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**Passing the frontiers of liquid phase glycerol partial oxidation over supported bimetallic catalysts**

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**Abstract:** In this paper, we compared the performances of monometallic and bimetallic (Au, Pt, Ag, Pd) catalysts supported on a basic alumina in the reaction of partial oxidation of glycerol in the liquid phase. A clear synergetic effect between metals was observed, especially when Au and Pt, Au and Pd, as well as Ag and Pt are associated. These three catalysts, characterized by relatively small mean particle size (*ie.*,  $4.44 \pm 2.18$  nm for AuPt,  $6.42 \pm 3.31$  nm for AuPd, and  $6.91 \pm 3.97$  nm for AgPt), enabled complete glycerol (GLY) conversion after 4 hours of reaction at room temperature, under atmospheric pressure (200 mL of a 0.3 M GLY solution, 0.5 g of catalyst, NaOH/GLY = 4 mol/mol, 1500 rpm, 650 mL O<sub>2</sub>/min). Moreover, it was possible to achieve more than 80% GLY conversion after 4 h of reaction at room temperature under atmospheric pressure with air bubbling (650 mL air/min) as an oxidation atmosphere. These unprecedented high performances in the glycerol partial oxidation reaction under such mild conditions paves the way to the possibility of industrial exploitation of this promising catalytic system.

## 1. Introduction

From over two decades scientists have been making substantial efforts to improve the reaction of partial glycerol oxidation in the liquid phase. This process is closely related with an intensively growing market of biofuels, especially with a fully commercialized production

of the first generation biodiesel, where each 1 ton of fats converted to biofuel generates approximately 100 kg of wastes, under the form of the so-called “*crude glycerol fraction*”.<sup>[1-3]</sup> With the aim of utilizing such a surplus of glycerol, this molecule can be converted to a number of value-added derivatives. Consequently, as a platform molecule it is an important raw material for future biorefineries.<sup>[1-4]</sup>

One of the most promising routes for glycerol valorization consists on catalytic partial oxidation in the liquid phase. Depending on the reaction conditions, including the catalyst choice, various important derivatives can be obtained, *i.e.*, glyceric acid, glycolic acid, tartronic acid, mesoxalic acid, lactic acid, glyceraldehyde, dihydroxyacetone, *etc.*<sup>[4-6]</sup> All of them have a market price highly exceeding that of pure glycerol.<sup>[6]</sup> Thus, each product obtained in this reaction, especially glyceric acid, glycolic acid and tartronic acid, has a potential market in pharmaceutical or personal care industries. Thus, many research papers were published in the field, especially discussing about: the effect of the nature of the active phase, of the introduction of various dopants and of the method for catalyst preparation, the influence of the initial reaction conditions (*e.g.*, initial pH of the reaction medium, temperature of the process, nature of the solvent and the oxidant, as well as the gaseous oxidant partial pressure...*etc.*), as well as the issue of impurities present in raw glycerol directly derived from biodiesel production units.<sup>[4-14]</sup> Although some non-noble metal catalysts have been tested in this reaction, it is still believed that noble metal supported catalysts, especially those based on gold, platinum, palladium and silver, are the most efficient ones in this process, showing good performance, especially under ambient temperature conditions.<sup>[14]</sup> Also, the activity of bimetallic systems have been intensively tested by various groups working on glycerol aerobic oxidation. After the works of Kimura,<sup>[15,16]</sup> who found that doping platinum with bismuth resulted in greatly improved selectivity to dihydroxyacetone, Dimitratos *et al.* used sol-immobilization method to prepare Au-Pd bimetallic particles (core-shell and alloyed) supported on graphene.<sup>[17]</sup> The next works on

bimetallic systems appeared shortly after and were reported by the groups of Dimitratos, Prati and Hutchings,<sup>[18-26]</sup> and also by Xu,<sup>[27]</sup> Zhao,<sup>[28]</sup> Yan,<sup>[29]</sup> Royker<sup>[30]</sup> and others. Most of the findings were briefly reviewed in the article of Sankar *et al.*, highlighting numerous benefits of bimetallic systems above monometallic catalysts: higher reaction rates - especially at lower temperatures, higher resistance to deactivation, as well as a better selectivity to the desired products (the selectivity depends on the catalyst composition, or the character of metallic phase: *e.g.* alloy, core-shell structure, average particles diameter, type of the support used... *etc.*).<sup>[31]</sup> From the literature, it is also known that Au alloyed bimetallic particles exhibit a clear synergistic effect for the oxidation of benzyl alcohol,<sup>[32]</sup> the transformation of several isomers of butanol and butanediol,<sup>[33]</sup> and also for the aerobic oxidation of *1,2*-propanediol, where AuPt/C catalysts showed impressive selectivity toward lactate.<sup>[34,35]</sup> Furthermore, the literature mentions also trimetallic systems, where the addition of gold to bimetallic Pt-Pd catalyst allowed twofold increase in the TOF during base-free oxidation of glycerol in the liquid phase.<sup>[36]</sup>

In this paper, a set of a bimetallic catalysts supported on basic alumina oxide is presented, showing excellent performance at 60 °C under 5 bar of oxygen pressure. Moreover, the bimetallic systems also exhibited high activity at room temperature and under atmospheric pressure using air bubbling as an oxidative atmosphere. The results have been also compared with the monometallic systems prepared in the same manner.

## 2. Results and discussion

### 2.1. Comparison of mono and bimetallic systems

All the catalysts listed in Table 1 were tested in the glycerol liquid phase oxidation, using typical reaction conditions, *i.e.*, 0.3 M of a glycerol solution at 60 °C, 5 bars of oxygen and an excess of NaOH in the reaction mixture (NaOH/GLY = 4 mol/mol). Analogous reaction conditions were also reported in our previous work describing performance of commercial alumina-supported Au, Pt and Pd catalysts,<sup>[14]</sup> and silver supported catalyst

prepared with formaldehyde as a reducing agent (the most efficient reducing agent for silver catalyst preparation)<sup>[37]</sup> (Table 2). These experiments showed that the most active system in the glycerol oxidation process was the commercial Au/Al<sub>2</sub>O<sub>3</sub> catalyst, characterized by a small mean particle diameter of  $4.65 \pm 2.63$  nm. The initial reaction rate for this system was  $12\,976 \text{ mol}\cdot\text{h}^{-1}\cdot\text{mol}_{\text{Me}}^{-1}$ , and 100% conversion could be achieved after the first 30 min under reaction.<sup>[14]</sup> The next most active catalysts were commercial Pt and Pd supported catalysts, with respective initial reaction rates of  $2\,898 \text{ mol}\cdot\text{h}^{-1}\cdot\text{mol}_{\text{Me}}^{-1}$  and  $1\,091 \text{ mol}\cdot\text{h}^{-1}\cdot\text{mol}_{\text{Me}}^{-1}$ . The least active was the Ag/Al<sub>2</sub>O<sub>3</sub> sample, prepared by chemical reduction method with formaldehyde ( $866 \text{ mol}\cdot\text{h}^{-1}\cdot\text{mol}_{\text{Me}}^{-1}$ ).<sup>[14]</sup> The monometallic catalysts used in this work, all prepared by chemical reduction method with sodium borohydride, showed slightly different order of the activity, *i.e.*, the platinum catalyst was more active than the gold supported sample (Table 2). The relatively big size of deposited gold particles (about 20 nm, Table 1) is the most probable explanation for this observation. Usually, Au-based systems are the most active ones in the glycerol oxidation process, but, at the same time, their activity and selectivity are “*size-sensitive*”.<sup>[4, 38-40]</sup> While the initial reaction rate of the Au-based catalyst was higher than that of the Pd-based sample ( $3\,446 \text{ mol}\cdot\text{h}^{-1}\cdot\text{mol}_{\text{Me}}^{-1}$  vs.  $984 \text{ mol}\cdot\text{h}^{-1}\cdot\text{mol}_{\text{Me}}^{-1}$ , respectively), the glycerol conversion increase with time was significantly slower (Figure S1). As a consequence, the glycerol conversion value recorded after 2 hours of reaction at 60 °C for the Au catalyst was lower than that over supported Pd (67.32% vs. 81.05%, respectively). Generally, the glyceric acid was the major product, and only the silver supported catalyst was characterized by different products distribution, with glycolic acid and formic acid as main products (typical behavior observed for this type of catalyst<sup>[37]</sup>).

