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Conversion of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over Au-based catalysts: optimization of active phase and metal-support interaction.

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Abstract

In the present work a series of Au- and Au-Cu-containing catalysts based on different carriers such as TiO₂ and CeO₂ were studied with a view to increasing the activity and selectivity in 5-hydroxymethylfurfural oxidation by optimizing the interaction both between the metals and with the support. The results obtained demonstrated the high activity in HMF oxidation of monometallic gold supported on ceria and titania. Nevertheless, although the particle size of gold on both supports was comparable, Au/CeO₂ showed significantly higher activity than Au/TiO₂, thus corroborating the theory that not only the gold particle size but also the support plays a key role in HMF oxidation in the aqueous phase. Indeed, pre-made uniform nanoparticles, used for catalyst preparation, were surface-bound by poly(N-vinyl-2-pyrrolidone) – the stabilizer used during nanoparticle synthesis – whose presence proved to prevent the interaction of active phases with CeO₂, worsening the catalytic activity of both monometallic and bimetallic systems. The pre-treatment of prepared catalysts was necessary to activate the materials, by maximizing the contact between the metal and the support and thus suggesting an important role of the ceria defects on 5-hydroxymethylfurfural oxidation to 2,5-furandicarboxylic acid.

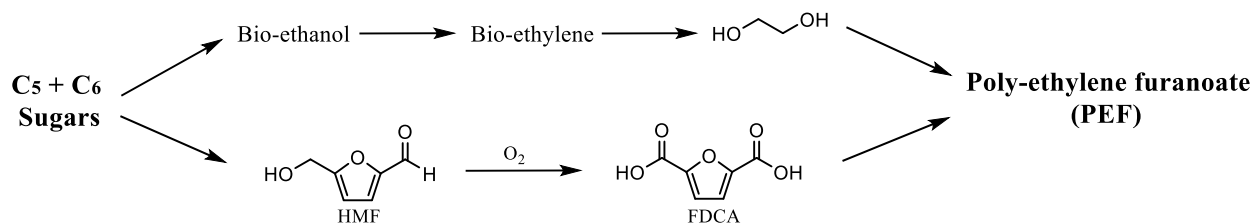
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1. Introduction

In the 21st century, the main issues related to the use of fossil fuels for the production of energy and chemicals are both their limited availability (being non-renewable) and the pollution caused by their use. Today the greenhouse effect, increased by the massive use of these non-renewable resources, is one of the world's most important problems. Biomasses are currently the most promising alternative to fossil fuels for the production of chemicals and fuels [1,2]. Nevertheless, the use of biomasses has sparked several controversies concerning ethical issues, for example the production of bio-ethanol, which uses mainly corn and sugar cane as raw materials [3]. For these reasons, today research is moving toward the use of biomasses derived from non-cultivable land and inedible raw materials, such as ligno-cellulosics [3,4].

In the transformation of biomass into chemicals, an important role is played by furfural derivatives which have functional groups in position five [6,7]. For instance, 5-hydroxymethyl-2-furfural (HMF) is a key precursor for the synthesis of derivatives with applications in the pharmaceutical and polymer industry [8-11]. It can be oxidized to obtain 2,5-furandicarboxylic acid (FDCA), a monomer for the synthesis of a new class of polymers, alternative to those obtained from terephthalic acid. The Department of Energy identifies 2,5-furandicarboxylic acid as a key platform molecule serving as a starting point for the synthesis of various polymers. The preparation of FDCA from HMF has been widely studied over the past 20 years and various methodology have been proposed for this oxidative process. Studied paths range from the use of stoichiometric oxidants, to heterogeneous metal catalysts or biochemical production [12,13]. At present, no commercial process to produce FDCA is in place. However, among others, Avantium Company is pursuing the use of FDCA to produce polyethylene furandicarboxylate (PEF) by replacing terephthalic acid, as shown in Scheme 1.

Scheme 1. The process for PFE production from monosaccharides



The exact routes utilized for HMF oxidation are not disclosed yet but likely the current technology for terephthalic acid production using cobalt-manganese-bromide catalyst is under evaluation. This system has drawbacks regarding the use of corrosive media and dangerous compounds, which make the process polluting [14-16]. Moreover, there are concerns regarding the purity of the product and of the final polymer.

Recently Au-supported catalysts have been found to be very active for HMF oxidation to FDCA [17, 18]. Many researchers have focused their attention on the study of the best supports and reaction conditions for improving FDCA yield [19-21]. Nevertheless, catalyst stability and process productivity remain low. According to the current research status, the preparation of bimetallic catalysts with controlled size and composition over different supports may be a promising way to improve catalyst activity and stability [23, 25]. Traditional synthetic techniques for supported metal catalysts typically involve the deposition of metal precursor onto high surface area supports, followed by various thermal activation treatments. Nevertheless, with bimetallic systems these methods often provide limited control over the structure and composition of bimetallic species, leading to significant compositional non-uniformity from particle to particle. The preparation of preformed colloidal nano-sols has been used for the controlled synthesis of monometallic and bimetallic catalysts [25, 26] with steric stabilizers such as polyvinylpyrrolidone (PVP) to protect the nanoparticles from excessive growth [27, 28]. Numerous examples of such catalytic systems have been documented in literature for oxidation reactions [29, 30].

In order to relate the catalytic activity with the nature of active species and the role of its interaction with the support, nanoparticle homogeneity is of crucial importance. This factor becomes even more significant when it comes to the comparison of bimetallic nanoparticles and monometallic ones. Thus, the colloidal nanoparticle size and structure control techniques become particularly advantageous in elucidating mechanisms over bimetallic catalysts.

In our previous works [23, 31] we synthesized titania-supported Au and Au/Cu species by using PVP-stabilized sols with controlled size, structure and composition prepared using an original process in water [32]. Unprecedented catalytic activity and stability was obtained with these catalytic materials in the oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid. Well-defined Au-Cu alloy nanoparticles supported on anatase TiO₂ were considerably more active

and selective toward HMF oxidation than their monometallic counterparts (i.e. Au/TiO₂ and Cu/TiO₂), which may be ascribed to Au site isolation effects caused by alloying. Moreover, reusability tests show that the Au-Cu-based catalysts were significantly more stable than gold ones [23].

In the present study, we report the preparation, characterization, and catalytic activity of CeO₂-supported Au, Cu and Au-Cu nanoparticles synthesized as metal colloids. Furthermore, we compared the established properties with those of analogous TiO₂-supported materials in order to optimize the catalyst activity in the selective oxidation of 5-hydroxymethylfurfural over these Au-based catalysts by tuning active-phase composition and metal-support interaction. Among different bimetallic catalysts, Au-Cu materials have recently attracted interest for the catalytic oxidation of CO, benzyl alcohol, and propene [33-35] and for the partial oxidation of methanol and ethanol [36,37]. Nevertheless, no systematic studies reporting the use of colloidal Cu and Au nanoparticles in the preparation of heterogeneous catalysts are available in the open literature. Therefore, further insight into the role of active-phase/metal oxide interface in HMF oxidation reaction can be obtained by using size-controlled Au and Au/Cu nanoparticles whose particle size is established before the deposition on the metal oxide support. Indeed, in this case, the effect of oxide supports in determining the size and dispersion of active phase is minimized because nanoparticles were synthesized before being immobilized on the oxide surface. Moreover, since the preparation of metal sols typically requires the use of polymer ligands to control metal nanoparticle growth and to stabilize colloids [38, 39] the effects of possible residual polymers attached to the metal surface and to the support during the immobilization process were investigated and discussed.

2. Experimental

2.1 Catalyst preparation

Au/CeO₂-, Au/TiO₂- and bimetallic Au-Cu-supported catalysts were prepared by the immobilization of preformed monometallic and bimetallic colloids on CeO₂ (VP AdNano 90, Evonik) and TiO₂ (DT51 Millennium Chemicals) surfaces. Mono and bimetallic nanoparticles were prepared using the method previously developed [23]. In brief, the necessary quantity of poly(vinylpyrrolidone) (PVP K25 Sigma Aldrich MW \approx 29000) used as a nanoparticle stabilizer

was added to a solution of NaOH in water. The solution was then heated to 95°C. At this temperature, β -D-glucose (Fluka) and an aqueous solution containing the metal precursors (HAuCl₄ and CuSO₄•5H₂O) in the desired ratio were added and stirred for 2.5 min. The ratio among PVP, β -D-glucose, NaOH, and metals was optimized for each gold and copper content [40-42]. Glucose and PVP metal ratios were selected to obtain small particle sizes with both monometallic and bimetallic sols, thus requiring a significantly higher quantity of PVP and glucose for bimetallic systems to foster particle nucleation instead of particle growth. In particular, Au, Au₃Cu₁, Au₁Cu₁, and Au₁Cu₃ sols were prepared by using PVP monomer/total metals molar ratios equal to 2.8, 5.8, 8.9, and 12, respectively. Before use, the as-prepared sols were concentrated and washed with distilled water using 50 KDa Amicon Ultra filters (Millipore) in order to eliminate the excess PVP and other reagents dissolved in aqueous media. Then Au and Au-Cu colloids were impregnated onto both TiO₂ and CeO₂ supports by maintaining the total metal loading at 1.5 wt%, while the Au:Cu ratio varied from 1:0 to 1:3 on a molar basis. For all samples, the impregnation solvent was evaporated by thermal treatment at 120°C. Some samples were calcined at 300°C. The catalyst samples are denoted as Au-S and Au_xCu_y-S, where x and y refer to the Au:Cu molar ratio and S to the support (i.e. Au₁Cu₁-Ce indicates a CeO₂-supported sample synthesized with 1.5%wt of bimetallic nanoparticles with an Au:Cu molar ratio of 1). Catalysts were characterized in detail by XRD, HR-TEM TGA, and BET analysis. To compare the catalysts with reference, monometallic Au/CeO₂ material was prepared by the deposition/precipitation method (see data reported in Figure S1). However, this method cannot be applied for the preparation of bimetallic systems. Table 1 shows the composition and characteristics of the catalysts studied in this work.

