

# A Career in Catalysis: Laura Prati

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**ABSTRACT:** This account celebrates the long and successful scientific career of Laura Prati, recalling her most important scientific achievements since the beginning of her work as a researcher in inorganic chemistry. Laura went through many aspects of liquid-phase heterogeneous catalysis, taking her first steps in the field of catalysts synthesis, where she pursued the development of innovative strategies for preparing catalysts until laying the foundations of the colloidal synthesis of metal nanoparticles, with particular interest in gold. Her investigations in colloids for catalysis had a natural outcome on catalysts synthesis and optimization. In her career, she dealt with liquid-phase oxidation reactions, with particular attention to biomass valorization processes. According to this, she could not help to deal also with hydrogenation and hydrogenolysis reactions, to which she dedicated herself, especially in the more recent years. Her discoveries have influenced many researchers in the area of heterogeneous catalysis and design of materials.

**KEYWORDS:** gold catalysis, oxidation, hydrogenation, alcohols, polyols, metal colloids



## 1. INTRODUCTION

Laura Prati was born in 1959 in Milan, Italy. She graduated in Chemistry (1983) at University of Milan, and received her specialization in “Tecniche Analitiche per la Chimica Organica Fine” from the Politecnico of Milano in 1985 and was awarded a Ph.D. in Industrial Chemistry in 1988. Since the beginning of her scientific career, she was involved in the field of the heterogeneous materials particularly applied to catalysis, being awarded a MONTEDIPE S.r.l. fellowship, concerning the project “Substitutive Catalysts of Noble Metals”. In 1989, she became a Researcher; in 1999, she became an Associate Professor of General Chemistry; and in 2017, she was a Full Professor. Since this year, she was elected as Head of the Department of Chemistry. Her research has focused on low-impact environmental catalytic methodologies as alternative processes of the stoichiometric ones based on organic synthesis. She introduced the use of gold as active metal in the aerobic selective oxidation of organic compounds, contributing to the developing of the unusual gold catalytic properties, the main one being the resistance to poisoning due to the overoxidation in the liquid-phase oxidation (Figure 1). Her skills include the preparation and the functionalization of materials for obtaining high metallic dispersed catalysts on oxides, active carbons, and mesoporous systems. The scientific results are reported in more than 150 publications on qualified international journals, h-index 53, 2 patents, and more than 100 communications at national and international congresses (7 invited). From 2002 to 2006, she was the Referent of the



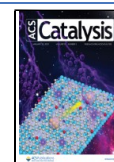
**Figure 1.** Laura Prati during a conference, showing the importance of Au in heterogeneous catalysis.

research topic concerning with liquid-phase gold-catalyzed oxidations, inside the European project AURICAT (HPRNN-

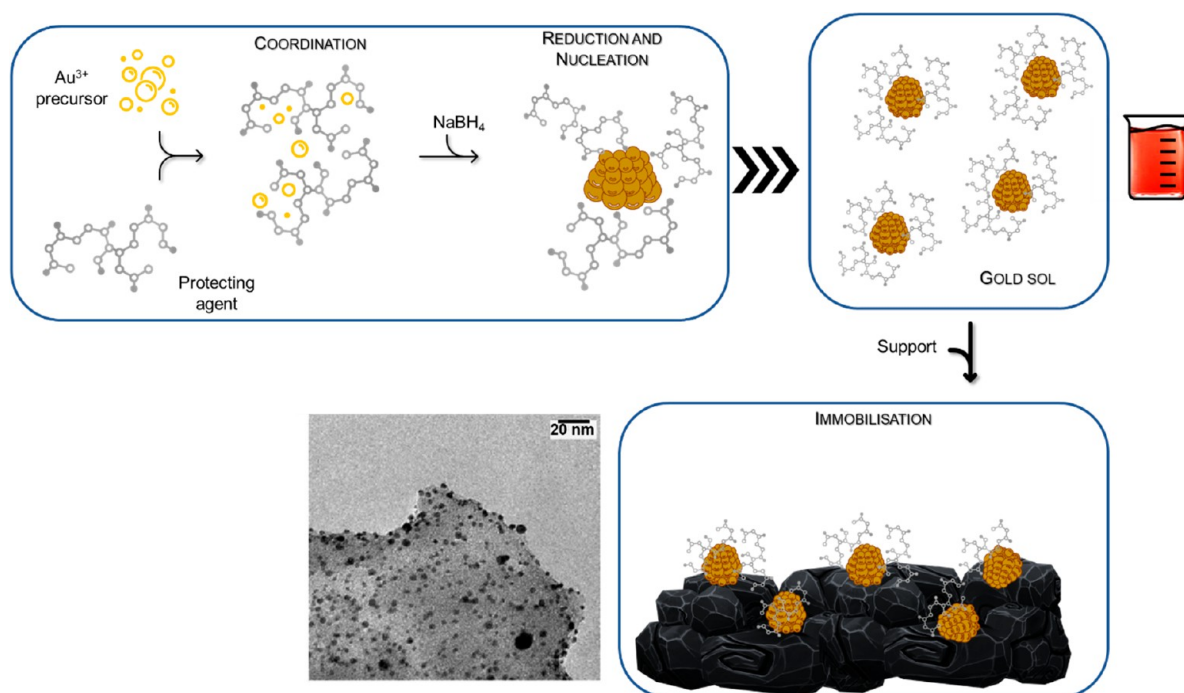
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## Scheme 1. Sol Immobilization Procedure