As shown in Table 2, most of the bimetallic systems were far more active than their monometallic counterparts, both in the terms of initial reaction rate and glycerol conversion observed after 2 hours under reaction. Only the PdPt and AgAu catalysts were less active than monometallic platinum and gold catalysts, respectively. However, in comparison to the

performance of the second monometallic analogue (*i.e.*, to respectively the monometallic palladium and silver catalysts), a significant improvement could be observed. Almost all the bimetallic catalysts enabled complete conversion of glycerol after 2 hours of reaction. Only the AgAu catalyst, with the largest particle size and the lowest initial reaction rate did not achieve full glycerol conversion, with a glycerol conversion of 67.7% after 2 hours of reaction, but this system also exhibited the highest selectivities to glycolic acid (26.8%) and formic acid (18.2%), thus partially reflecting the behavior of the monometallic silver supported catalyst. The main product over AgAu catalyst was glyceric acid (GA), which can be related with the typical behavior of gold known to be selective to this compound. Other catalysts promoted mostly the conversion of GLY to GA, as well as the subsequent deeper oxidation to tartronic acid (TARTA) and oxalic acid (OXALA). Figure S1 show the evolution of the GLY conversion and selectivity as a function of time over monometallic and bimetallic catalysts at 60 °C under 5 bars of oxygen. It should be noted that test with physical mixture of monometallic catalysts did not give results as good as those observed over the corresponding bimetallic system. For example, glycerol conversion over physical mixture of Ag and Pt monometallic catalysts resulted in 56.1% conversion and 83.4% selectivity to GA (2 hours at 60°C under 5 bars of O<sub>2</sub>), while the corresponding AgPt catalyst enabled almost full conversion of glycerol under the same reaction conditions (Table 2). Significant difference could also be observed between the initial reaction rates, respectively of 1 772 mol·h<sup>-1</sup>·mol<sub>Me</sub><sup>-1</sup> for physical mixture of monometallic Ag and Pt catalysts, and of 12 474 mol·h<sup>-1</sup>·mol<sub>Me</sub><sup>-1</sup> for the corresponding bimetallic AgPt system. Such obvious synergism between metals in the multi-metallic systems was also previously reported by the groups of Prati<sup>[18]</sup> and Hutchings.<sup>[25]</sup>

## 2.2. Oxidation at room temperature over bimetallic systems

Because four of the prepared bimetallic catalysts allowed achieving complete conversion of glycerol after 2 hours of test at 60 °C, the next step was to carry out the reaction without external heating, *i.e.*, at room temperature (25 °C). The results are shown in Table 3. Initial reaction rates were lower than those observed at 60 °C (Table 2), but still almost full glycerol conversion (above 97%) was observed after 2 h of reaction under 5 bars O<sub>2</sub>, using the AgPt, AuPd and AuPt systems. Similar bimetallic systems reported previously in the literature were noticeably less active, as about 40% glycerol conversion could be obtained after 24 hours of reaction over 1 wt.% Au-Pt/MgO catalyst.<sup>[24,25]</sup> We then decided to study the effect of oxygen pressure over these highly active catalysts.

## 2.3. Effect of oxygen pressure and catalyst amount

The main goal of these additional catalytic tests was to check the performance of the bimetallic systems under reduced oxygen pressure as well as the effect of the catalyst amount on the glycerol conversion. All the tests were performed at room temperature using the AuPt system, *i.e.*, one of the most active bimetallic catalysts. The results in Figure 1 clearly show that the use of atmospheric oxygen (bubbling at the rate of 650 mL/min) at room temperature still gives excellent performances. While the initial reaction rate decreased from 9 842 mol·h<sup>-1</sup>·mol<sub>Me</sub><sup>-1</sup> (5 bars of O<sub>2</sub>), through 2 964 mol·h<sup>-1</sup>·mol<sub>Me</sub><sup>-1</sup> under 1 bar O<sub>2</sub>, to 1 835 mol·h<sup>-1</sup>·mol<sub>Me</sub><sup>-1</sup> for the test at  $P_{atm}$ , glycerol conversion after 90 minutes was practically complete (99.4-100%), irrespective on the oxygen pressure. Furthermore, the differences between the product selectivities were practically negligible, *i.e.*, with a selectivity to GA of 48-54%, to GLYCA of 16-18%, and to FA of 10-12%. Finally, the selectivities to deeper oxidation products were respectively 13-17% to TARTA and 3-5% to OXALA. Similarly, a change in the catalyst amount from 0.5 g to 0.1 g also did not affect significantly the selectivity. Namely: for 50% glycerol *iso*conversion, selectivities to GA, TARTA and OXALA were 58-

59%, 3-5%, and 2-3%, respectively. Only the selectivities to FA and GA slightly decreased with the decrease in the catalyst amount (from 16% to 13% in the case of FA, and from 22% to 16% for GLYCA, respectively).

From the industrial point of view such results can be very satisfying, especially that the repeatability of the tests results was very high and the bimetallic catalyst could be reused without significant change in performances (Figure S2). However, a possibility of replacing the oxygen with air, especially under atmospheric pressure and at room temperature, would make the process much more economical. This is described in the next section.

#### 2.4. Tests at room temperature under air bubbling

For the tests under bubbling air (650 mL/min), a typical laboratory pressure pump was used to provide air directly to the reactor *via* a tube dipped in the solution. Again, no external source of heating was used, and the reaction was carried out using 200 mL of a 0.3 M GLY solution, base (NaOH/GLY = 4 mol/mol) and 0.5 g of bimetallic catalyst. The results obtained after 2 h of reaction are shown in Table 4. The initial reaction rate was significantly lower than that observed with 5 bars of oxygen (Table 3), and, in most cases, its value did not exceed  $500 \text{ mol}\cdot\text{h}^{-1}\cdot\text{mol}_{\text{Me}}^{-1}$ . The highest initial reaction rate was observed over the AuPt catalyst ( $706 \text{ mol}\cdot\text{h}^{-1}\cdot\text{mol}_{\text{Me}}^{-1}$ ), although it was less than half of the value obtained under atmospheric pressure using pure oxygen flow. A very good glycerol conversion, close to 50%, could be obtained after 2 hours of reaction. Concerning the products distribution, an important increase in the selectivity to lactic acid could be observed (up to 14%), while the selectivity to oxalic acid was almost negligible. In each case, the dominant product was glyceric acid, with a selectivity usually between 70-82%. Only AuPt and AgAu catalysts were less selective to GA (60.69% and 51.58%, respectively), and clear promotion of an oxidative decomposition reaction leading to formic acid and glycolic acid (of which both selectivities were over 10%) could be observed. It is worth to underline that prolonging the reaction time up to 240 minutes enabled further increase in the glycerol conversion to 82-83% over PdPt and AuPd catalysts,



and to 74% over the AuPt sample. The selectivities to the main products did not vary between each other, and stayed at the same level. The corresponding pictures presenting the changes of conversion and selectivities as a function of the reaction time for the tests at room temperature under air bubbling are shown in Figure S3. Additional experiments with the AuPt system supported on pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (3  $\mu$ m fine powder with a specific surface area of 100-120 m<sup>2</sup>/g) showed that the conversion of glycerol at room temperature under bubbling air still can be improved, reaching 97% after 4 hours of reaction (52% selectivity to GA, 19% to LA and 12% to TARTA). Previously, Garcia *et al.* reported 90% of glycerol conversion using air as an oxidant under atmospheric pressure. However, they carried out the reaction for 8 hours over PdBi/C at 60 °C.<sup>[41]</sup> Similar results were also obtained by Breiner *et al.* who reported 92-99% glycerol conversion after 4 hours at 40-60 °C under atmospheric pressure, using 3 wt.% Pt/C catalyst (10 g for 700 mL of 1.08 M GLY solution) and also two types of Pd-Pt-Bi/C catalysts.<sup>[42]</sup> Also, Galhardo *et al.* working at the temperature of 60 °C reported 20% glycerol conversion and 58% selectivity to GA during 6 hours of glycerol oxidation under 8 bars of synthetic air over a PtNi/AC(MH) catalyst.<sup>[43]</sup>