2.2 Analytical methods

Catalyst surface areas were measured by N₂ physisorption apparatus (Sorpty 1750 CE instruments) and the single-point BET analysis method, in which samples were pre-treated under a vacuum at 120°C.

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 α , λ =1.5418 Å). All catalysts were analyzed in the region of 10-80° 2 θ , counting for 20 sec at each 0.05° step. However, for the evaluation of the metal crystallite size for the supported catalysts, a second acquisition was performed in the 2 θ range 36-46°, counting

for 400 sec at each 0.03 step. In fact, the coherence length of the Au crystalline domains was evaluated through the single-line profile fitting of the reflection at 2θ 38.2° for Au-CeO₂ catalysts. Crystallite size values were calculated using the Scherrer equation from the full width at half maximum intensity measurements.

Transmission Electron Microscopy (TEM) observations have been carried out using a FEI Tecnai F20 TEM equipped with a Schottky emitter and operating at 200 keV. The instrument is equipped with a Fischione High Angle Annular Dark Field Detector (HAADF) for Scanning Transmission Electron Microscopy (STEM) investigations and with an Energy Dispersive X-Ray Spectrometer (EDX) for X-rays microanalysis. The samples were grinded in a mortar and treated with ultrasound in isopropyl alcohol. A droplet of the resulting finely dispersed suspension was evaporated at room temperature and atmospheric pressure on a holey carbon film.

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.

The oxidation behavior of different samples was studied via Temperature Programmed Oxidation using a Thermoquest TPDRO instrument under 5% O₂/He flow (20 ml·min⁻¹). The temperature was raised from 60 to 650°C with a heating rate of 10°C min⁻¹ followed by an isothermal step at 650°C for 30 min.

2.3 Oxidation of HMF

The oxidation of HMF was carried out using an autoclave reactor of 100 mL capacity, equipped with a mechanical stirrer (0–600 rpm) and measurement tools for 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 O₂ (5 bar) and then pressurized at 10 bar. If not indicated otherwise, the temperature was increased to 70°C and the reaction mixture was stirred at approximately 400 rpm for 4 h. Initial time (time zero) for the reaction was taken when the set point temperature was reached (after 15 min of heating). At the end of the reaction, the reactor was cooled down to room temperature and the solution was filtered. Then, 4 mL of water were added to an aliquot of the reaction solution (1 mL) before analysis with an Agilent Infinity 1260 liquid chromatograph equipped with a Aminex HPX-87H 300 x 7.8 mm column using a 0.005 M

H₂SO₄ solution as mobile phase. The compound identification was achieved by calibration using reference commercial samples.

3. Results and discussion

3.1 Catalysts characterization

The surface area and average Au crystal size for the prepared catalysts are listed in Table 1. Surface areas similar to supports were obtained in the case of gold supported over TiO₂ and CeO₂, thus indicating that gold nanoparticle deposition did not lead to a significant change in the texture of supporting materials. Conversely, the impregnation with bimetallic Au/Cu sols pointed out that the deposition somewhat affects the textural properties of ceria and titania, while samples with the higher Cu/Au metal ratio showed a significant reduction in surface area. This is probably due to the presence of a higher organic content in bimetallic systems. As a matter of fact, the organic layer surrounding metal nanoparticles may occlude the oxide porosity, thus leading to a decrease in the surface area. To confirm this hypothesis, the as-synthesized materials were characterized by TGA and DTA (Figures 1A and 1B). The TGA curves of the as-synthesized ceria-supported samples (Figure 1A) show two distinct weight losses; i) a lower weight loss between 50 and 150°C, due to the physically adsorbed water, and ii) a higher weight-loss, in the temperature range of 200–300°C, which is associated with an exothermal process (Figure 1B) ascribable to the burning-off of the adsorbed poly(N-vinyl-2-pyrrolidone) (PVP) in the sample. Indeed, the decomposition of PVP has been reported to occur at higher temperatures (400-600°C) in the absence of active metals [43,44], but between 200°C and 450°C in the presence of noble metals such as Pt [45]. The observed catalyst's weight loss in TG analysis increased from approximately 2 wt.% to 10 wt.% by increasing the Cu content in the materials (Table 2).

During metal sol preparation, the weight ratios of PVP to total metals varied from 2.8 to 12, while the metal loading was always equal to 1.5 wt. %; therefore, the observed increase of the weight loss may be mainly attributed to the higher amount of PVP present over samples with the highest copper content. These results are confirmed by the comparison of the weight loss observed for TiO₂-supported materials (Table 2) prepared using the same preformed sols [29], which show exactly the same trend. In addition, the exothermicity associated with the PVP decomposition significantly increased by increasing the Cu content in the active phase (Figure 1B); this trend

explains the decrease observed in the surface area of the catalysts with high copper content. Moreover, the data reported in this table show that the temperature of PVP combustion depends on the support, thus indicating that ceria promotes PVP decomposition.

Figure 2 shows XRD patterns for gold and gold/copper catalysts at different metal ratios. This analysis revealed the presence of diffraction peaks related to the CeO₂ phase in the cubic crystal structure of fluorite-type, while no peaks related to gold species were evidenced using standard XRD acquisition procedures, thus suggesting that very small gold and gold/copper nanoparticles were formed, consistent with the previous findings [31]. Nevertheless, if a more accurate XRD acquisition was used, a small broad peak at about 38.2° 2θ was evidenced, which was attributed to metallic gold and/or the Au/Cu alloy. The average diameters of the metallic particles, estimated from this peak by the Scherrer's equation, are given in Table 1. Very small Au particles were obtained in all samples.

Gold and gold/copper species over CeO₂ were investigated by high-resolution TEM imaging. Figure 3 A and B displays some representative TEM images of the Au and Au/Cu supported catalysts and the corresponding size distribution histograms. The dispersed agglomerates include ceria particles with a mean diameter of 10-15 nm. Gold and gold/copper nanoparticles are embedded in the ceria network. This study reveals a significant homogeneity in the size distribution of Au and Au/Cu particles supported over TiO₂ and CeO₂. Both metals are in close contact with the supports and dark field images (not shown) confirm that the metallic nanoparticles are evenly distributed. Au and Au/Cu nanoparticles are present an almost spherical shape with very narrow diameter distribution (5-6 nm) confirming results obtained from XRD.

3.2 Catalytic tests

HMF conversion in blank experiments

Preliminary experiments have been devoted to blank tests, by reacting HMF in an aqueous solution with HMF:NaOH ratio of 1:4, at 70°C and ambient pressure, both under air and under N₂, in the absence of any catalytic system (Figure 4). These experiments made it possible to verify that no oxidation occurred under these conditions; nevertheless, as already reported in our previous work [23] and in the recent Vuyyuru paper [46], a significant amount of 5-hydroxymethylfurfural was degraded in these basic conditions. Figure 4 shows 40% of HMF conversion at 70°C already after 10 minutes, without the formation of any detectable oxidation products. The reaction mixture

turned from colorless to yellow and then to red with the reaction time. After 30 minutes, HMF was totally converted and the solution became brownish. The formed degradation products were soluble in water at high pH (pH= 13), but they were insoluble in acidic conditions. In fact, when some drops of HCl were added, the formation of a black precipitate was observed. In these reaction conditions, aldol condensation should not be possible due to the absence of species with alpha hydrogen; therefore, the mechanism should be different from that obtained in acidic condition [47]. However, even if these degradation products are formed with a different reaction pathway, they behave like humins, which are formed in acidic conditions. Indeed, Piccolo et al. [48] have treated some organic matter in basic conditions using NaOH and obtained the precipitation of some humic acids by lowering the pH with HCl up to the value of 1.

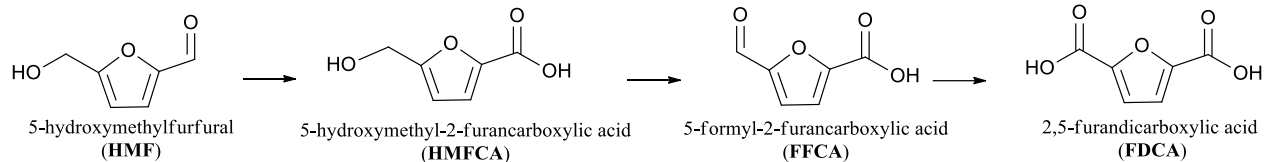
Generally, humins have coiled conformations cross-linked by weak forces such as Van der Waals bonds, but when the pH is lowered, both the formation of intermolecular hydrogen bond and the rearrangement of the conformation are observed. Probably, the HMF degradation products, obtained in basic conditions, are similar to humins and are arranged in coil conformations; at low pH values, however, these aggregates become insoluble in water and tend to precipitate, due to their rearrangement.

Scientific literature extensively reports the positive effects of the addition of homogeneous bases on the performance of HMF oxidation. Actually, the rate of HMF oxidation depends strongly on the presence of NaOH, and the base seems to promote the formation of 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA), that can be further oxidized by the metal catalyst [18]. However, in the absence of an active catalyst, the basic environment leads to the formation of by-products that cannot be easily identified. Therefore, it is important to develop active catalysts that rapidly oxidize HMF and intermediate products, thus avoiding their fast degradation in reaction conditions.

As-prepared samples: effect of active phase composition

It has been reported that the oxidation of HMF to FDCA over gold-based catalysts comprises two steps: i) the aldehyde oxidation to form HMFCFA and ii) the oxidation of the alcohol to FDCA, through the formation of 5-formyl-2-furancarboxylic acid (FFCA) as intermediate (Scheme 2) [16, 20, 21, 49].

Scheme 2. The reaction scheme in HMF oxidation to FDCA.



According to previous works, the formation of HMFCFA, via the hemiacetal [22], is a very fast reaction and it is strongly influenced by the amount of base and reaction temperature while the subsequent transformation of the HMF hydroxyl group is the rate-limiting step [49]. Furthermore, sometimes the formation of 2,5diformylfuran (DFF) has been observed, mainly in the absence of both a base and with metals other than gold [15].

