect, crystal size values (Table 2) estimated using the Scherrer equation indicated ~4 nm for gold and ~3–3.5 nm for Au/Cu sols, confirming the coarser size of the monometallic system. These results were also confirmed by TEM analysis on supported samples [11] that indicated a particle size decreases when introducing Cu into the Au nanoparticles.

#### Table 2

Particles size distribution estimated by DLS (d-DLS) and XRD (d-XRD) analysis on prepared sols.

Sol	d-DLS (nm)	PDI	d-XRD (nm)
Au	21	0.20	4.0
Au <sub>3</sub> Cu <sub>1</sub>	17	0.22	4.0
$Au_1Cu_1$	18	0.27	3.5
Au <sub>1</sub> Cu <sub>3</sub>	20	0.37	3.0
Au <sub>1</sub> Cu <sub>6</sub>	120	0.45	n.d.

n.d. = not detectable.



**Fig. 2.** XRD data for all Au and Au/Cu preformed nanoparticles. The vertical lines correspond to the  $(1 \ 1 \ 1)$  peak position for Au. Legend: (a) Au sol; (b) Au<sub>3</sub>Cu<sub>1</sub> sol; (c) Au<sub>1</sub>Cu<sub>1</sub> sol; (d) Au<sub>1</sub>Cu<sub>3</sub> sol; (e) Au<sub>1</sub>Cu<sub>6</sub> sol.

#### 3.2. Catalyst characterization

XRD, BET, TGA and XPS have been used to determine the structure and morphology of the gold and gold/copper nanoparticles deposited on TiO<sub>2</sub>. The structural properties of the Au/TiO<sub>2</sub> and Au–Cu/TiO<sub>2</sub> catalysts are shown in Table 1. In the case of Au/TiO<sub>2</sub>, the surface area values are very similar to the TiO<sub>2</sub> support, indicating that deposition of the gold sol did not produce a significant change in the total porosity. On the other hand, immobilization of the bimetallic colloid induces a more significant decrease in catalyst surface area. The effect of active phase content on this parameter is evident and the BET surface area data are linearly correlated with the total metals loading and on copper content in the active phase, showing a significant decrease for samples with higher metals content.

Fig. 3 compares the weight loss analysis for prepared samples. The minor weight loss at temperatures lower that 100 °C corresponds to the release of adsorbed water while the more significant



**Fig. 3.** Thermogravimetric analysis in air of  $TiO_2$  supported catalysts with different Cu:Au atomic ratio. (1) Au– $TiO_2$ ; (2)  $1.5Au_3Cu_1$ –Ti; (3)  $1.5Au_1Cu_1$ –Ti; (4)  $1.5Au_1Cu_3$ –Ti.



**Fig. 4.** XRD patterns of the TiO<sub>2</sub> supported catalysts with different gold:copper atomic ratio. (a) 1.5Au-Ti; (b) 1.5Au<sub>3</sub>Cu<sub>1</sub>-Ti; (c) 1.5Au<sub>1</sub>Cu<sub>1</sub>-Ti; (d) 1.5Au<sub>1</sub>Cu<sub>3</sub>-Ti. In the insert: magnification of the reflection at  $2\theta$  44.3°; utilized to evaluate the Au crystal size.

weight loss observed between 200 °C and 400 °C can be assigned to the decomposition of the organic capping agent (PVP) and reducing agent (glucose) chemisorbed onto the catalysts surface [17–19]. Weight loss significantly increases by increasing the Cu content in the active phase and can be related to the higher amounts of stabilizer and glucose necessary to synthesize sols at higher Cu:Au atomic ratio.

A typical series of XRD patterns for the prepared systems is shown in Fig. 4 that represents the XRD pattern for sample at 1.5 wt% total metal content and increasing Au/Cu ratio. Comparison with the pattern of pure titania reveals that most of the reflections stem from the support (anatase TiO<sub>2</sub>). For all catalysts, a high metal dispersion was observed since, in addition to the titania reflections, only weak and broad peaks corresponding to the most intense metallic gold reflection were detected at 44.3°. This reflection can be assigned to the (2 0 0) plane of fcc gold. The average size of gold nanoparticles, as calculated from this reflection using the Scherrer equation, is given in Table 1. As a general observation, these results indicated that the impregnation of the Au and Au/Cu sols on TiO<sub>2</sub> support generates a high metal dispersion despite of the fact that partial aggregation, difficult to avoid during the deposition



**Fig. 5.** Au 4f XPS spectra of the monometallic Au/TiO<sub>2</sub> catalysts (normalized to the same intensity). (a) 0.5Au–Ti, (b) 1.0Au/Ti, (c) 1.5Au/Ti, (d) 2.0Au–Ti.

process, leads to a slightly higher mean particle size in comparison to preformed nanoparticles.