## 2.5. Global discussion

A series of bimetallic catalysts supported on basic alumina oxide were prepared by a one-pot chemical reduction method using sodium borohydride alkaline solution. This reductant is usually recommended by the literature for efficient recovery of noble metals (*i.e.*, Au, Pt, Pd and also Ag, all recovered in a fully reduced state) from various solutions.<sup>[45-47]</sup> Other types of chemical reductants usually shows limited efficiency in the synthesis of reduced monometallic catalysts, *i.e.*, hydrazine (N<sub>2</sub>H<sub>4</sub>) incompletely reduces palladium and promotes the deposition of undesired large Pt particles (up to 160-260 nm average diameter),<sup>[48]</sup> while formaldehyde (HCHO), very efficient in the synthesis of active silver catalysts,<sup>[37]</sup> shows a poor reducing power in respect to gold and palladium. Herein, an alkali

solution of NaBH<sub>4</sub> enabled synthesizing fully reduced mono and bimetallic systems with fine nanoparticles exhibiting relatively small average diameters (from *ca.* 3 to *ca.* 32 nm, Table 1, Figure S4). Furthermore, XPS studies confirmed fully reduced state of the metal particles (Figure S5). Small shifts in the BE values were observed for the bimetallic catalysts compared to the monometallic samples, which is especially well seen for Au 4f<sub>7/2</sub> region (Table 1). According to previous reports, they reflect metal-metal interactions, due to the formation of bimetallic alloy nanoparticles.<sup>[22]</sup> Lack of Me<sup>+δ</sup> species on the catalyst surface after the aerobic oxidation of glycerol reaction, evidenced by XPS (Table S1), confirmed a good stability of the catalysts (recycling test results in Figure S2b). This issue is especially important in the case of Pt and Pd containing catalysts, which are known from their relatively weak oxygen-resistance.<sup>[21,22,31,49]</sup> However, addition of gold to the composition usually diminishes this problem, especially when a uniform alloy is present on the support surface. According to the literature, the beneficial effect in terms of stability and activity can be clearly seen only in the case of uniform alloys, while the samples with inhomogeneous composition and partial metal segregation are usually less promising.<sup>[49]</sup> Our test with the AgPt supported catalyst and the physical mixture of corresponding monometallic samples support this statement, as a 7-fold increase in the initial reaction rate (from 1 772 mol·h<sup>-1</sup>·mol<sub>Me</sub><sup>-1</sup> to 12 474 mol·h<sup>-1</sup>·mol<sub>Me</sub><sup>-1</sup>) clearly confirms a synergism between metals in the bimetallic system. Also, TEM microscopy confirmed that most of the bimetallic catalysts are characterized by very uniform and quite narrow particle size distributions (Table 1, Figure S4). Only AgPd catalyst was characterized by a broader particle size distribution, typical for monometallic silver catalyst. However HR-TEM did not allow to distinguish between separate metals, suggesting the presence of an uniform alloy. Furthermore, very similar values of Ag and Pd atomic surface concentrations measured by XPS (Ag at.% / Pd at.% = 0.95) suggest homogenous and uniform distribution of both metals on the catalyst surface.

Comparison of the catalytic results clearly reflects the synergism between the loaded metals. After 2 hours of reaction at 60 °C, under 5 bars O<sub>2</sub> pressure (Table 2), the conversion of glycerol over bimetallic catalysts was by far higher than that over their monometallic analogues. Very high reaction rates resulted in almost complete glycerol conversion within the first 30-60 min of reaction.

Obviously, the catalytic performances depend on many factors, especially the size of the metal particles, the nature of the support, and the presence of a base in the reaction medium. In our experiments most of the catalysts were characterized by relatively similar mean particle diameters, between 3 and 8 nm, and only monometallic Ag, Au and AgPt catalysts contained larger particles. All the catalysts were synthesized by the same method using the same type of the support, and, also, all the experiments were performed while maintaining the same NaOH/GLY molar ratio. The presence of base in the reaction medium is usually crucial for initial activation of the glycerol molecule over silver and gold, where the first step is the hydrogen abstraction from one of the primary hydroxyl groups of glycerol, leading to glycerate *via* subsequent oxidation.<sup>[25]</sup> In the case of Pd and Pt catalysts, an initial dehydrogenation *via* hydrogen abstraction is also possible, although, according to the literature, it is a relatively slow process, often considered as impossible for both Ag and Au.<sup>[21,25]</sup> In the next steps, GA formed in primary reactions can undergo further oxidation, first to tartronic acid and then to mesoxalic acid, although the latest is relatively unstable and readily undergo decarboxylation to oxalic acid.<sup>[5]</sup> Furthermore, both Au and Ag exhibit high activity in the oxidative C-C bond cleavage, leading to various C1 and C2 derivatives, especially to glycolic acid and formic acid. According to the literature, a high cleavage potential can be related with the presence of H<sub>2</sub>O<sub>2</sub>, most probably formed *in-situ* through O<sub>2</sub> reduction by metal hydride.<sup>[21]</sup> In fact, this molecule induces secondary, non-selective oxidation reactions.<sup>[5,28]</sup> Moreover, it has been reported by Davis *et al.* that Au catalysts are more active and selective in the formation of H<sub>2</sub>O<sub>2</sub> compared with Pd catalysts, which are

characterized by higher decomposition rate of  $\text{H}_2\text{O}_2$ .<sup>[31,44,50]</sup> Indeed, the selectivity to formic and glycolic acids was the highest over both gold and silver supported monometallic catalysts, while monometallic palladium was characterized by the highest selectivity to glyceric acid (about 80%). The introduction of a second metal to Ag and Au catalysts (especially Pd) significantly lowered the selectivity to C-C cleavage reactions (Figure S1). Only the AgAu catalyst showed a high potential in glycolic acid formation (selectivity to GLYCA about 25%). This behavior is somewhat similar to that of monometallic Ag and Au systems, *i.e.*, under the same reaction conditions (2 h of reaction at 60°C, 5 bars  $\text{O}_2$ ), the selectivity to GLYCA was about 42% using Ag/ $\text{Al}_2\text{O}_3$  and 13% over Au/ $\text{Al}_2\text{O}_3$ . Other bimetallic catalysts showed an important selectivity to tartronic acid (close to 50%), a secondary oxidation product derived from subsequent oxidation of glyceric acid.

A decrease in the reaction temperature to the room temperature significantly lowered the initial reaction rates (Table 3), and also affected deep oxidation reactions leading to tartronic acid. The selectivity to TARTA recorded after 2 hours of reaction exceeded 20% only for the AuPt and the AgPt catalysts (for other systems it was less than 10%). Moreover, at room temperature the selectivities to formic acid and glycolic acid over AuPd and AuPt catalysts were visibly higher (increase by a factor of 1.5-2.6), and only the PdPt bimetallic catalyst maintained low selectivity to C-C oxidative cleavage reactions (selectivity to FA and GLYCA after 2 h of reaction at room temperature were 4.9% and 5.9%, while at 60°C they were 4.4% and 4.1%, respectively). Replacing the oxygen with air and operating under atmospheric pressure further lowered the initial reaction rates, as well as deep oxidation reactions. The selectivity to GA increased due to the lower oxidation rate to TARTA. Oxalic acid was practically absent in the reaction mixture, while an interesting change in the selectivities to FA and GLYCA could be observed. With an excess of oxidant, the selectivity to glycolic acid was higher than that to formic acid, while under air bubbling an opposite trend was observed (Tables 3 and 4 respectively). Explanation of this phenomenon requires

further investigation, although it is worth to mention that glycolic acid can be also formed *via* retro-aldol reaction, which leads directly to glycolate from glycerate.<sup>[5,21]</sup> Finally, an increase of lactic acid formation (growth in selectivity from about 1% up to 6-14%) during reaction under bubbling air can be explained by appearance of C-H bond abstraction under basic conditions, leading to 2-hydroxypropanal or *l*-hydroxypropan-2-one (possibility confirmed previously by DFT calculations<sup>[5]</sup>), which are the reactive intermediates in the lactic acid production. In fact, according to the literature, a benzilic acid rearrangement of pyruvaldehyde to lactic acid commonly occurs in alkaline solution.<sup>[51]</sup>

### 3. Conclusion

In this work, the performance of bimetallic systems based on Ag, Au, Pt and Pd were evaluated in the glycerol liquid phase partial oxidation reaction, these metals being the most frequently used in the literature for this reaction. The bimetallic systems prepared by the same chemical reduction method using sodium borohydride as a reducing agent showed excellent performances in the process, due to the presence of small very active nanoparticles (mean diameter varying from 3.21 nm for PdPt, 4.44 nm for AuPt; through intermediate values of 6.42 nm and 6.91 nm for AuPd and AgPt, respectively, up to 7.59 nm for AgAu and 15.43 nm for AgPd) enabling softening the reaction conditions: It was indeed possible to run the reaction at room temperature using air bubbling at atmospheric pressure. The best results after 4 hours of oxidation under air were obtained above AuPt, AuPd and PdPt systems, enabling around 80% conversion of glycerol at room temperature and glyceric acid as main product (selectivity up to 80%). An evident synergism between the metallic particles could be observed, as the initial reaction rates achieved over bimetallic systems were far better than the rates above the monometallic catalysts (up to 32 fold), and also compared to that of corresponding physical mixtures of two monometallic catalysts (7 fold). Further, the bimetallic catalysts could be recycled without significant loss in activity, making these systems good candidates for industrial perspectives.