Firstly the effect of Au:Cu ratios over CeO₂-supported materials was studied, for a total metal loading of 1.5% wt. (Figure 5). Results indicate that pure ceria support is inactive in the oxidation, forming very small amount of HMFCFA acid and by-products derived from HMF degradation. Conversely, the oxidation of HMF over Au and Au/Cu samples resulted in the formation of both HMFCFA and FDCA. FFCA was observed only in low reaction time tests, whereas DFF was never formed.

For all samples, after the 4 h reaction HMF conversion was always complete but remarkable differences were shown amongst catalysts in terms of products selectivity. In particular, the selectivity toward FDCA decreased significantly for Cu-containing samples compared to monometallic catalysts, due to the slower oxidation of HMFCFA. TOF data, calculated as moles of formed FDCA produced referred to reaction time (4h) and Au moles, turned out to be equal to 12.9 h⁻¹, 7.4 h⁻¹ and 11.4 h⁻¹ for Au-Ce, Au₃Cu₁-Ce and Au₁Cu₁-Ce, respectively.

These results are very different from those observed with titania-supported materials [23], where the presence of Cu in the active phase led to a considerable increase in catalytic performance compared to Au-based materials. In particular, the comparison of the effect of Cu content using TiO₂ and CeO₂ supports (Figure 6) indicates that the monometallic Au-Ce sample was the most active ceria-supported catalyst, while for titania-supported materials higher activity was observed with bimetallic systems. Indeed, the use of a CeO₂ support seems to depress the positive effect of Cu, observed in the case of TiO₂-supported catalysts

In order to discuss on the reasons for the different behaviour shown by CeO₂ and TiO₂, it must be reported that Au supported on ceria is very active in the oxidation of a variety of molecules

[50, 51]. In general, CeO₂ is known as an excellent redox support due to its superior physicochemical properties compared to conventional supports, due to both the large number of oxygen vacancies and the easy Ce⁴⁺/Ce³⁺ redox transition, with both significant oxygen mobility and storage capacity. Corma and co-workers showed that Au/CeO₂, especially in catalysts with nanocrystalline CeO₂ support, is particularly effective for the oxidation of alcohols to the corresponding aldehyde [52]. These catalysts were shown to be more active than supported Pd catalysts available at that time [53]. Later on, Corma and Iborra [49] showed that a similar catalyst was effective for the oxidation of HMF but reusable at a limited extent only.

The role of the CeO₂ support in gas-phase reactions was reported to be correlated to its capacity either to facilitate oxygen transfer to the metal so to stabilize cationic Au, or to activate molecular oxygen [54]. Moreover, several works [55-59] demonstrated that all these events, i.e., oxygen mobility, activation of O₂, and cationic Au formation system are strongly dependent on Au-CeO₂ interfacial interaction.

In this work, the synthesis of Cu-containing nanoparticles required a considerable quantity of capping agent to control the growth of particles during preparation; this led to significantly larger amounts of organics around Cu-containing nanometals, which might prevent the proper interaction between active phase and CeO₂, thus influencing the reactivity. As a matter of fact, the comparison of TPO profiles for monometallic and bimetallic samples (Figure 7) indicates that the bimetallic catalyst contains a significantly higher quantity of organics than the monometallic one. This is also confirmed by TG analysis, with the main combustion step shown at 230-240°C, while the first small peak at 150°C is ascribable to the desorption of CO₂ from the sample. This last signal is also present in the analysis of the CeO₂ support alone.

Due to the mentioned phenomena, and because a proper interaction between the active phase and the support appears to be necessary in order to maximize the efficiency of these catalysts, we concluded that the greater amount of capping agent in Au/Cu bimetallic systems might be detrimental for catalytic activity, finally being responsible for the relevant differences shown between TiO₂- and CeO₂-based systems. Indeed, the nanoparticle size effect on the activity could be excluded because the size of the preformed nanoparticles was very similar for all catalysts regardless of support type, as demonstrated by XRD and TEM analysis.

Concluding, that the activity of TiO₂-supported catalysts seems to be more influenced by the nature of the nanoparticle species. Conversely, the activity of CeO₂-supported systems is

mainly influenced by the interaction between Au and ceria; in this case, bimetallic nanoparticles were less active.

As-prepared samples: effect of reaction temperature and time

Catalytic experiments were also performed with the Au₃Cu₁-Ce catalyst by varying the reaction temperature (Figure 8), and the activity was compared with the performance shown with the TiO₂ supported system containing the same active phase. A strong effect of temperature was observed on products distribution. The results obtained confirmed that the studied catalysts display a very high activity for the oxidation of the aldehydic functionality of HMF, forming a high quantity of HMFCFA also at low temperature. Nevertheless, the oxidation of the primary alcohol side-chain, which is necessary to form FDCA via intermediate (FFCA, is more demanding and proceeds at a significant rate at temperatures higher than 80°C). In both catalysts, after 4-hour reaction at 95°C, a selectivity of FDCA higher than 90% was achieved. By-products were not detected under reported conditions, and HMF was exclusively oxidized to HMFCFA and then to FDCA.

A typical profile of products is shown in Figure 9, plotting HMF conversion and selectivities as a function of reaction time with the Au-Ce catalyst, at 95°C. In these conditions, complete conversion of HMF was obtained as soon as the reaction mixture reached the temperature of 95°C. Since neither HMFCFA nor 2,5-dihydroxymethylfurfural were formed in the absence of catalyst, the presence of the Cannizzaro reaction could be excluded [60]. A very low amount of FFCA was shown during the initial stage of the reaction, but it rapidly converted into FDCA. Indeed, the rate-determining step for FDCA production is the oxidation of the HMF hydroxymethyl group [49]. Other by-products (e.g., DFF) were not formed, and after 4 hr of reaction a very pure FDCA solution was obtained (Figure S2).

Catalyst stability and reusability

Since catalysts based on supported Au were reported to lose rapidly activity due to Au leaching and/or active phase blocking by competitive adsorption, the stability of the Au/CeO₂ and Au-Cu/CeO₂ catalysts was studied carefully. Figures 10 and 11 show the results of the reusability studies using Au-Ce (Figure 10) and Au₃Cu₁-Ce (Figure 11). Unexpectedly, both monometallic and bimetallic catalysts showed a rapid increase of activity after repeated catalytic tests. Similar

trends were not observed in the case of TiO₂-supported materials [23,31]. In fact, in our previous papers we reported that with monometallic TiO₂-supported catalysts a rapid decline of activity was shown, while bimetallic Au/Cu materials were highly stable and resistant to poisoning. Since metal leaching during HMF oxidation was excluded by chemical analysis (XRF analysis revealed that no Au, Cu, or Ce species were dissolved in the reaction mixture), the unusual activation effect shown may be attributable to a modification of the interaction between the surface of the nanoparticles and CeO₂ during the reactivity experiments.

As already discussed, it is known that the changes induced either by the support on metal particles or viceversa are mainly restricted to the atoms at the interface or at the perimeter of the nanoparticles, where the reactants can interact simultaneously with both the oxidic support and the metal catalyst. Moreover, reducible supports, such as CeO₂, can provide activated oxygen [61] and stabilize cationic gold [62]. These functions have been ruled out in gold-based catalysts when the latter are used in gas-phase reactions [63]. However, the capability of Au to activate CeO₂ is strongly improved by the interaction between the latter and metal particles, and this cooperative effect can be hindered by the presence of the residual capping agent (PVP) used.

On the other hand, it is likely that during reaction the removal of the capping agent takes place, thus increasing the support-nanoparticle interaction and leading to an increase of the activity during the repeated uses. In order to verify this hypothesis, an in-depth study of the effect of capping agent removal on Au and Au/Cu catalysts was performed.

Treated catalysts: effect of capping agent removal

Capping ligands such as surfactants and polymers are widely utilized for the synthesis of nanometals to control their size and shape [64]. Moreover, it has also been found that the ligands chemisorbed on the nanoparticles can hinder the reagents access to the active surface [65-68]. PVP is among the most commonly used capping ligands in the chemical synthesis of nanometals. The wrapping of PVP around metal nanoparticles results in a metallic core-porous PVP shell architecture with a coordination of the carbonyl group and nitrogen atom of the pyrrolidone ring with the nanoparticle. Chemisorbed ligands were found to poison the catalytic activity of metals by lowering the accessibility of reactants to the metal surface [69]; moreover, it was observed that PVP interaction with metal nano-crystals is accompanied by charge transfer [70]. This interaction can modify the structure of metal colloids, sometimes with beneficial effects on the catalytic performance [71]. Indeed, Baumer's work reports a number of benefits that such ligand shells may

have for heterogeneous catalysis, including the tuning of strong metal–support interaction (SMSI) effects [72].

Previous results obtained by our research group [23,31] demonstrated that the PVP presence over Au and Au/Cu TiO₂-supported catalysts does not prevent their activity in HMF oxidation. Nevertheless, catalysis over CeO₂-supported samples seems to indicate an important effect of the capping agent on both Au-CeO₂ and Au/Cu-CeO₂ catalysts; therefore, further experiments were conducted on these materials in order to investigate their catalytic behavior after removal of the PVP stabilizer.

Various studies have reported about the difficulties met during the removal of the residual capping agent from nanoparticles [73, 74]. Different strategies, such as chemical and thermal treatments of catalysts [75,77] may be used. We tested two different treatments with the aim of obtaining surface-clean Au and Au/Cu species over CeO₂: i) catalyst washing in autoclave using reaction conditions (T=70°C, 4h, 10 bar of oxygen pressure, with Metal:NaOH molar ratio equal to 0.01:4), but in the absence of HMF, and ii) thermal treatment at T=300°C. The results obtained are summarized in Table 3.

The washing treatment of the Au-Ce sample in reaction conditions significantly boosted the activity; indeed, FDCA selectivity over this sample increased from 47% (Table 3, entry 1) to 92% (Table 3, entry 2). Gold-supported nanoparticles retained their dimension and TPO analysis confirmed the cleaning of the catalyst surface.