CT-2002–00174). In 2007, she was funded by Fondazione Cariplo on “Metal Based Nanostructures Materials for Catalysis” and in 2009 on the project “Metallic Nanoparticles: The Issue of Stability for Their Application”. She received a grant from Consiglio Nazionale delle Ricerche (CNR, National Research Council) bilateral project Italy-Hungaria on the project: Supported bimetallic Au–Cu and Au–Ag catalysts in selective alcohol (benzyl alcohol, glycerol) oxidation reactions: Au/Cu(Ag) atomic ratio, Au/Cu(Ag) structure and support effect”. In 2017, she was granted by TOTAL on the project “Catalyst for Future”. She was a Visiting Professor at Université Pierre et Marie Curie (Paris) [June–July 2015] and at Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México (Mexico City) [November 2015 and 2017].

## 2. THE ORIGINS OF A “GOLDEN CAREER”: GOLD CATALYSIS FOR REACTIONS IN LIQUID PHASE FROM MONOMETALLIC TO BIMETALLIC SYSTEMS

At the core of the modern catalysis science is the fundamental awareness that a multidisciplinary approach must be implemented to tackle future challenges and opportunities. This paradigm is well-reflected by the above-summarized scientific career of Laura Prati, where material science and inorganic chemistry were combined with organic, physical, and analytical chemistry methods in shaping a knowledge-based design of heterogeneous catalysts.

In the early 1990s, Laura began her research on heterogeneous catalysis for the chemo-selective oxidation of diols and phenols by using molecular oxygen. The attention was initially focused on copper-based catalysts.<sup>1–4</sup> Meanwhile, a few years earlier, the research team of Prof. Haruta had demonstrated that nanostructured gold was able to oxidize carbon monoxide, even at low temperatures,<sup>5</sup> while a team led by Prof. Hutchings had reported the unique activity of cationic gold in acetylene hydrochlorination.<sup>6</sup> These were years of

significant growth in the field of catalysis by gold. The review of Bond and Thompson well-summarized the main achievements of gold in the area of catalysis of that period and the promising future of gold for catalytic applications.<sup>7,8</sup>