#### 4. Experimental Section

##### *Materials:*

The materials for catalysts preparation included: silver nitrate (99.0%, ACS grade reagent), ammonium tetrachloroplatinate (II), palladium (II) nitrate dihydrate, and sodium borohydride (> 96% NaBH<sub>4</sub>) - all purchased from Sigma Aldrich; hydrogen tetrachloroaurate (III) trihydrate (HAuCl<sub>4</sub>) purchased from Alfa Aesar; and the support - activated basic alumina (activity stage I according to the Brockmann activity grades, 70-230 mesh powder for column chromatography, pH 8.5-10.5 of 10% water suspension, SSA 195.7 m<sup>2</sup>/g) from Merck. Anhydrous glycerol 99% (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) and purum sodium hydroxide (NaOH) from Sigma–Aldrich were used for the catalytic tests.

##### *Catalysts preparation*

To yield supported (bi-)metallic nanoparticles, a method of chemical reduction with sodium borohydride we reported elsewhere was used.<sup>[37,48]</sup> Namely, the alumina support powder was suspended in a solution of metallic precursor in water of which the pH was adjusted at 8 by using a 2 M NaOH solution. Then, a 2 M sodium borohydride aqueous basic solution (2 M NaOH) was added dropwise to the alumina suspension. After vigorous mixing for 90 min, the suspension was filtered, solid was washed with distilled water (200 cm<sup>3</sup>) and dried at 110 °C for 24 h.

##### *Catalysts characterization*

The actual metal loading was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Vista Pro Varian) performed for Au, Pt and Pd monometallic and bimetallic systems. X fluorescence spectroscopy (XRF) using an S2 Ranger Bruker spectrometer equipped with a Pd X-ray tube was applied for silver-containing samples, due to weak sensitivity of ICP towards Ag<sup>+</sup> cations. The total amount of deposited metals in monometallic samples was between 0.95 wt.% and 1.42 wt.%, while the total loading in

bimetallic systems was between 1.4 and 1.6 wt.% (Table 1). In this last case, the ratio between supported metals was close to 1.

The XRD analysis was performed at room temperature using a D8 Advanced apparatus from Bruker AXS instrument, and the JCPDS database was used to interpret the diffractograms. The samples were scanned within the  $5^\circ < 2\theta^\circ < 90^\circ$  range with a rate of  $0.02^\circ$  per step and a scan time of 3 s per step. The noble metals were almost not detected using XRD (Figure S6), mainly due to their relatively low content and also to the relatively small size of well dispersed particles. Only the most intense reflections could be observed together with the diffraction lines characteristic for the commercial, basic alumina support (mixture of  $\gamma$ -alumina, Boehmite and Gibbsite phases).

TEM FEI Tecnai G2-20 twin electronic microscope, working with an accelerating potential of 20 kV, was used for microscope observation of the catalysts. The particle size distribution was calculated using the Visilog 6.5 software by counting at least 300 particles over multiple areas for each sample (Figure S4).

The oxidation states of the metals on the surface of the fresh and used catalysts were analyzed using XPS (VG ESCALab 220XL from Thermo Fisher Scientific) equipped a monochromatized aluminum source ( $Al_{K\alpha} = 1486.6$  eV). The high-resolution spectra were recorded with a 40 eV pass energy, and the value of the C1s core level (284.6 eV) was used for calibration of the energy scale. Curve fitting was performed using the CasaXPS software using a Shirley-type background subtraction (Figure 5S). The corresponding photoelectron peak binding energy (BE) values (Table 1) measured for fresh catalysts were similar to those reported in the literature for reduced noble metals species, *i.e.*, 368.1 – 368.4 eV for Ag 3d<sub>5/2</sub>, 83.7 – 84.2 eV for Au 4f<sub>7/2</sub>, 335.5 – 335.7 eV for Pd 3d<sub>5/2</sub>, and 71.4 – 71.8 eV for Pt 4f<sub>7/2</sub>.<sup>[49, 52-54]</sup> In each case, note that the value of the Al 2p level was  $74.6 \pm 0.2$  eV.

*Catalytic performances evaluation*

Liquid phase partial oxidation of glycerol was carried out in a 300 cm<sup>3</sup> semi-batch stainless steel reactor equipped with a turbine, 4 baffles, a thermocouple, and a gas supply system. In each experiment under oxygen pressure, 200 cm<sup>3</sup> of a pure glycerol solution in water (0.3 M) were heated to the selected temperature (for the tests at room temperature, no external heating was supplied), and the reaction was started when the calculated amount of NaOH with a selected catalyst (0.5 g) were flushed into the reactor, and the system was pressurized with oxygen (1-5 bar). For the tests under atmospheric pressure, oxygen or air were delivered to the reactor zone by bubbling.

The products were periodically sampled and analyzed with an Agilent 1200 HPLC equipped with a reflective index detector and Rezex ROA-Organic Acid H<sup>+</sup> column (300 x 7.8 mm). The identification and quantification of the obtained products were performed by comparison with the corresponding calibration curves.

**Supporting information**

Supporting Information is available from the Wiley Online Library or from the authors.

**Acknowledgements**

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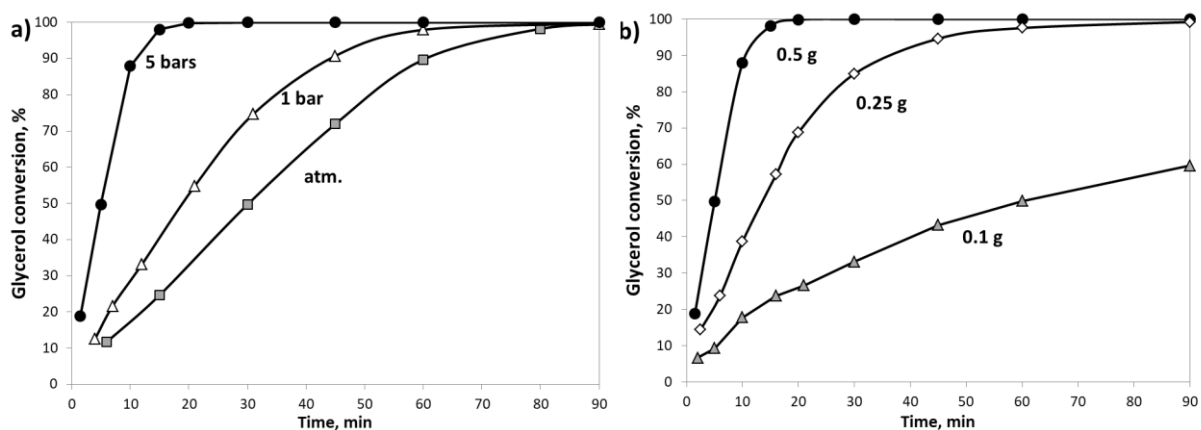
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**Figure 1.** Test at room temperature using the PtAu catalyst. (a) Effect of oxygen pressure for the reaction over 0.5 g of catalyst (“atm” means bubbling O<sub>2</sub> under atmospheric pressure); (b) Effect of the catalyst amount for the reaction under 5 bars of oxygen. Other reaction conditions: 200 mL of a 0.3 M GLY solution, NaOH/GLY = 4 mol/mol, 1500 rpm.