Similar results (FDCA selectivity 92%) were obtained by decomposing the capping agent with thermal treatment. TG and TPO analysis demonstrated the decomposition of PVP at this temperature. Nevertheless, the average size of the gold nanoparticles, as evaluated by XRD and TEM on the calcined sample, underwent a slight increase, from 6 to 7.2 nm. This is not surprising since Au nanoparticles are frequently observed to sinter after thermal treatment carried out in order to remove the organic ligands [66]; however, the low exothermicity associated to this treatment, due to the relatively low PVP content, made it possible to limit the particle growth.

Reported results indicate that the trend observed during Au-Ce sample repeated use is related to the PVP removal during reaction, and that the metal-CeO₂ interface plays a pivotal role in the oxidation of HMF.

The same treatments were carried out with the bimetallic catalyst Au₃Cu₁-Ce. The results obtained (Table 3, entry 4 and 5) indicate that the simple washing of the catalyst did not improve

the catalytic activity at all, while the obtained FDCA selectivity remained 22% after this treatment. As previously reported, it must be pointed out that Cu-containing nanoparticles were prepared with a higher PVP amount, due to the difficulty in controlling the particle growth in preformed Au/Cu sols; therefore, this high PVP content seems to be more difficult to remove. Moreover, the affinity of PVP with Cu/Au nanoparticles might be higher, due to the ability of PVP to form complex compounds with Cu [77].

Zhang and co-workers recently studied the removal of PVP on Au nanoparticles using NaBH_4 in water [78]; they demonstrated that the hydride derived from sodium borohydride has a higher binding affinity to nanoparticles than PVP. Moreover, a redox cycle was shown to remove PVP from nanoparticles [45]. These results could explain the different activation obtained by treating Au/Cu samples in reaction conditions either with HMF (during re-use tests) or without HMF (entry 5 in Table 3); in fact, HMF oxidation may foster the displacement of PVP from the nanoparticle surface, finally inducing a higher metal- CeO_2 interaction while significantly increasing FDCA formation.

TPO analysis on $\text{Au}_3\text{Cu}_1\text{-Ce}$ samples after pre-treatment in reaction conditions (Figure 12) confirmed the incomplete removal of PVP from the catalyst surface. Although the TPO signal is significantly lower than that of the $\text{Au}_3\text{Cu}_1\text{-Ce}$ sample before treatment, indicating that the washing procedure is effective in removing most of PVP, the treatment might not completely eliminate the PVP dislocated at the interface between Au and CeO_2 , thus limiting the metal-support interaction.

Very different results were obtained after the thermal treatment of the $\text{Au}_3\text{Cu}_1\text{-Ce}$ catalyst at 300°C in air. In this case, the thermal treatment completely decomposed the stabilizer, which resulted in a significantly increased FDCA selectivity; the latter increased from 22% (Table 3 entry 4) to 41% (Table 3 entry 6). However, the very high exothermicity related to PVP combustion strongly conditioned the average size of the Au/Cu nanoparticles, which showed a considerable sintering phenomenon. In this case, the heat developed during the thermal treatment was higher than that one for Au-supported catalysts, because a higher PVP content was used to synthesize Au/Cu nanoparticles. Indeed, the particle size increased from 5 to 21 nm, making it difficult to discriminate, in the observed effect of FDCA yield increase, amongst various effects, i.e., the influence of particle size, phase segregation, and metal-oxide interface. As a matter of fact, the activity in alcohol oxidation was reported to be affected by particle size; the optimum particle size was shown to be around 3-5 nm [79-81].

Nevertheless, our data demonstrated that large Au particles (size > 20 nm) are also able to oxidise HMF with high selectivity, if a suitable interaction with the ceria support is guaranteed. These data confirm some recently reported results on the conversion of aromatic alcohols [82] over unsupported bulk Au, which showed that the interaction between the gold surface and the aromatic ring enhances the overall efficiency of the active site even in the presence of large particles .

In order to distinguish between the effect of particle size and that one derived from PVP removal, the decomposition of PVP was also obtained by calcination of the Au₁Cu₃-Ce sample at 300°C after washing in reaction conditions. The lower exothermicity, due to the lower stabilizer content, made it possible to control the particle size growth, which increased to 11 nm only, instead of 21 nm for the unwashed sample. This two-stage decomposition of PVP significantly promoted the catalyst activity, while the FDCA selectivity increased from 41% (Table 3, entry 6) to 71% (Table 3, entry 7), thus confirming the significant effect of the active phase particle size on catalytic performance.

The mechanism of HMF reaction is still a matter of debate. Davis and coworkers [83] demonstrated the important role of hydroxyls for the liquid phase oxidation of alcohols catalysed by Au; they proposed that the role of O₂ in aqueous media is an indirect one, that not involves incorporation into the acid products but instead regenerates hydroxide ions, removing the electrons from the Au surface [84]. However, no comments are reported in the literature regarding the possible role of CeO₂. Results reported here indicate that the metal-CeO₂ interface plays a pivotal role, similarly to what is observed in gas-phase reactions. Since the rate-controlling step of the reaction appears to be the oxidation of HMFCA [53], it may be proposed that ceria acts as an oxygen (or hydroxyl) pump, by releasing and adsorbing the oxidizing species through the Ce⁺⁴/Ce⁺³ redox process, as also suggested by Corma and co-workers [85]. Nevertheless, this effect is observed only in the presence of a close contact between the metal and the support, thus suggesting an important role of the ceria defects induced by the metal presence [86].

4. Conclusions

The use of preformed metal nanoparticles with well-defined size and composition supported over titania or ceria was used to explore the role of the metal–support interaction in the oxidation of HMF over Au and Au/Cu catalysts. The deposition of preformed nanoparticles is not support-dependent [87], which made it possible to investigate the support effect on the activity and

selectivity in HMF oxidation to FDCA. Results obtained demonstrate that CeO₂ is the most effective support for obtaining active and selective catalysts for FDCA synthesis. However, pre-made uniform nanoparticles, used for catalyst preparation, were surface-bound by poly(N-vinyl-2-pyrrolidone) (PVP), the organic capping agents used for nanoparticle synthesis, and the presence of this stabilizer hindered the chemical interaction between the active phase and CeO₂. Indeed, the pre-treatment of catalysts was necessary in order to remove the PVP, allow the interaction between ceria and metal nanoparticles at the interface and finally activate the catalyst, events which led to the enhancement of catalytic performance..

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Table 1. Structural parameters and chemical composition of Au and Au-Cu supported over CeO₂ and TiO₂.

Catalyst	Total metal loading (% wt.)	Gold content (% wt.)	Copper content (% wt.)	Surface Area (m ² /g)	Au crystallite size (nm)*
CeO ₂	-	-	-	89	-
Au-Ce	1.5	1.5	-	85	6.0
Au ₃ Cu ₁ -Ce	1.5	1.34	0.16	62	5.0
Au ₁ Cu ₁ -Ce	1.5	1.14	0.36	53	5.0
Au ₁ Cu ₃ -Ce	1.5	0.76	0.74	49	5.0
TiO ₂	-	-	-	83	-
Au-Ti	1.5	1.5	-	74	6.5
Au ₃ Cu ₁ -Ti	1.5	1.34	0.16	72	5.0
Au ₁ Cu ₁ -Ti	1.5	1.14	0.36	64	5.0
Au ₁ Cu ₃ -Ti	1.5	0.76	0.74	60	5.0

* estimated from XRD

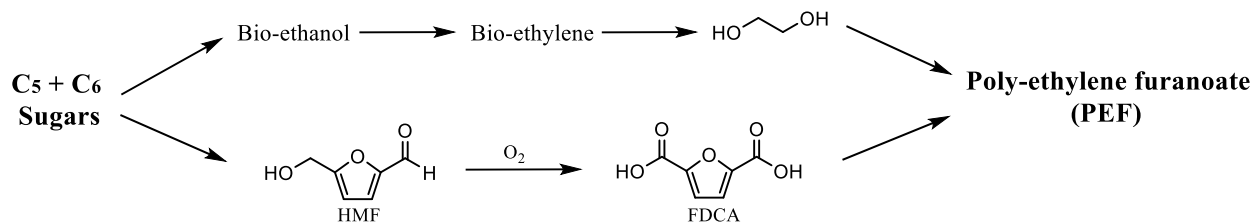
Table 2. Weight loss and PVP decomposition temperature of the Au and Au-Cu supported over CeO₂ and TiO₂.

Catalyst	T (°C)	Weight loss (%)
Au-Ce	236	1.9
Au ₃ Cu ₁ -Ce	240	3.1
Au ₁ Cu ₁ -Ce	236	5.4
Au ₁ Cu ₃ -Ce	250	9.7
Au-Ti	312	2.0
Au ₃ Cu ₁ -Ti	310	3.5
Au ₁ Cu ₁ -Ti	320	5.5
Au ₁ Cu ₃ -Ti	301	9.8

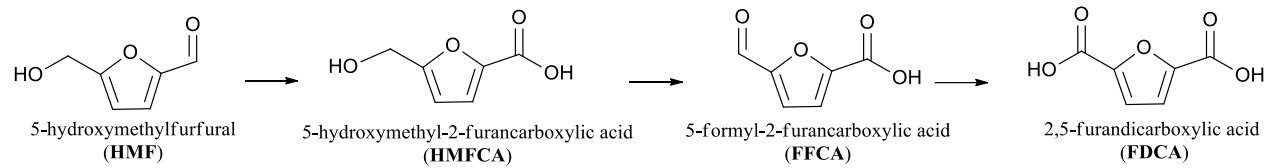
Table 3. Comparison of the selectivity to the reaction products obtained with treated and untreated catalysts (see text for details on the treatment procedure used). For all reactions the HMF conversion was total. Reaction conditions: Temperature = 70°C, reaction time 240 min, O₂ pressure 10 bar, HMF: Metal: NaOH molar ratio 1:0.01:4.