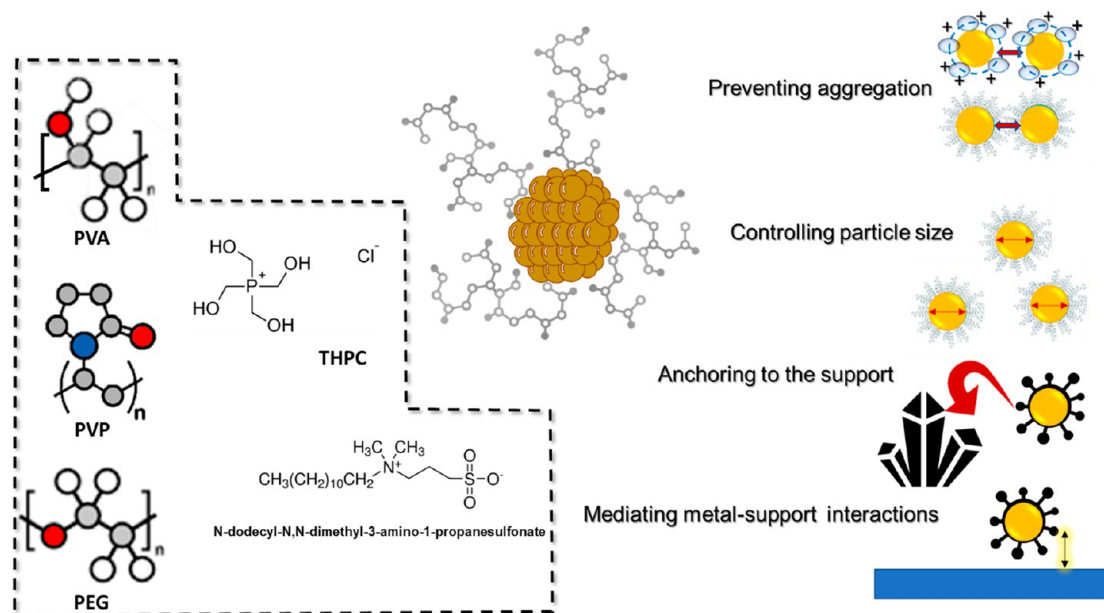
Gold was considered to be a poorly active metal until the 1980s. The possibility to finely disperse gold in the form of small nanoparticles (2–6 nm) on a support imposed a reconsideration of the catalytic potential of gold. Besides the above-mentioned reactions, the gold-catalyzed hydrogenation of CO<sub>2</sub> to methanol was investigated by Baiker et al.,<sup>9</sup> while Schmidbauer et al.,<sup>10</sup> Teles et al.,<sup>11</sup> and Hashmi and co-workers<sup>12,13</sup> discovered the enormous potential of homogeneous gold catalysis in the addition of alcohols to alkynes and in phenol synthesis, respectively. In parallel, the praiseworthy surface characterization studies of Goodman and co-workers<sup>14,15</sup> and the reports by Flytzani-Stephanopoulos and co-workers<sup>16,17</sup> on the role of the cationic form of gold provided useful insights on the nature and structure of active sites in gold-based catalysis.

These fascinating seminal studies stimulated Laura’s interest in catalysis by gold and drove her to perform research devoted to the investigation of the catalytic activity of gold in the oxidation of diols in liquid phase.

At that stage, literature investigations had mainly focused on the catalytic oxidation of polyols and C<sub>2</sub>/C<sub>3</sub> diols using palladium on carbon or platinum on carbon as catalysts. Despite their high activity, these catalysts promoted over-oxidation and C–C bond cleavage, resulting in poor selectivity, which, together with the poisoning effect of O<sub>2</sub>, limited the large-scale application of Pd/C and Pt/C catalysts. In this view, the unique capability of gold to favor molecular adsorption of O<sub>2</sub> over the dissociative one was promising insofar as it could prevent subsurface oxygen diffusion and then minimize the poisoning effect of oxygen.

Starting from these premises, in the first studies, activated carbon was selected as the reference support for gold-based catalysts and ethane-1,2-diol and propane-1,2-diol were studied

Scheme 2. Most Employed Protecting Agents and Their Role in Catalyst Preparation by Sol Immobilization



as model substrates. Surprisingly, 1% Au supported on activated carbon was proven to be an effective catalyst able to convert ethane-1,2-diol in alkaline solution and under mild conditions (70 °C, 2 atm O<sub>2</sub>, substrate/metal ratio = 1000, NaOH/substrate molar ratio = 3) with remarkable selectivity toward mono-oxygenation (90% selectivity in glycolate at very high conversion (94%)) and improved stability.<sup>18</sup> When tested under similar conditions, Pd/C and Pt/C were more active but less selective, Cu/C promoted C–C bond cleavage, and Ir/C was inactive. In addition, gold catalyst was less sensitive to poisoning, being recyclable up to 10 times without a loss of activity nor a significant decrease in selectivity.<sup>18</sup> The reported high activity and superior stability of Au/C catalyst in the liquid-phase oxidation of diols set a new important milestone in the rising “golden age” of heterogeneous catalysis, especially in the area of heterogeneous liquid-phase catalysis and, later, in gas-phase catalysis.