**Table 1.** Characterization of fresh bimetallic catalysts. Elemental Analysis (ICP/XRF), mean particle diameter (TEM) and binding energies (XPS).

Cat.	Metals composition by EA <sup>a)</sup> [Me wt.%]				Mean particle diameter by TEM [nm]	BE [mV] by XPS			
	Au	Pt	Pd	Ag		Au 4f <sub>7/2</sub>	Pt 4f <sub>7/2</sub>	Pd 3d <sub>5/2</sub>	Ag 3d <sub>5/2</sub>
Au	1.21	-	-	-	20.01 ± 10.01	84.1	-	-	-
Pt <sup>b)</sup>	-	1.03 <sup>b)</sup>	-	-	2.95 ± 1.12 <sup>b)</sup>	-	71.4 <sup>b)</sup>	-	-
Pd	-	-	0.95	-	4.33 ± 1.58	-	-	335.5	-
Ag <sup>c)</sup>	-	-	-	(1.42) <sup>c)</sup>	31.8 ± 17.20 <sup>c)</sup>	-	-	-	368.1 <sup>c)</sup>
AuPt	0.76	0.74	-	-	4.44 ± 2.18	84.2	71.6	-	-
AuPd	0.89	-	0.76	-	6.42 ± 3.31	83.8	-	335.6	-
AgAu	0.81 (0.80)	-	-	0.07 (0.77)	7.59 ± 8.01	83.7	-	-	368.4
PdPt	-	0.72	0.66	-	3.21 ± 1.08	-	71.8	335.6	-
AgPt	-	0.82 (0.85)	-	0.20 (0.52)	6.91 ± 3.97	-	71.7	-	368.4
AgPd	-	-	0.73 (0.71)	0.10 (0.54)	15.43 ± 20.52	-	-	335.7	368.4

<sup>a)</sup> Elemental Analysis by ICP, values in brackets are presenting the metal composition estimated by XRF analysis.

<sup>b)</sup> data from Ref. [16]

<sup>c)</sup> data from Ref. [15]

**Table 2.** Initial reaction rates, glycerol conversions and selectivities after 2 h of reaction over the prepared catalysts at 60°C. Other reaction conditions: 5 bars O<sub>2</sub>, 200 cm<sup>3</sup> of a 0.3 M GLY solution, NaOH/GLY = 4 mol/mol, 0.5 g of catalyst and a stirring speed of 1500 rpm).

Active metal(s)	Initial reaction rate, [mol·h <sup>-1</sup> ·mol <sub>Me</sub> <sup>-1</sup> ]	Conversion and selectivity after 2 hours of reaction, [%]						
		<i>C</i> <sub>GLY</sub>	<i>S</i> <sub>OXALA</sub>	<i>S</i> <sub>TARTA</sub>	<i>S</i> <sub>GA</sub>	<i>S</i> <sub>GLYCA</sub>	<i>S</i> <sub>LA</sub>	<i>S</i> <sub>FA</sub>
Au	3 446	67.32	0	2.40	67.07	14.75	2.89	12.89
Pt <sup>a)</sup>	9 491 <sup>a)</sup>	97.25 <sup>a)</sup>	6.90 <sup>a)</sup>	24.17 <sup>a)</sup>	49.05 <sup>a)</sup>	7.65 <sup>a)</sup>	4.16 <sup>a)</sup>	7.92 <sup>a)</sup>
Pd	984	81.05	4.93	9.63	69.40	9.62	0	6.29
Ag	394	23.63	0.73	0.27	18.84	42.69	2.02	35.34
AuPt	19 854	100	12.26	47.51	20.95	10.93	0	8.13
AuPd	8 058	100	11.42	55.47	14.88	6.36	6.48	4.85
AgAu	1 382	67.73	0	3.63	51.40	26.77	0	18.20
PdPt	6 478	100	12.21	51.01	23.13	4.12	4.94	4.41
AgPt	12 474	99.63	9.21	32.81	43.54	4.29	4.01	6.14
AgPd	2 497	96.61	1.09	20.40	58.32	6.73	5.10	8.28

<sup>a)</sup> data from Ref.<sup>[16]</sup>

Abbreviations: *C*<sub>GLY</sub> – glycerol conversion, *S*<sub>*i*</sub> – selectivity to *i* component: GA – glyceric acid, GLYCA – glycolic acid, TARTA – tartronic acid, OXALA – oxalic acid, FA – formic acid, LA – lactic acid.



**Table 3.** Initial reaction rates, glycerol conversions and selectivities after 2 h of reaction over bimetallic catalysts operating at room temperature. Other reaction conditions: 5 bars O<sub>2</sub>, 200 cm<sup>3</sup> of a 0.3 M GLY solution, NaOH/GLY = 4 mol/mol, 0.5 g of catalyst and a stirring speed of 1500 rpm).

Active metal(s)	Initial reaction rate, [mol·h <sup>-1</sup> ·mol <sub>Me</sub> <sup>-1</sup> ]	Conversion and selectivity after 2 hours of reaction, [%]						
		C <sub>GLY</sub>	S <sub>OXALA</sub>	S <sub>TARTA</sub>	S <sub>GA</sub>	S <sub>GLYCA</sub>	S <sub>LA</sub>	S <sub>FA</sub>
AuPt	9 842	100	6.93	29.25	33.39	18.66	0	11.63
AuPd	2 655	98.35	1.99	7.78	63.73	15.91	0.91	9.67
AgAu	437	23.45	0	5.79	53.80	24.48	0	15.94
PdPt	1 558	65.82	3.33	9.97	74.82	5.91	1.05	4.91
AgPt	5 146	97.34	6.80	21.38	55.01	8.94	0.49	7.38
AgPd	1 184	57.59	3.42	6.66	70.06	10.10	0.70	8.92

For the abbreviations' meaning, please refer to the footnote of Table 2.

**Table 4.** Initial reaction rates, glycerol conversions and selectivities after 2 h of reaction over basic alumina supported bimetallic catalysts tested at room temperature and using bubbling air as an oxidant (reaction conditions: RT,  $P_{\text{atm}}$ , 650 mL air/min, 200 cm<sup>3</sup> of 0.3 M GLY solution, NaOH/GLY = 4 mol/mol, 0.5 g of catalyst and a stirring speed of 1500 rpm).

Active metal(s)	Initial reaction rate, [mol·h <sup>-1</sup> ·mol <sub>Me</sub> <sup>-1</sup> ]	Conversion and selectivity after 2 hours of reaction, [%]						
		$C_{\text{GLY}}$	$S_{\text{OXALA}}$	$S_{\text{TARTA}}$	$S_{\text{GA}}$	$S_{\text{GLYCA}}$	$S_{\text{LA}}$	$S_{\text{FA}}$
AuPt	706	43.58	1.40	2.11	60.69	11.75	11.01	12.85
AuPd	296	49.36	0	6.22	81.59	1.43	6.29	3.31
AgAu	77	5.94	0	2.42	51.58	10.32	14.08	17.90
PdPt	449	50.67	0	5.90	74.31	2.65	10.02	5.96
AgPt	439	36.01	0	5.41	80.03	2.32	7.26	4.13
AgPd	148	13.64	0	2.91	77.63	4.43	9.08	5.96

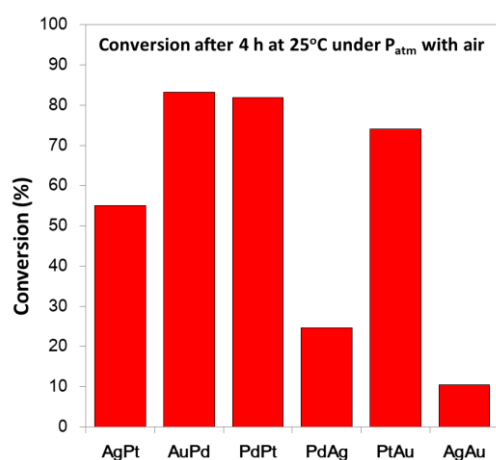
For the abbreviations' meaning, please refer to the footnote of Table 2.