Results of the XPS characterization of the titania-supported nanoparticles are presented in Table 3 and Figs. 5–7. Analysis of the Au 4f region for both monometallic and bimetallic samples encompassed the range 83.2–83.8 eV, this range is consistent with the Au(0) oxidation state [20,21]. The majority of the reported energies (Table 3) are lower than that for bulk gold (*ca.* 84 eV), and while a shift lower (*ca.* –0.3 eV) is indicative of the lower coordination of gold atoms, the lower bound of this range is indicative of the rounded nature of the metallic Au nanoparticles [22], and consistent with the microscopy data presented in our previous work [11]. The lower binding energy observed for the Au 4f<sub>7/2</sub> for the Au–Cu supported materials could be due to the following reasons: (i) the



Fig. 6. Cu 2p<sub>3/2</sub> XPS spectra of the bimetallic Au-Cu/TiO<sub>2</sub> catalysts (normalized to the same intensity). (a) 0.5Au<sub>1</sub>Cu<sub>1</sub>-Ti, (b) 1.0Au<sub>1</sub>Cu<sub>1</sub>-Ti, (c) 1.5Au<sub>1</sub>Cu<sub>1</sub>-Ti, (d) 2.0Au<sub>1</sub>Cu<sub>1</sub>-Ti.

Table 5	
XPS binding energies of Au/TiO2 and Au-Cu/TiO	$O_2$ catalysts.

Samples	BE Au 4f <sub>7/2</sub>	Oxidation state	BE Cu 2p <sub>3/2</sub>	Oxidation state	%Au	%Cu	Au/Cu
0.5%Au/TiO <sub>2</sub>	83.6	Au(0)	0		1.25	0	
1%Au/TiO <sub>2</sub>	83.7	Au(0)	0		2.44	0	
1.5%Au/TiO2	83.8	Au(0)	0		4.08	0	
2%Au/TiO <sub>2</sub>	83.7	Au(0)	0		5.18	0	
0.5%(AuCu)/TiO2	83.2	Au(0)	931.9 (82), 932.6 (18)	$Cu(0) Cu(\delta^+)$	0.78	0.57	1.36
1%(AuCu)/TiO2	83.3	Au(0)	931.6 (67.2), 932.9 (32.8)	$Cu(0) Cu(\delta^+)$	1.44	0.84	1.71
1.5%(AuCu)/TiO <sub>2</sub>	83.6.0	Au(0)	931.7 (66.7), 932.4 (33.3)	$Cu(0) Cu(\delta^+)$	1.63	1.63	1.0
2%(AuCu)/TiO2	3.7	Au(0)	931.9(67.0),933.2 (33.0)	$Cu(0) Cu(\delta^+)$	2.07	1.16	1.78

smaller particle size of the Au-Cu particles as it has been observed by Makee and co-workers [20] and (ii) electron transfer from copper to gold atoms. The later can be explained as gold is more electronegative than copper according to Pauling's electronegativity table therefore we could expect some electron transfer shifting of gold core levels toward lower binding energies [23,24]. However, the Cu 2p peak centered at ca. 932 eV is lower than the expected bulk value (932.7 eV) and that observed for smaller clusters of Cu [25] and this contradicts the explanation of an electron transfer from copper to gold. In view of this, we suggest that the dominant factor for the lower core level observed for Au  $4f_{7/2}$  is mainly due to the smaller particle size of the Au-Cu particle. While the FWHM of the Cu  $2p_{3/2}$  peak is almost twice that of, for example the corresponding O 1s, Ti 2p and Au 4f (FHWM ~ 1.1 eV), this could possibly in part be attributed to broadening of the Cu signal within the Au-Cu intermetallic [26], coupled with possible oxide formation which would present as a shoulder to the higher binding energy side, suggesting that the major component is metallic Cu within a Cu-Au alloy, whereby the shift is a result of charge transfer between the Cu and Au atoms within the alloy [27]. This is consistent with HRTEM data wherein a Cu/Au alloy in bimetallic samples was confirmed [11]. The weak Cu 2p signal precludes identification of any Cu(II) species from shake-up structure and similarly a direct identification of the oxidation state using the Auger parameter while in principle is possible, in practice for low-loading supported catalysts it is difficult due to the very weak Auger LMM signal and possible X-ray induced reduction of the ionic species.

#### 3.3. Catalytic tests

The partial oxidation of 5-hydroxymethyl-2-furfural (HMF) over the Au–Cu nanoparticles supported on  $TiO_2$  resulted in the formation of 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) and furandicarboxylic acid (FDCA) (Scheme 1). In some reactions, byproducts derived from HMF degradation were observed, this being an indication of the low activity of catalysts for HMF oxidation. In addition, the repeated absence of the 5-formyl-2-furancarboxylic acid intermediate (FFCA) in our experiments seems to confirm that the oxidation of the hydroxyl group in 5-hydroxymethyl-2-furfural is the rate limiting step of the reaction while FFCA, if formed, is quickly transformed to FDCA.