Entry	Sample	Treatment	FDCA Sel. (%)	HMFCFA Sel (%)	Active phase dimension (nm)
1	Au-Ce	As is (dried 120°C)	47	53	6.0
2	Au-Ce	Washed in reaction conditions	92	8	6.5
3	Au-Ce	Thermal treated 300°C	91	9	7.2
4	Au ₃ Cu ₁ -Ce	As is (dried 120°C)	22	78	5.0
5	Au ₃ Cu ₁ -Ce	Washed in reaction conditions	22	78	6.0
6	Au ₃ Cu ₁ -Ce	Thermal Treated 300°C	41	59	21.0
7	Au ₃ Cu ₁ -Ce	Washed in reaction conditions and thermal treated 300°C	71	29	11.0

Scheme 1. The process for PFE production from monosaccharides



Scheme 2. The reaction scheme in HMF oxidation to FDCA.



Figures

Figure 1. Thermogravimetric analysis (A) and differential thermal analysis (B) in air of CeO₂-supported catalysts with different Au:Cu atomic ratios. (1) Au-Ce; (2) Au₃Cu₁-Ce; (3) Au₁Cu₁-Ce; (4) Au₁Cu₃-Ce.

Figure 2. XRD patterns of CeO₂-supported catalysts with different Au:Cu atomic ratios. 1) Au-Ce; 2) Au₃Cu₁-Ce; 3) Au₁Cu₁-Ce; 4) Au₁Cu₃-Ce. In the insert: magnification of the reflection at 2θ 38,2° which was used to evaluate the Au crystal size.

Figure 3. Representative TEM images of the Au- and Au/Cu-supported catalysts. (A) Au-Ce sample dried at 120°C and (B) Au₃Cu₁-Ce sample dried at 120°C.

Figure 4. Effect of reaction time on HMF degradation. Reaction conditions: no catalyst, no O₂ pressure, temperature 70°C, ambient pressure, HMF:NaOH 1:4 molar ratio.

Figure 5. Product selectivity on CeO₂-supported catalysts at different Au:Cu atomic ratios. Results are given at total conversion of HMF. Reaction conditions: temperature 70°C, reaction time 240 min, O₂ pressure 10 bar, HMF:Metal:NaOH molar ratio 1:0.01:4. Legend: ■HMFCa, ■FDCA, ■by-products.

Figure 6. Comparison of FDCA selectivity on CeO₂- and TiO₂-supported catalysts at different Au:Cu atomic ratios. Results are given at total conversion of HMF. The only products observed were FDCA and HMFCa. Reaction conditions: temperature 70°C, reaction time 240 min, O₂ pressure 10 bar, HMF:Metal:NaOH molar ratio 1:0.01:4. Legend: ■CeO₂ ■TiO₂.

Figure 7. TPO analysis of CeO₂ as is (a), Au-Ce (b) and Au₃Cu₁-Ce (c) supported catalysts.

Figure 8. HMFCa (closed symbols) and FDCA (open symbols) selectivity as a function of the reaction temperature over Au₃Cu₁-Ce (■,□) and Au₃Cu₁-Ti (▲,△) catalysts. For all reactions, the HMF conversion was total. The only products observed were FDCA and HMFCa. Reaction conditions: reaction time, 240 min, O₂ pressure 10 bar, HMF:Metal:NaOH molar ratio 1:0.01:4. The insert shows the final mixture after reaction at different temperatures with Au₃Cu₁-Ti.

Figure 9. HMF conversion and products selectivity as a function of reaction time. Catalyst Au-Ce. Reaction conditions: temperature 95°C, O₂ pressure 10 bar, HMF:Metal:NaOH molar ratio

1:0.01:4. Legend: HMF conversion (●), HMFCFA selectivity (▲), FFCA selectivity (×), FDCA selectivity (◆). Initial time (time zero) for the reaction is when the temperature of 95°C was reached (after 15 min heating from a.t). The insert shows the final mixture after reaction at different times.

Figure 10. Reusability study for the oxidation of HMF using Au-Ce catalyst. HMFCFA (■) and FDCA (■) selectivities are given at total conversion. Reaction conditions: temperature 70°C, reaction time 240 min, O₂ pressure 10 bar, HMF:Metal:NaOH molar ratio 1:0.01:4.

Figure 11. Reusability study for the oxidation of HMF using Au₃Cu₁-Ce catalyst. HMFCFA (■) and FDCA (■) selectivities are given at total conversion. Reaction conditions: temperature 70°C, reaction time 240 min, O₂ pressure 10 bar, HMF:Metal:NaOH molar ratio 1:0.01:4.

Figure 12. TPO analysis of Au₃Cu₁-Ce catalysts. Legend: (a) untreated Au₃Cu₁-Ce; (b) Au₃Cu₁-Ce washed in reaction conditions; (c) Au₃Cu₁-Ce washed in reaction conditions and then calcined at 300°C.

Figure 1. Thermogravimetric analysis (A) and differential thermal analysis (B) in air of CeO₂-supported catalysts with different Au:Cu atomic ratios. (1) Au-Ce; (2) Au₃Cu₁-Ce; (3) Au₁Cu₁-Ce; (4) Au₁Cu₃-Ce.

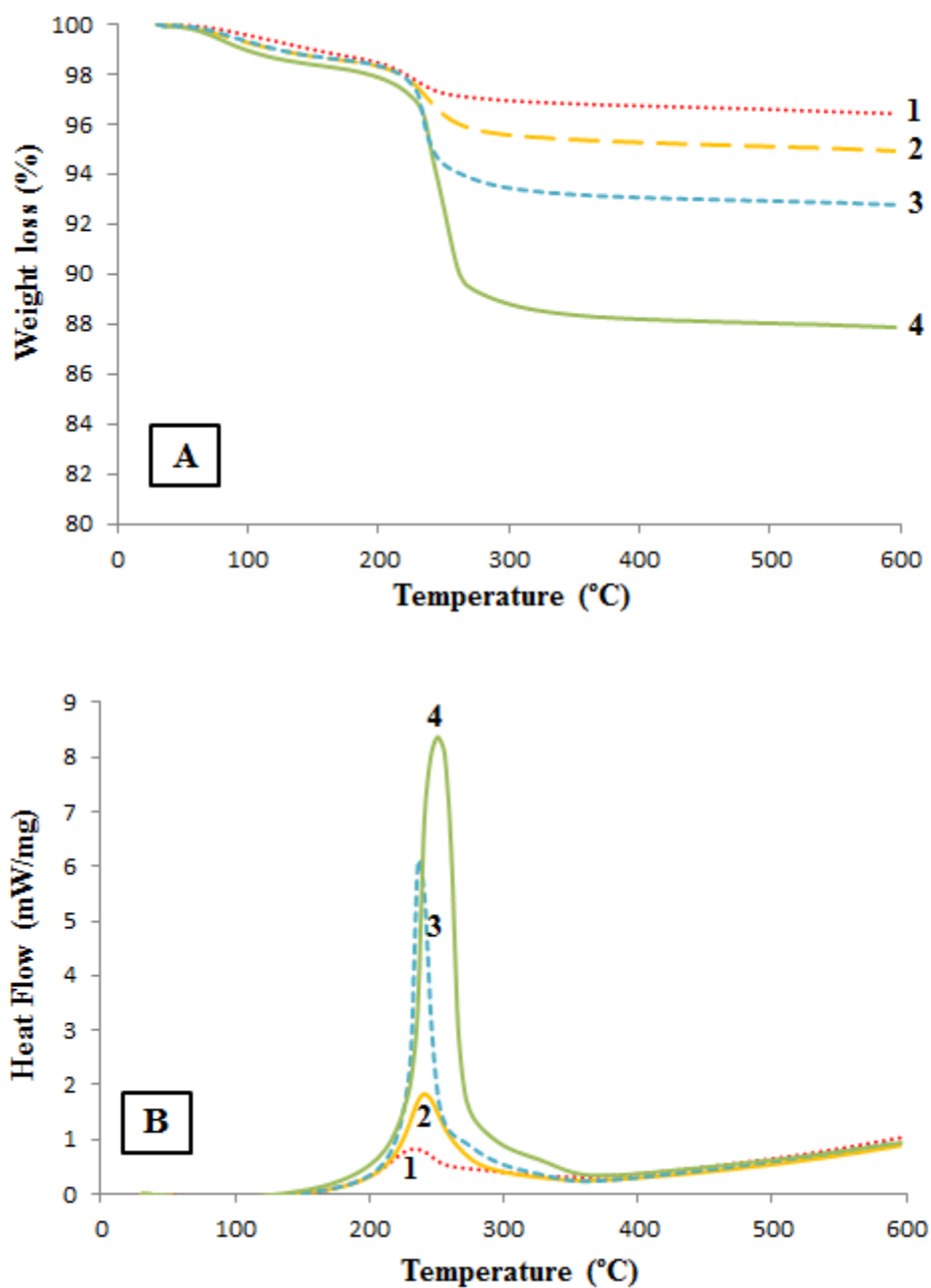


Figure 2. XRD patterns of CeO₂-supported catalysts with different Au:Cu atomic ratios. 1) Au-Ce; 2) Au₃Cu₁-Ce; 3) Au₁Cu₁-Ce; 4) Au₁Cu₃-Ce. In the insert: magnification of the reflection at 2 θ 38,2° which was used to evaluate the Au crystal size.