**Table of contents:** Bimetallic catalysts showed excellent performances in the reaction of glycerol partial oxidation in the liquid phase. Almost full conversion could be achieved over the AuPt/Al<sub>2</sub>O<sub>3</sub> catalyst at room temperature under atmospheric air bubbling as an oxidative atmosphere, paving the way towards potential industrial applications using such mild conditions.

**Keywords:** glycerol, liquid phase oxidation, ambient reaction conditions, noble metal catalysts, air as oxidant

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### Passing the frontiers of liquid phase glycerol partial oxidation over supported bimetallic catalysts



## Supporting Information

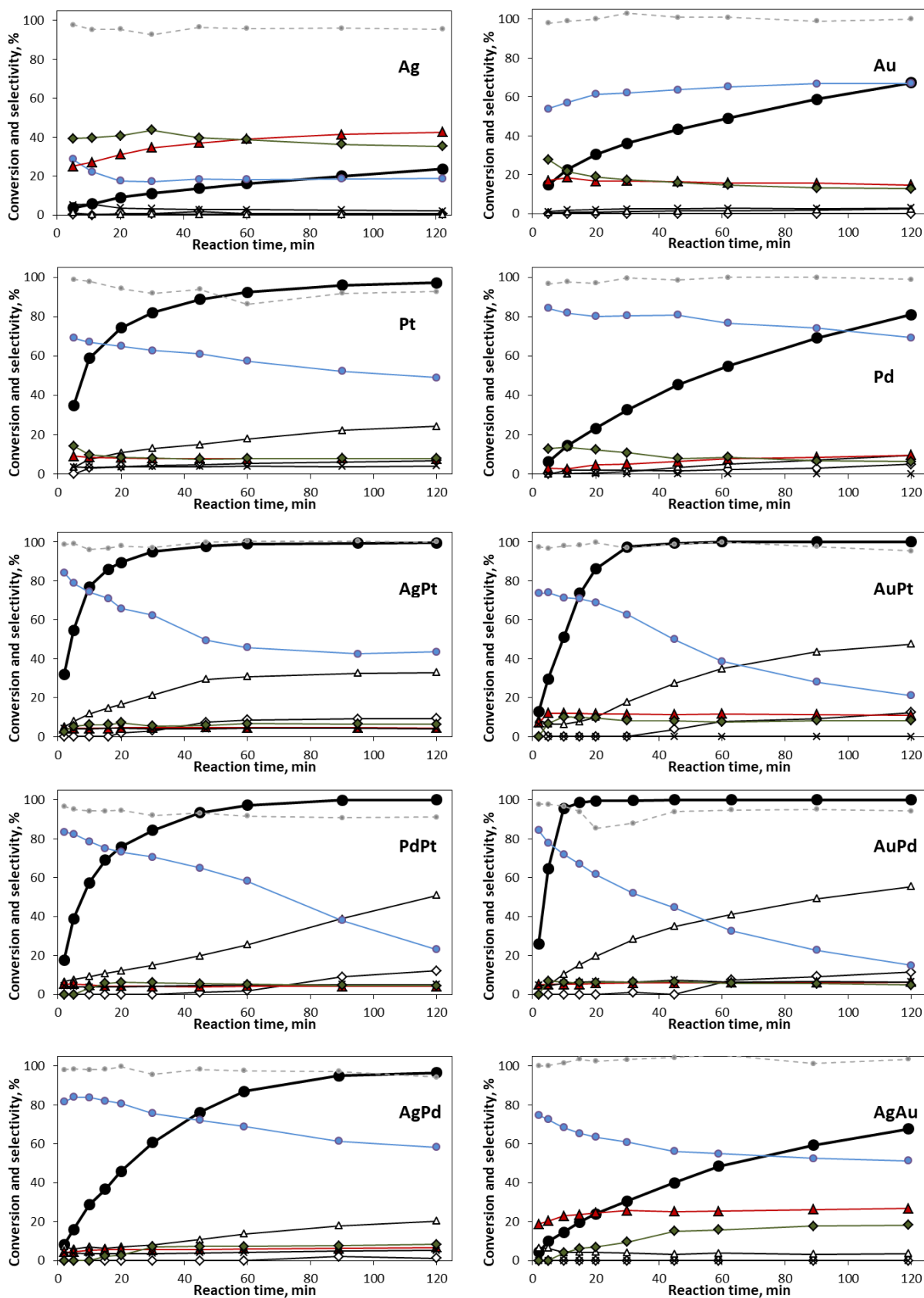
### **Passing the frontiers of liquid phase glycerol partial oxidation over supported bimetallic catalysts**

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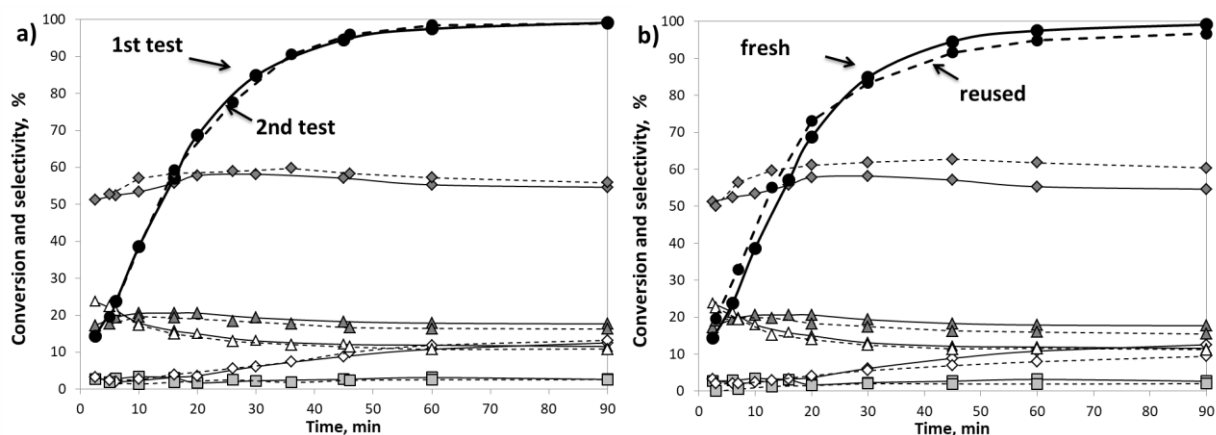
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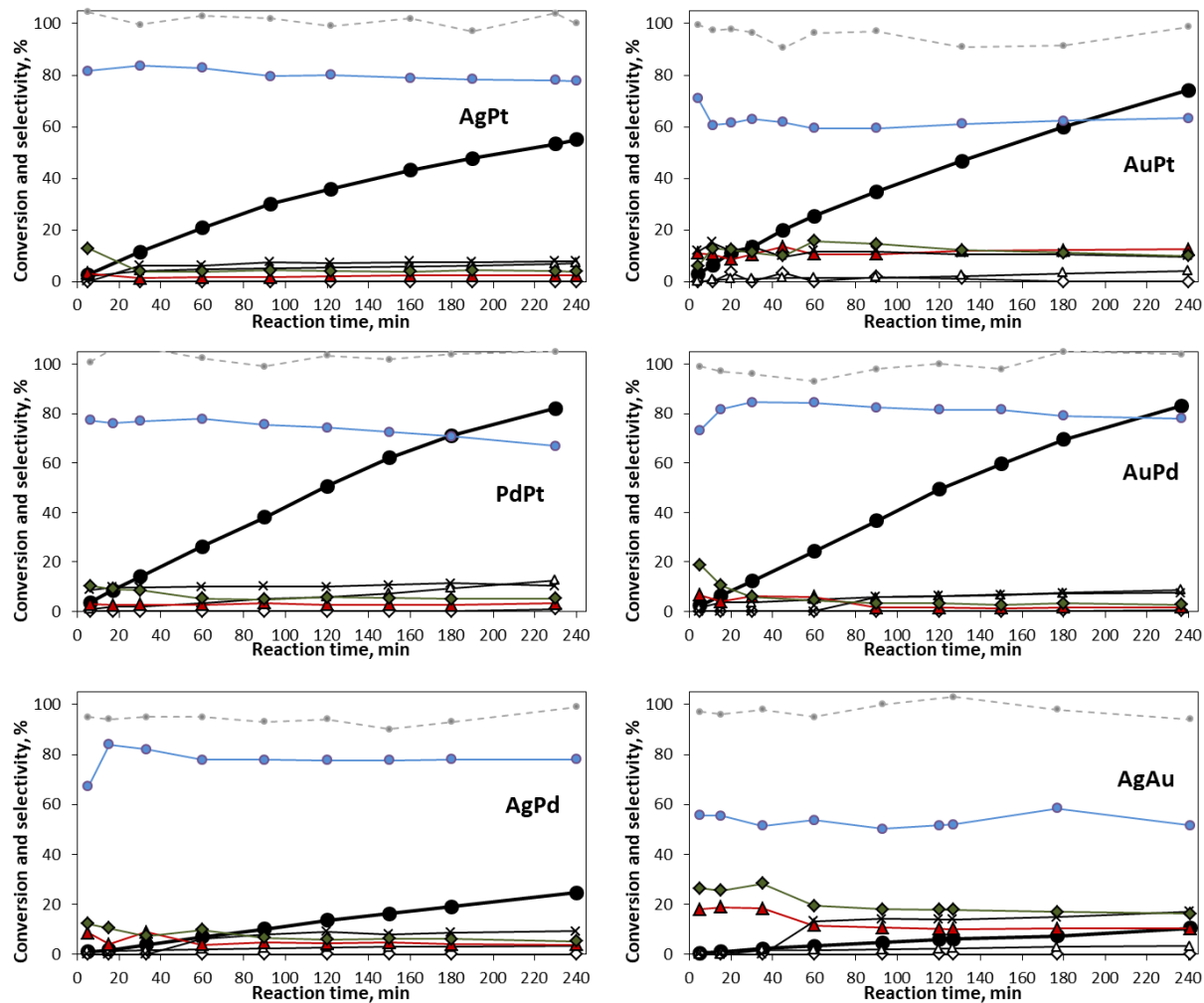
**Figure S1.** Glycerol conversion (●) and selectivities to glyceric acid (●), glycolic acid (▲), oxalic acid (◆), tartaric acid (△), lactic acid (x), formic acid (◇), and carbon balance (dotted line) as function of time over monometallic and bimetallic catalysts. Reaction conditions: 60 °C, 5 bars O<sub>2</sub>, 0,5 g of catalyst, 200 mL of a 0.3 M GLY solution, NaOH/GLY = 4 mol/mol, 1500 rpm.