In our studies catalytic tests over  $1.5Au-TiO_2$  and  $1.5Au_1Cu_1-TiO_2$  samples at different metal loadings were firstly carried out. The next step was the catalytic study of bimetallic samples with different Au-Cu contents and the same total metal loading (1.5%), in order to evaluate the effect of nanoparticles composition on the reaction.



Fig. 7. Au 4f XPS spectra of the bimetallic Au-Cu/TiO<sub>2</sub> catalysts (normalized to the same intensity). (a)  $0.5Au_1Cu_1$ -Ti, (b)  $1.0Au_1Cu_1$ -Ti, (c)  $1.5Au_1Cu_1$ -Ti, (d)  $2.0Au_1Cu_1$ -Ti.

Fig. 8 shows the comparison in catalytic activity of monometallic and bimetallic samples, containing 0.5-1.5 wt% of total metal content, at different active phase loadings. The reaction was performed under optimized conditions:  $60 \,^{\circ}$ C, 240 min, 10 bar of oxygen pressure, HMF:metal loading:NaOH molar ratio 1:0.01:4 [11].

It is worth noting that at the end of 4h reaction time, total conversion of HMF was obtained with all catalysts. Nevertheless, from reported results, it is evident that bimetallic Au-Cu materials display improved yield to FDCA with respect to their corresponding monometallic catalysts. Moreover, the optimum Au-Cu weight loading for the highest FDCA yield was 1.5% metal on the titania support. Taking into account crystallite size data for the bimetallic samples, an increase of metal loading did not affect significantly the mean metal particle size. The mean particle size for the 0.5-2 wt% Au-Cu/TiO<sub>2</sub> catalyst is in the range 4–5 nm. Hence, considering that the metal particle size is similar the observed difference in activity, should be more related to either the Au/Cu surface composition or the oxidation state of Au and Cu. XPS data revealed that the most active bimetallic catalyst (1.5 wt%Au-Cu/TiO<sub>2</sub>) was characterized by a Au/Cu=1 surface composition, with gold in metallic state and the majority of Cu species in the presence of Cu(0) and  $Cu(\delta^+)$ , whereas the surface composition of the 0.5 wt%,



Scheme 1.



**Fig. 8.** Catalytic activity for the synthesis of FDCA on supported Au ( $\blacksquare$ ) and Au/Cu ( $\Box$ ) catalysts with different metals loading. Reaction conditions: 60°C, 240 min, 10 bar of oxygen pressure, HMF:metal loading:NaOH molar ratio 1:0.01:4.

1.5 wt% and 2.0 wt% of Au–Cu/TiO<sub>2</sub> catalysts are enriched in gold (Au/Cu = 1.3–1.8). These results indicate that for obtaining the highest activity for HMF transformation there is an optimum surface composition (Au/Cu = 1) and the presence of Au in metallic state and Cu species in (0,  $\delta^+$ ) oxidation state favor selectivity toward FDCA.

Taking into account that the most active catalyst was based on the 1.5 wt% Au-Cu/TiO<sub>2</sub> catalyst with 1/1 nominal atomic ratio, the effect of Au:Cu ratios was systematically studied. Fig. 9 shows the performance of catalysts containing different Au:Cu ratios, for a metal loading of 1.5%. Also in this case, for all studied samples, after the 4h of reaction, the HMF conversion was always complete but, among these samples, strong differences appear in terms of product selectivity. In particular, the selectivity toward the desired product, the FDCA, increased significantly for 1.5Au<sub>3</sub>Cu<sub>1</sub> and 1.5Au<sub>1</sub>Cu<sub>1</sub> samples with respect to monometallic systems and afterwards strongly decreased as the Cu content in the catalyst formulation further increased. TOF data, calculated as moles of formed FDCA divided by reaction time (4h) and moles of Au, resulted to be  $5.5 h^{-1}$ ,  $14.5 h^{-1}$  and  $14 h^{-1}$  for  $1.5 Au_1 1.5 Au_3 Cu_1$  and  $1.5 Au_1 Cu_1$ respectively. The lack of FDCA, but also the limited formation of HMFCA and the presence of high amount of by-products (mainly consisting of oligomers) in the experiments with high copper



**Fig. 9.** Products selectivities on catalysts at different Au:Cu atomic ratios. Results are given at total conversion of HMF. Reaction conditions: 70 °C, 240 min, 10 bar of oxygen pressure, HMF:metal loading:NaOH molar ratio 1:0.01:4. Legend: (□) HMFCA, (■) FDCA, (■) by-products.