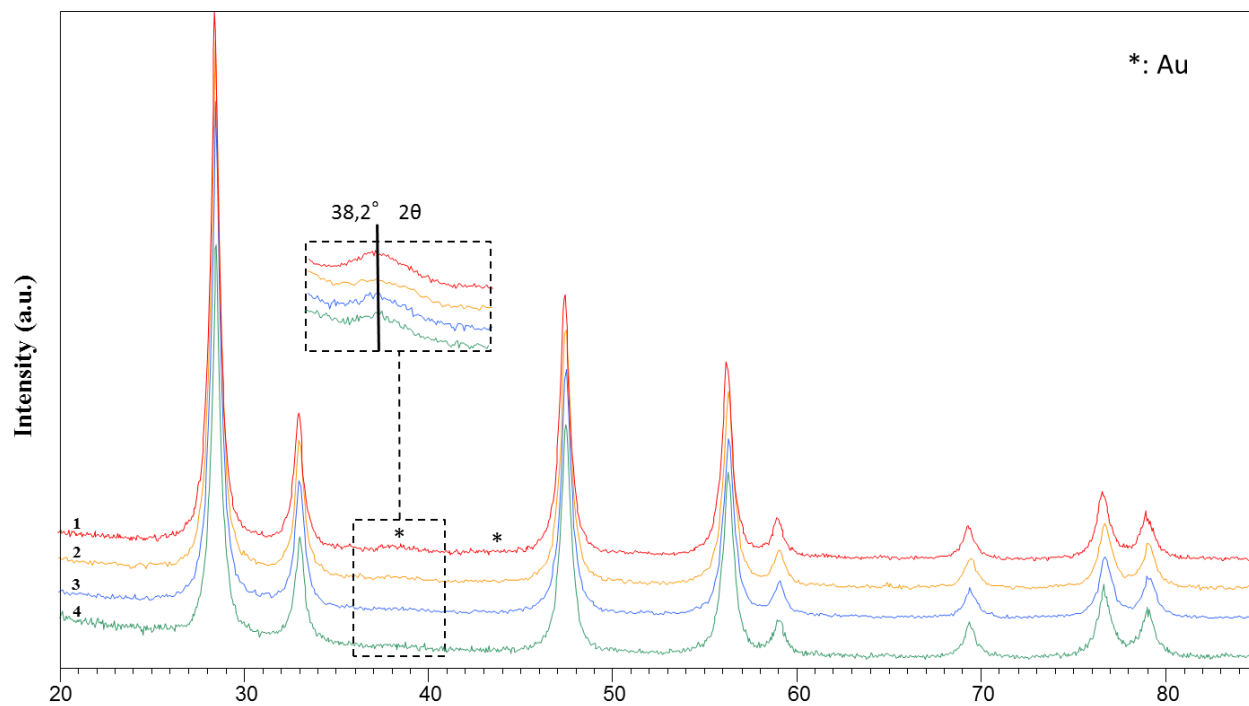
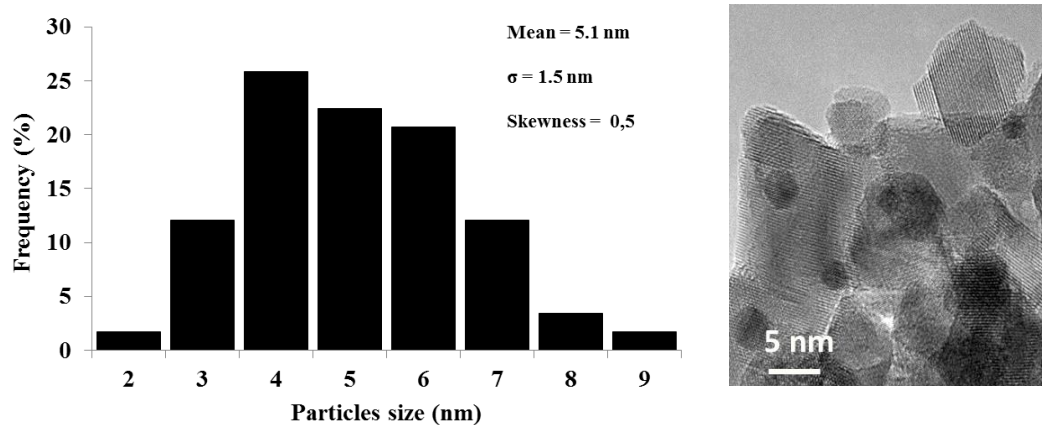


Figure 3. Representative TEM images of the Au- and Au/Cu-supported catalysts. (A) Au-Ce sample dried at 120°C and (B) Au₃Cu₁-Ce sample dried at 120°C.

A



B

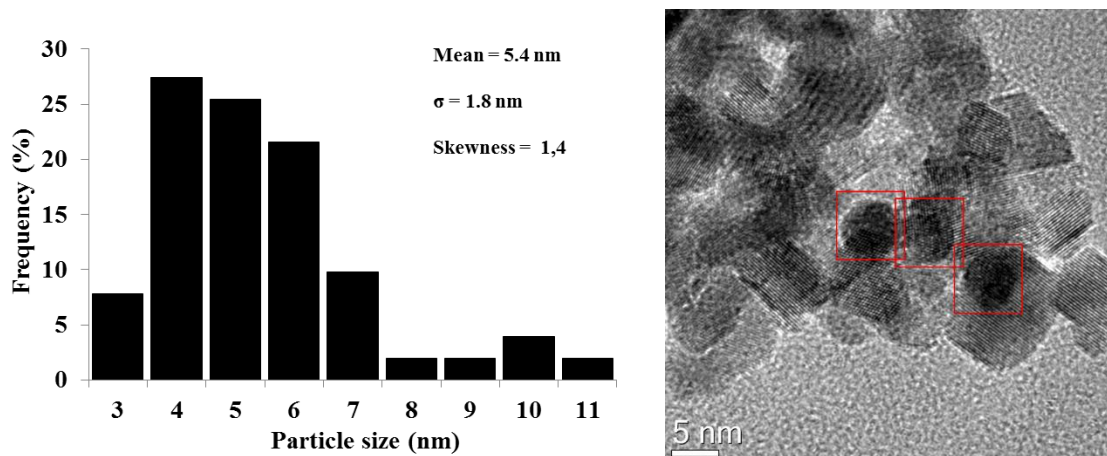


Figure 4. Effect of reaction time on HMF degradation. Reaction conditions: no catalyst, no O₂ pressure, temperature 70°C, ambient pressure, HMF:NaOH 1:4 molar ratio.

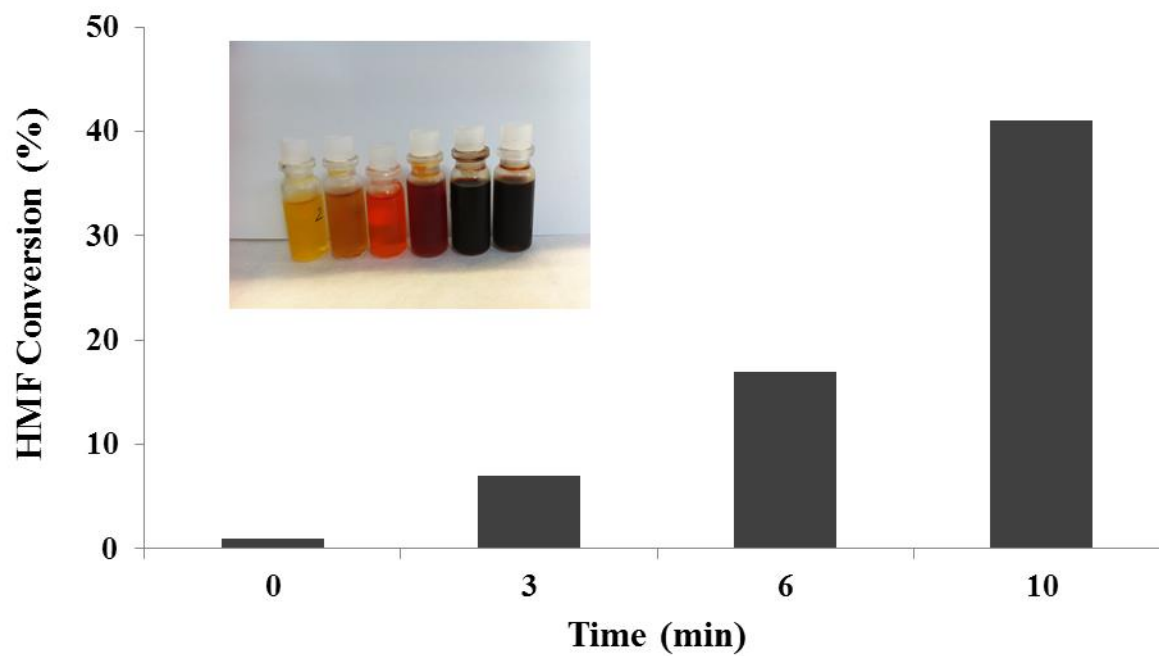


Figure 5. Product selectivity on CeO₂-supported catalysts at different Au:Cu atomic ratios. Results are given at total conversion of HMF. Reaction conditions: temperature 70°C, reaction time 240 min, O₂ pressure 10 bar, HMF: Metal: NaOH molar ratio 1:0.01:4. Legend: ■ HMFCA, ■ FDCA, ■ by-products.