**Figure S2.** Test at room temperature over the AuPt catalyst. (a) Repeatability of the results – two separate experiments with 0.25 g of fresh catalyst; (b) Possibility of reusing the catalyst – reaction with 0.25g fresh AuPt and reaction with 0.25 g of catalyst recovered after complete process of GLY oxidation at 60 °C under 5 bars of O<sub>2</sub>.

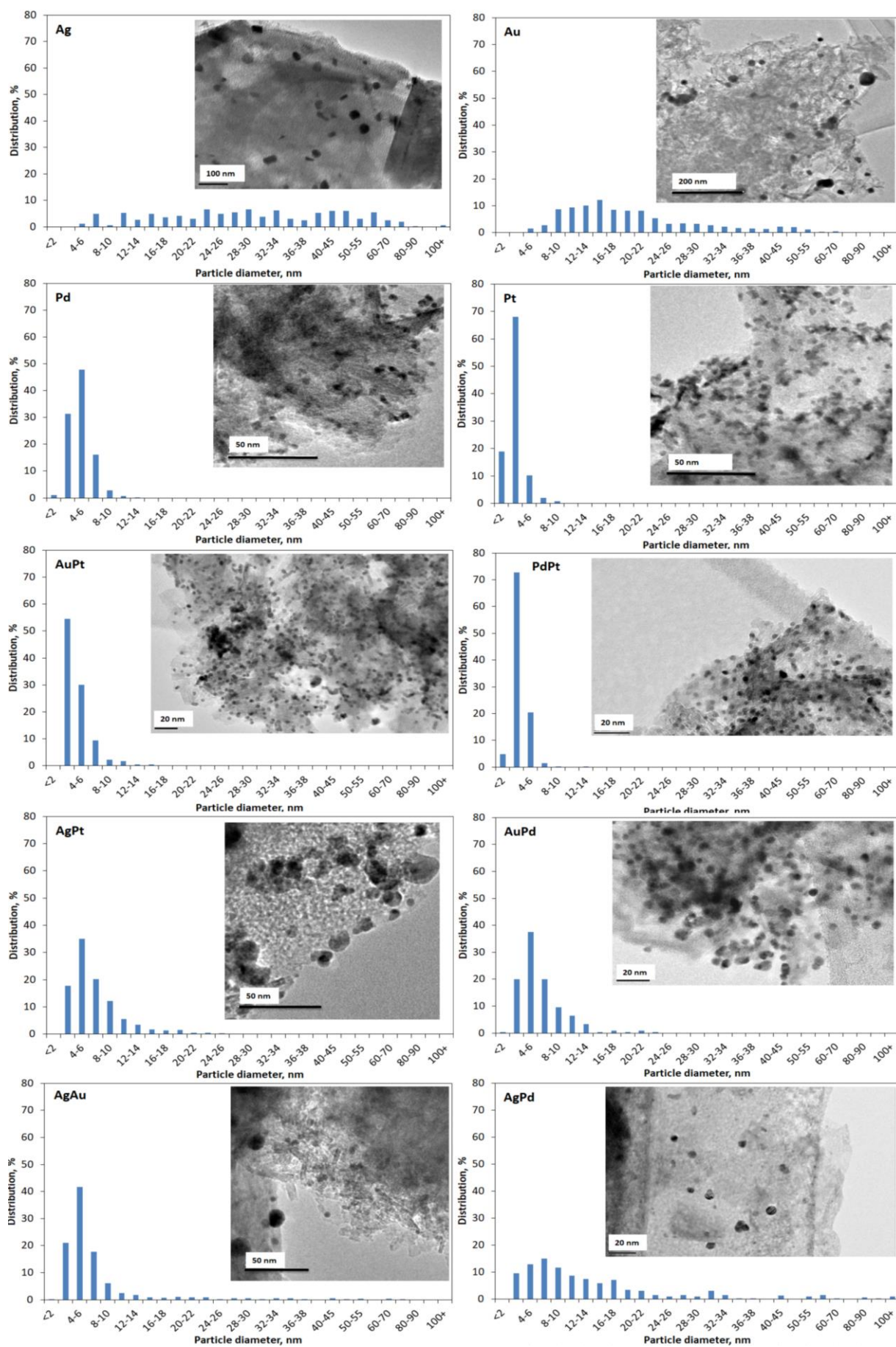
Reaction conditions: 60° C, 5 bars O<sub>2</sub>, 200 mL of a 0.3 M GLY solution, NaOH/GLY = 4 mol/mol, 1500 rpm.

Symbols: (●) GLY conversion, (◆) selectivity to GA, (▲) selectivity to GLYCA, (△) selectivity to FA, (◇) selectivity to TARTA, (■) selectivity to OXALA.