**Fig. 10.** FDCA (solid line) and HMFCA (dotted line) selectivities as a function of reaction temperature over  $1.5Au_1Cu_1$ -Ti ( $\blacktriangle$ ,  $\triangle$ ) and  $1.5Au_3Cu_1$ -Ti ( $\blacksquare$ ,  $\Box$ ) catalysts. For all reaction the HMF conversion was total. Reaction conditions: 240 min, 10 bar of oxygen pressure, HMF:metal loading:NaOH molar ratio 1:0.01:4.

content samples, suggest the prevalent degradation of HMF over these materials.

As indicated from characterization, gold nanoparticles on titania tend to be slightly larger than Au/Cu supported nanoparticles, and this may be one of the factors controlling the reactivity of these materials. Nevertheless,  $1.5Au_3Cu_1-TiO_2$ ,  $1.5Au_1Cu_1-TiO_2$ and  $1.5Au_1Cu_3-TiO_2$  have very similar mean crystallite sizes, hence the effect of active phase composition must account for the lower activity observed with the catalysts containing higher than Cu:Au = 1 atomic ratio. As a consequence, the inferior selectivity to oxidized products obtained with catalysts at high copper contents emphasises the importance of the Au:Cu ratio to achieve copper promotion on gold and suggests that Cu acts as a gold promoter and/or dispersing agent [24] only if present in a Au:Cu ratio higher than 1:1.

Catalytic experiments were also performed over the more selective catalysts  $(1.5Au_3Cu_1-TiO_2 \text{ and } 1.5Au_1Cu_1-TiO_2)$  by varying reaction temperature (Fig. 10). A strong effect of this parameter was observed on products distribution. In effect, obtained results confirmed that studied catalysts display a very high activity for the oxidation of the aldehydic functionality of HMF molecule, forming high quantity of HMFCA also at low temperature. Nevertheless, the oxidation of the primary alcohol side-chain, which is necessary to form the FDCA, presumably *via* the corresponding aldehyde (FFCA), is more demanding and proceeds with a significant rate at temperature higher than 80 °C. On both catalysts, after 4 h of reaction at 95 °C, a yield higher than 90% of FDCA was achieved. By-products were not formed in any of the studied conditions and HMF was exclusively oxidized to HMFCA and subsequently to FDCA.

Stability of the catalyst under operative conditions was evaluated by re-using it in consecutive runs. The catalyst was filtered off, washed with water and dried before the new run using fresh HMF/NaOH solution. FDCA yields during 3 runs for monometallic 1.5Au–Ti sample and bimetallic 1.5Au<sub>3</sub>Cu<sub>1</sub>–TiO<sub>2</sub> and 1.5Au<sub>1</sub>Cu<sub>1</sub>–TiO<sub>2</sub> catalysts after 4 h are shown in Fig. 11. Significant deactivation was observed on repeated tests over Au/TiO<sub>2</sub> catalyst. According to previous studies, deactivation mainly occurs due to the active phase being blocked by competitive adsorption [6]. However, this deactivation was not so evident for bimetallic samples and the stability increases, by increasing the Cu content in the active phase. The 1.5Au<sub>1</sub>Cu<sub>1</sub>–TiO<sub>2</sub> catalyst only presents a slight decrease of FDCA yield confirming the importance of Au site isolation in the bimetallic systems due to the alloying with Cu present in this material.



**Fig. 11.** Reusability study for the oxidation of HMF using 1.5Au–Ti, 1.5Au<sub>3</sub>Cu<sub>1</sub>–Ti and 1.5Au<sub>1</sub>Cu<sub>1</sub>–Ti as catalysts. FDCA yield is given at total conversion of HMF. Reaction conditions: 240 min, 60 °C, 10 bar of oxygen pressure, HMF:metal loading:NaOH molar ratio 1:0.01:4. Legend: FDCA yield during (**■**) 1° use, (**□**) 2° use and (**■**) 3° use.

#### 4. Conclusions

We have characterized and studied the activity for HMF oxidation to FDCA of TiO<sub>2</sub>-supported Au and Au-Cu catalysts. The catalysts were synthesized from pre-formed nanoparticles via colloidal methods of different compositions. The presence of Cu, which by itself was not active in the desired reaction, allowed a remarkable increase of the catalytic performance with respect to the Au-only catalyst. This could be attributed to the generation of alloyed bimetallic nanoparticles in the range 2-6 nm. The catalyst containing 1.5 wt% of total metal and an Au/Cu atomic ratio of 3/1 presented the best catalytic activity, which allowed an efficient transformation of the intermediate HMFCA into FDCA, which is the rate limiting step of the process. Additionally, the Cu/Au mixed systems improve reusability of the catalyst recovered by filtration; in fact, the loss of activity of the reused Au-Cu catalysts was much lower than that shown by the monometallic Au material. In addition, the stabilization effect due to Cu presence in the active phase seems significantly connected with the Cu amount, the bimetallic system with Au/Cu atomic ratio of 1 showing the highest level of reusability.

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