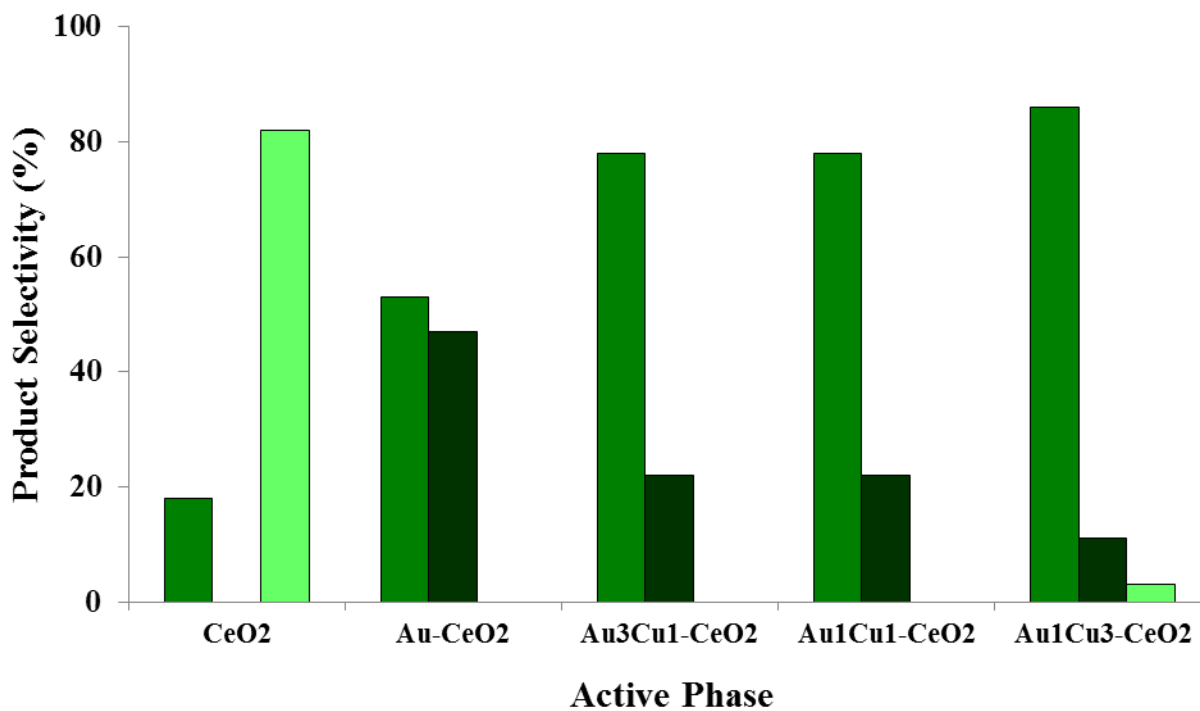


Figure 6. Comparison of FDCA selectivity on CeO₂- and TiO₂-supported catalysts at different Au:Cu atomic ratios. Results are given at total conversion of HMF. The only products observed were FDCA and HMFCFA. Reaction conditions: temperature 70°C, reaction time 240 min, O₂ pressure 10 bar , HMF:Metal:NaOH molar ratio 1:0.01:4. Legend: ■CeO₂ ■TiO₂.

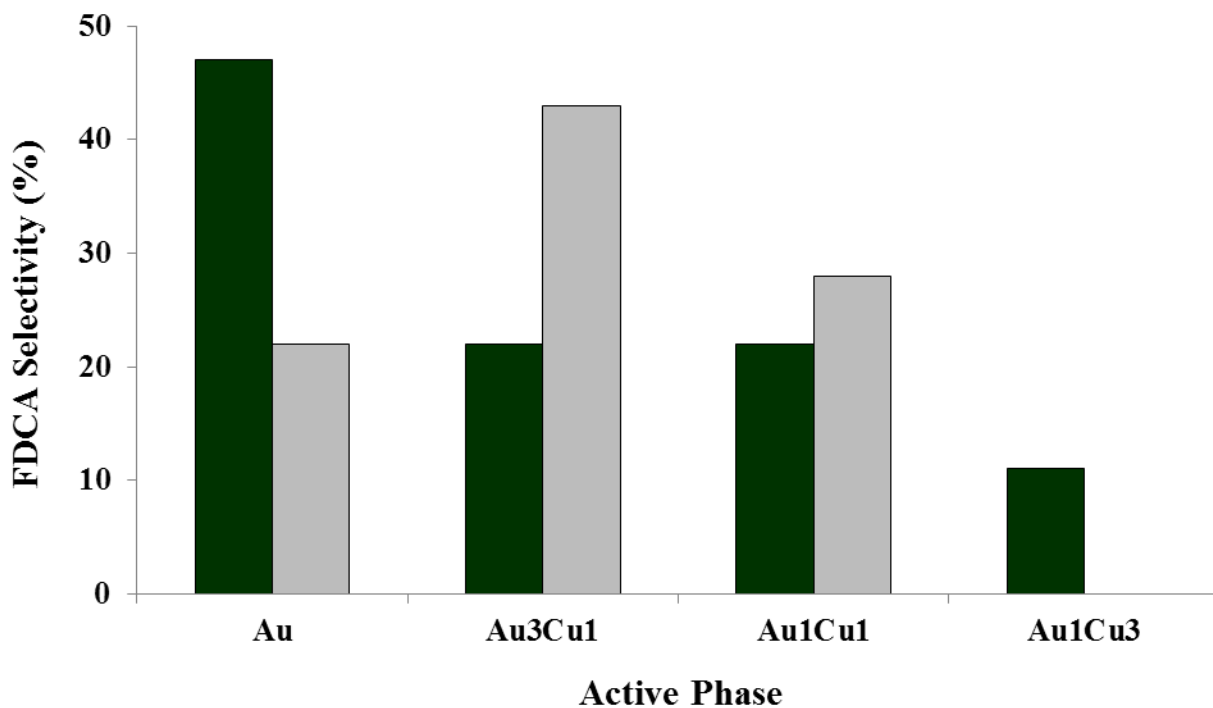


Figure 7. TPO analysis of CeO₂ as is (a), Au-Ce (b) and Au₃Cu₁-Ce (c) supported catalysts.

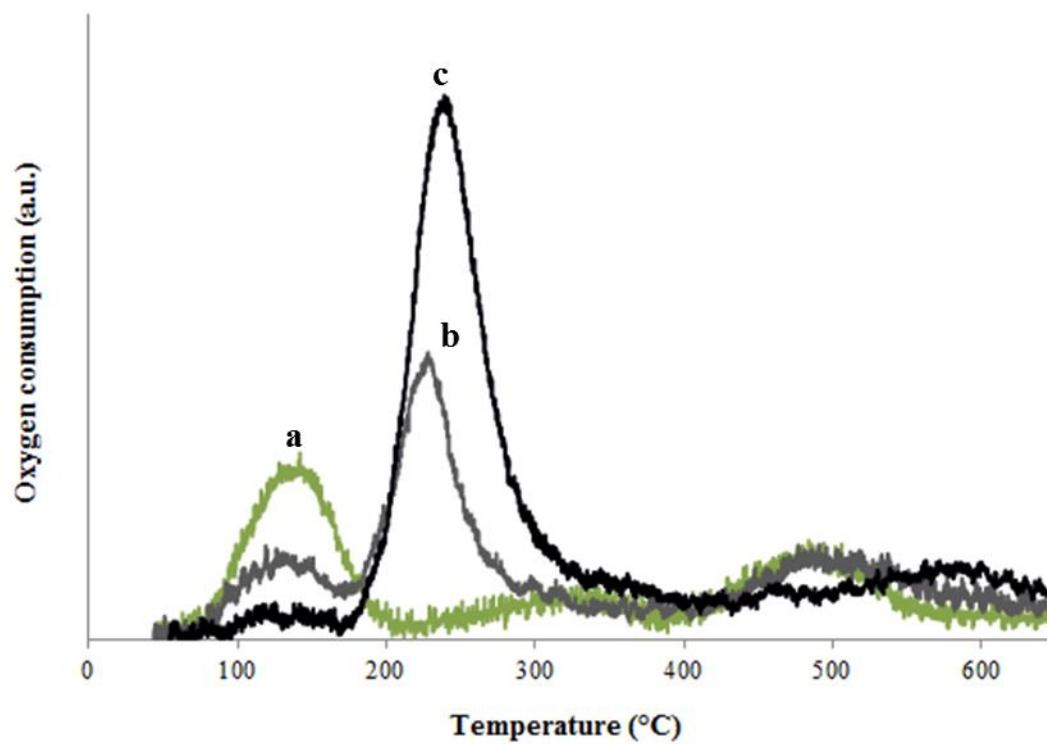


Figure 8. HMFCA (closed symbols) and FDCA (open symbols) selectivity as a function of the reaction temperature over Au₃Cu₁-Ce (■,□) and Au₃Cu₁-Ti (▲,△) catalysts. For all reactions, the HMF conversion was total. The only products observed were FDCA and HMFCA. Reaction conditions: reaction time, 240 min, O₂ pressure 10 bar, HMF:Metal:NaOH molar ratio 1:0.01:4. The insert shows the final mixture after reaction at different temperatures with Au₃Cu₁-Ti.

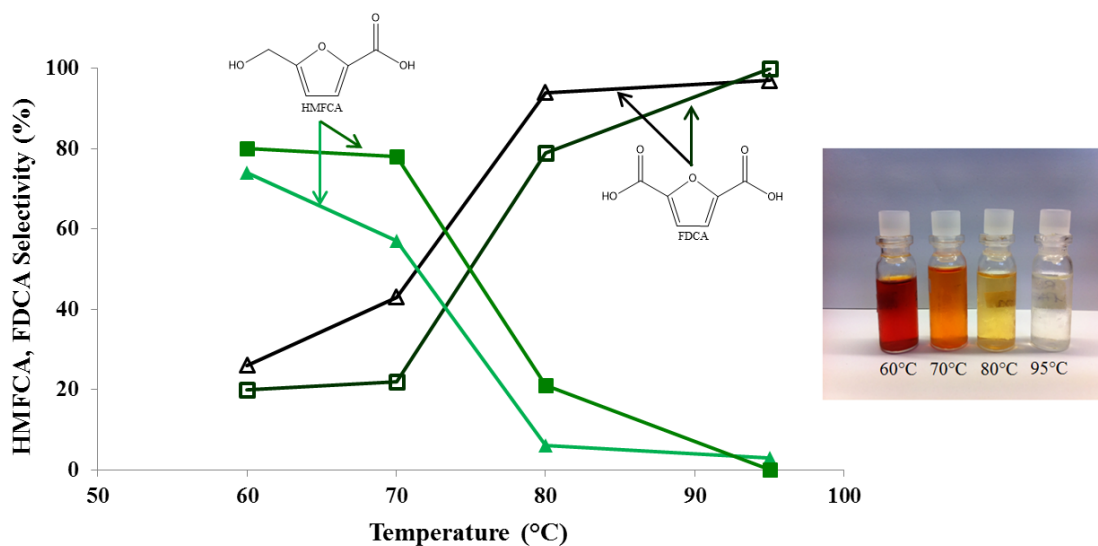


Figure 9. HMF conversion and products selectivity as a function of reaction time. Catalyst Au-Ce. Reaction conditions: temperature 95°C, O₂ pressure 10 bar, HMF: Metal: NaOH molar ratio 1:0.01:4. Legend: HMF conversion (●), HMFCFA selectivity (▲), FFCA selectivity (×), FDCA selectivity (◆). Initial time (time zero) for the reaction is when the temperature of 95°C was reached (after 15 min heating from a.t). The insert shows the final mixture after reaction at different times.