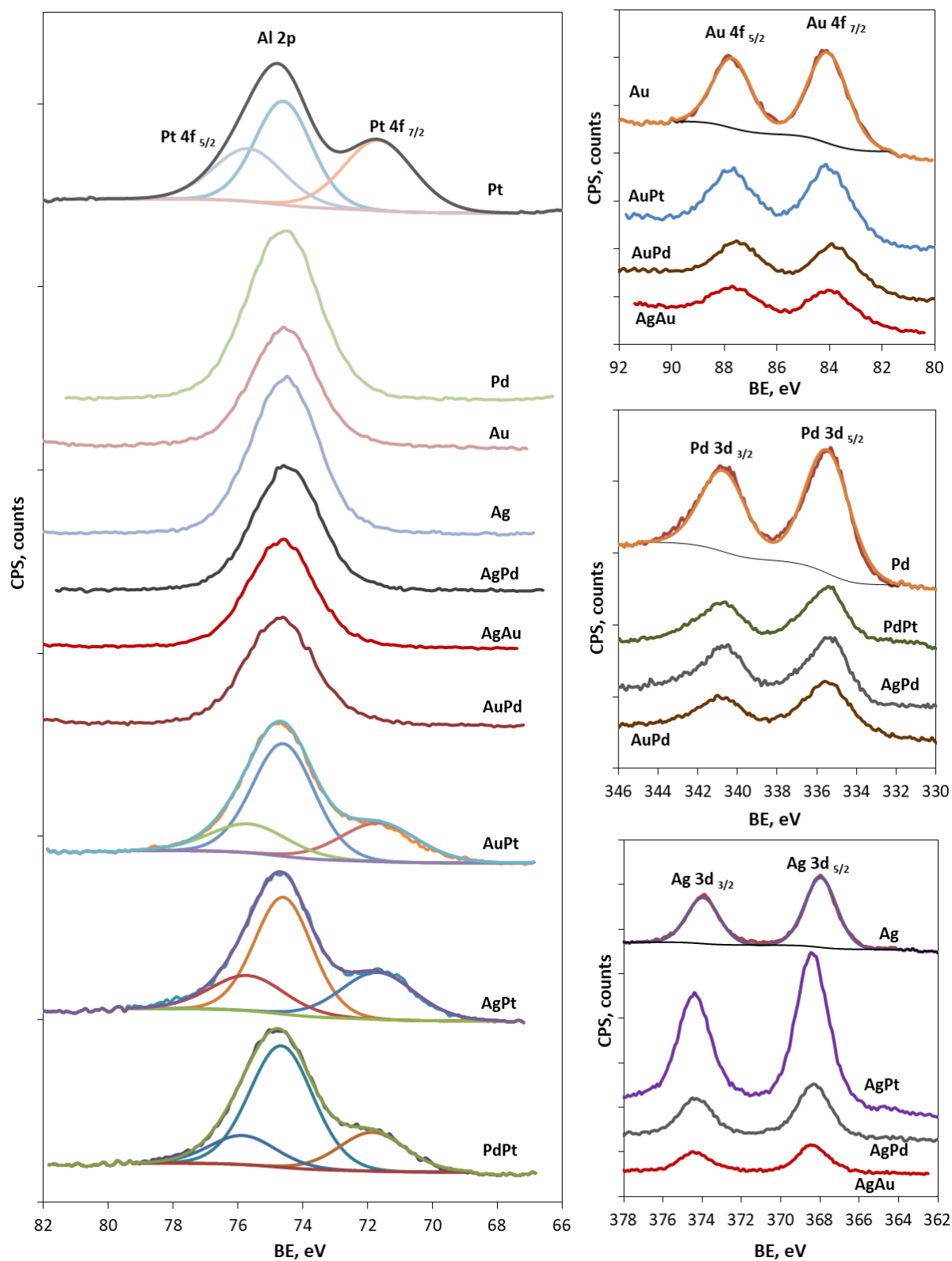
**Figure S3.** Glycerol conversion (●) and selectivities to GA (●), GLYCA (▲), OXALA (◆), TARTA (Δ), LA (x), FA (◆), and carbon balance (dotted line) as a function of time over bimetallic catalysts.

Reaction conditions: Room temperature, atmospheric pressure, 650 mL/min air flow, 0.5 g of catalyst, 200 mL of a 0.3 M GLY solution, NaOH/GLY = 4 mol/mol, 1500 rpm.

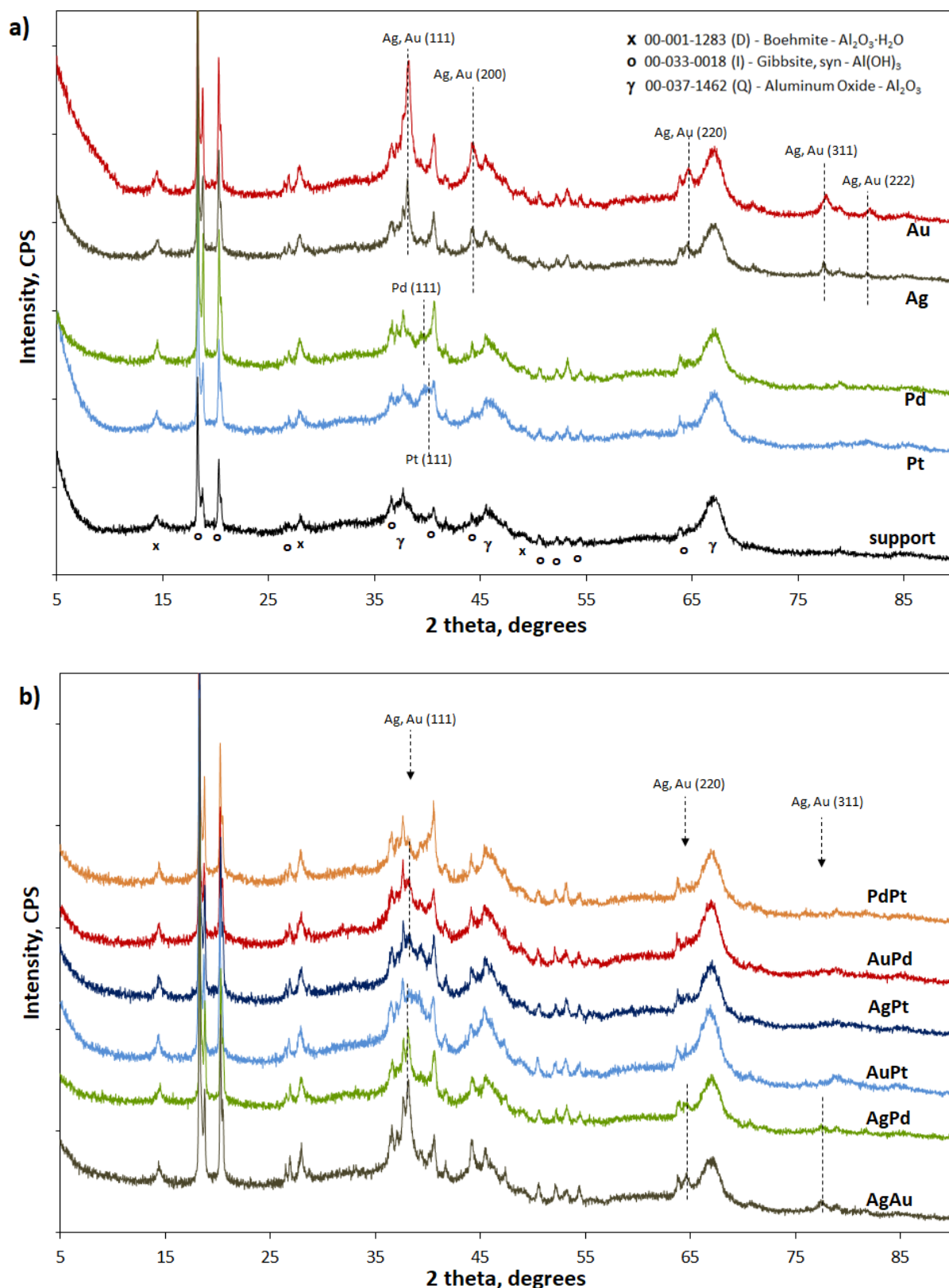


**Figure S4.** Particle size distribution histograms with representative TEM images (inserts).





**Figure S5.** XPS spectra of the Al 2p level with Pt 4f peaks identified by fitting (left graph) and Au 4f, Pd 3d and Ag 3d levels (right graphs from the top) observed for monometallic and bimetallic fresh noble metals catalysts supported on basic alumina oxide.



**Figure S6.** XRD diffractograms of monometallic noble metals catalysts and bare support (a), and of bimetallic catalysts supported on basic alumina (b). Corresponding JCPDS files: Pt (00-001-1194), Pd (01-087-0637), Ag (01-089-3722), Au (04-0784).

**Table S1.** XPS binding energy values (XPS) for the bimetallic catalysts recovered after glycerol oxidation test at 60° C under 5 bars O<sub>2</sub>.

Cat.	BE [eV] by XPS			
	Au 4f <sub>7/2</sub>	Pt 4f <sub>7/2</sub>	Pd 3d <sub>5/2</sub>	Ag 3d <sub>5/2</sub>
AuPt	83.9	71.5		
AuPd	83.6		335.1	
AgAu	83.5			367.7
PdPt		71.4	335.3	
AgPt		71.3		368.0
AgPd			335.4	367.9