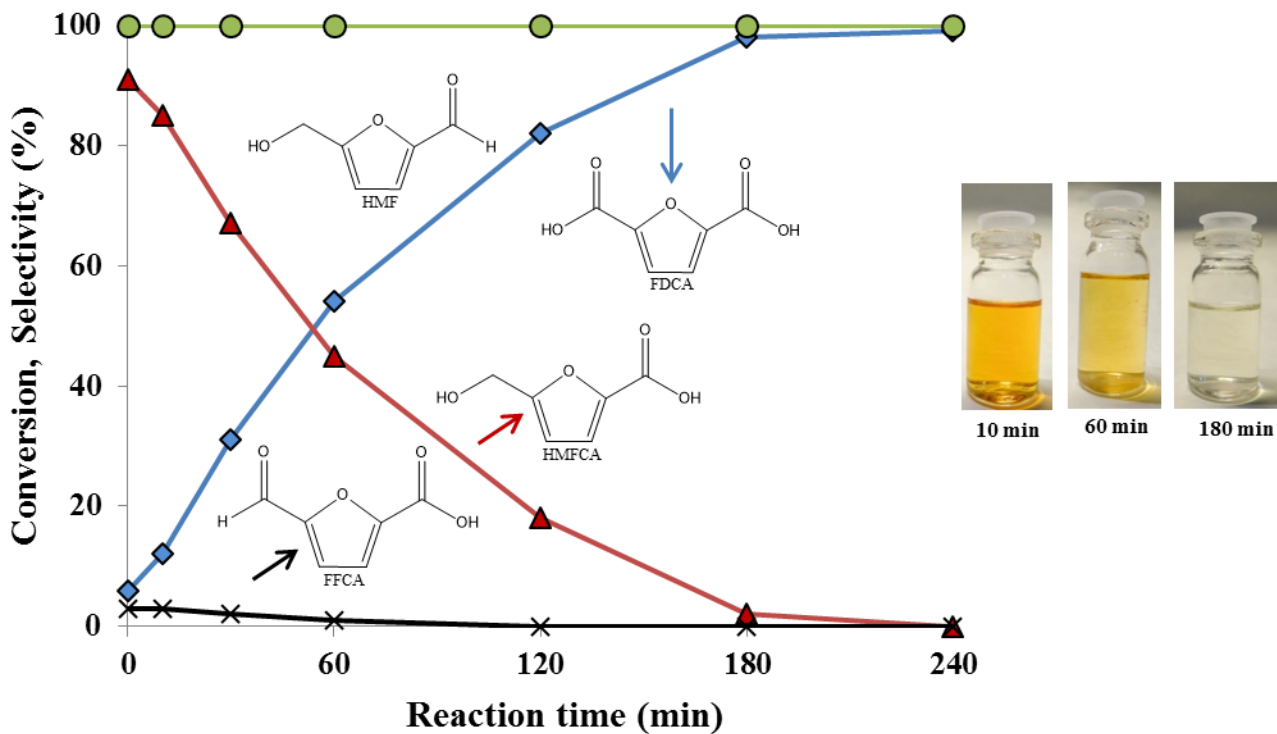


Figure 10. Reusability study for the oxidation of HMF using Au-Ce catalyst. HMFCFA (■) and FDCA (■) selectivities are given at total conversion. Reaction conditions: temperature 70°C, reaction time 240 min, O₂ pressure 10 bar, HMF:Metal:NaOH molar ratio 1:0.01:4.

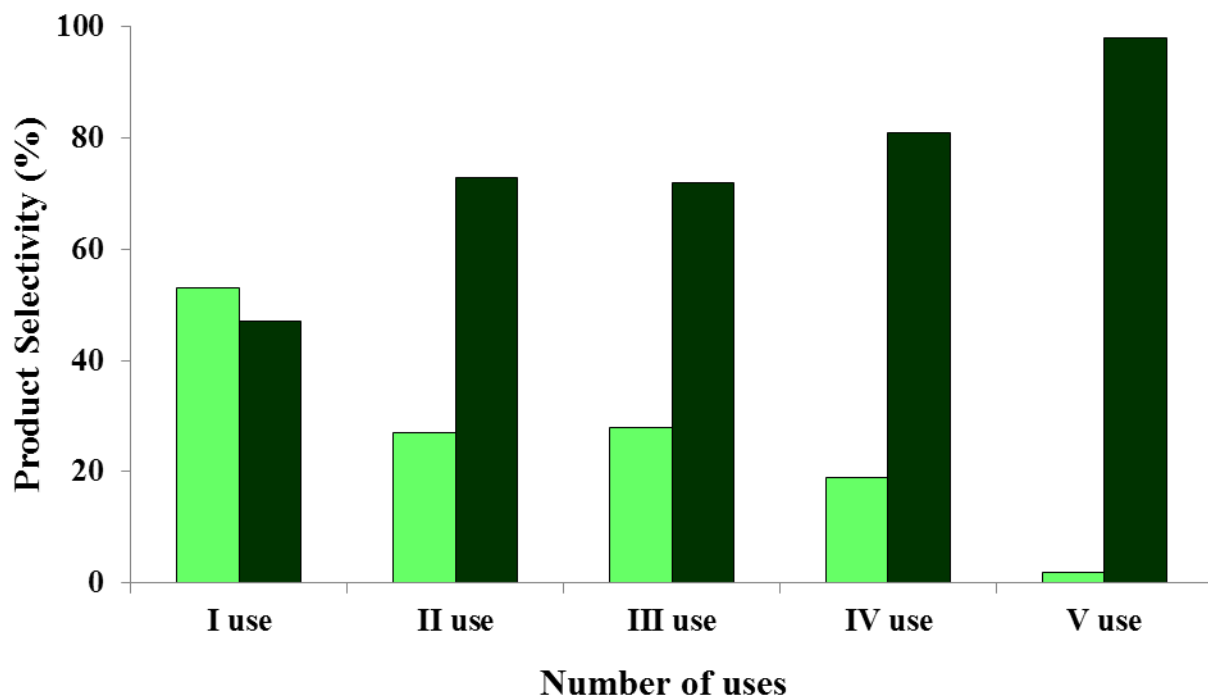


Figure 11. Reusability study for the oxidation of HMF using Au₃Cu₁-Ce catalyst. HMFCFA (■) and FDCA (■) selectivities are given at total conversion. Reaction conditions: temperature 70°C, reaction time 240 min, O₂ pressure 10 bar, HMF: Metal: NaOH molar ratio 1:0.01:4.

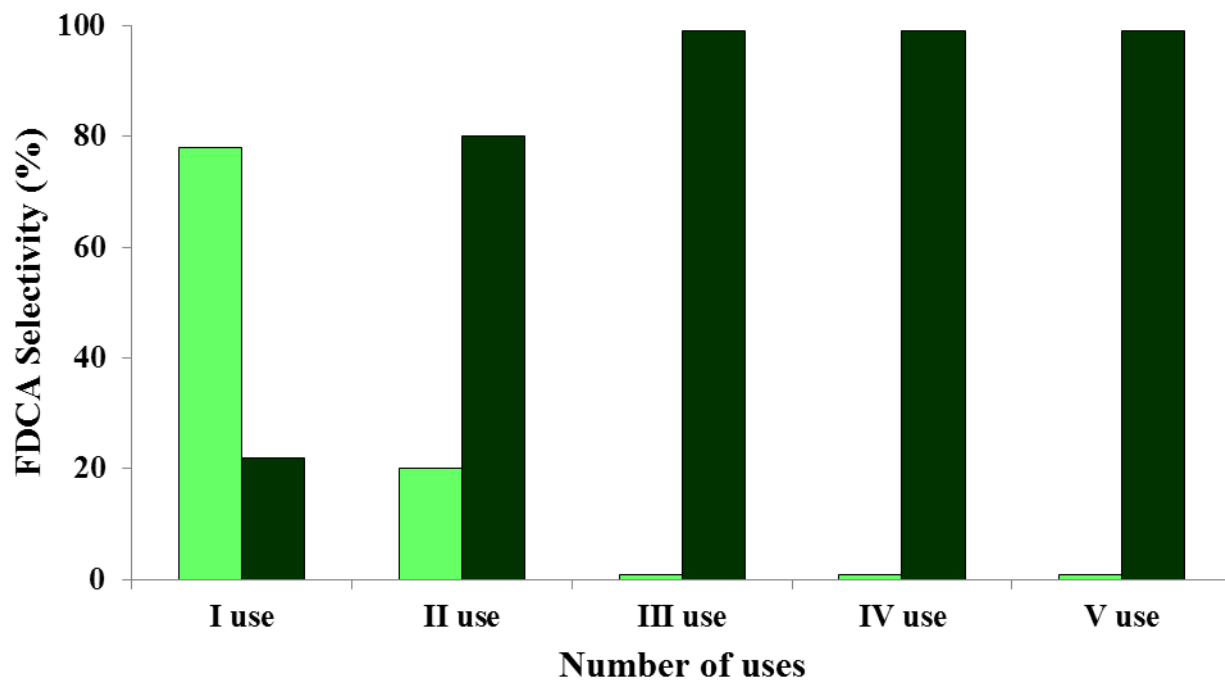


Figure 12. TPO analysis of $\text{Au}_3\text{Cu}_1\text{-Ce}$ catalysts. Legend: (a) untreated $\text{Au}_3\text{Cu}_1\text{-Ce}$; (b) $\text{Au}_3\text{Cu}_1\text{-Ce}$ washed in reaction conditions; (c) $\text{Au}_3\text{Cu}_1\text{-Ce}$ washed in reaction conditions and then calcined at 300°C .