However, right from these first studies, it was clear that the catalytic behavior of gold catalysts was influenced by many important parameters, such as (i) the particle size, (ii) the type of support, (iii) the metal–support interaction, (iv) the different preparation methods, and (v) the reaction conditions.<sup>19</sup> The development of gold-based catalysts for liquid-phase reactions thereby demanded actions on several fronts.<sup>20</sup> First, a prerequisite for an optimal design of gold-based catalyst was the setting-up of a synthetic procedure to deposit gold nanoparticles with controlled particle size and high dispersion, independently on the choice of support. So far, coprecipitation, deposition–precipitation and chemical vapor deposition (CVD) were the most often used methods for the deposition of gold nanoparticles onto oxidic supports to produce Au-based catalysts for gas-phase reactions. However, all these methods failed to produce small and highly dispersed Au aggregates on activated carbon, which, on the other hand, had been demonstrated to be the most suitable support for Au catalysts to be used in the liquid phase.<sup>19</sup> A major breakthrough was made by Laura and her co-workers,<sup>21</sup> when they prepared size-controlled gold nanoparticles supported on activated carbon through immobilization of a

prereduced gold sol (sol immobilization method), by adopting a protocol proposed by Grunwaldt et al. for the preparation of Au/TiO<sub>2</sub> and Au/ZrO<sub>2</sub> catalysts for the low-temperature oxidation of CO.<sup>22</sup> The sol immobilization method consisted in the chemical reduction of gold precursor (NaAuCl<sub>4</sub> or HAuCl<sub>4</sub>) in the presence of a protecting agent (polymer, surfactant, polar molecule, etc.) and the subsequent immobilization of gold nanoparticles on a support (Scheme 1).

Interestingly, the activity of Au/C catalyst prepared by the sol immobilization in the oxidation of ethane-1,2-diol was at least 2-fold higher (ca. 80% conversion) than that of analogous catalysts prepared by more conventional methods (43% and 22% conversion for Au/C catalysts prepared by deposition precipitation and impregnation, respectively). The unique activity of Au/C catalyst prepared by the sol immobilization was derived by two concomitant effects: the enhanced dispersion of gold nanoparticles (Au NPs) on the support surface and the controlled particle size of Au.

Unlike gas-phase CO oxidation, where it has been reported that uniform 2-nm Au NPs represented the most active phase,<sup>23</sup> in liquid phase oxidation processes the effect of particle size was more complex.

Specifically, Au NPs having mean particle size of 7–8 nm were obtained by depositing preformed Au NPs on activated carbon, and these Au NPs resulted to be more active and selective than those with larger or smaller particle sizes. These effects were essentially affected by the interaction between metal NPs and support and their extent depended on the nature of the support, on the molecular size and structure of the protecting agent, on the protecting agent/Au weight ratio (w/w) (Scheme 2).<sup>24</sup>

The protecting agent emerged as an essential ingredient in the sol immobilization method and its role deserves to be thoroughly investigated. It foremost forms an organo-shell, which provides stabilization and prevents aggregation of metal NPs in the sol. Moreover, protecting agent molecules confer additional functionalities and modify the surface charge of gold NPs. Typically, the surface of Au NPs is negatively charged, due to the presence of adsorbed anions. Embedding polar or

ionic character, the protecting agent molecules adsorbed on the metal surface can alter its surface charge. By this way, they may mediate the anchoring of Au NPs on the support, resulting in a more effective interaction with the support and allowing preserving the original particle size and morphology during the immobilization step. Among the most employed protecting agents, tetrakis(hydroxymethyl-)phosphonium chloride (THPC, which acts also as a reducing agent and provides electrostatic stabilization) produced small, mono-dispersed Au NPs (2–4 nm). However, high THPC/Au ratio was necessary to keep the original particle after immobilization on support.<sup>25</sup> Improved stabilization could be achieved when both electrostatic and steric effects were involved. This was the case of polymers, such as poly(ethylene glycol) (PEG), poly(vinylpyrrolidone) (PVP) and, in particular, poly(vinyl alcohol) (PVA), which provide double protection and ensure good stabilization. In particular, the use of PVA not only enabled the maintenance of sol particle dimension, even after immobilization on the carbon support, but it also generated highly active Au NPs with mean Au diameter centered at 7 nm. The latter were able to quantitatively oxidize ethylene glycol (EG) after 1 h (substrate/catalyst ratio = 1000 mol/mol, substrate/NaOH molar ratio = 1,  $p_{O_2}$  = 2 atm,  $T$  = 70 °C).<sup>26</sup>

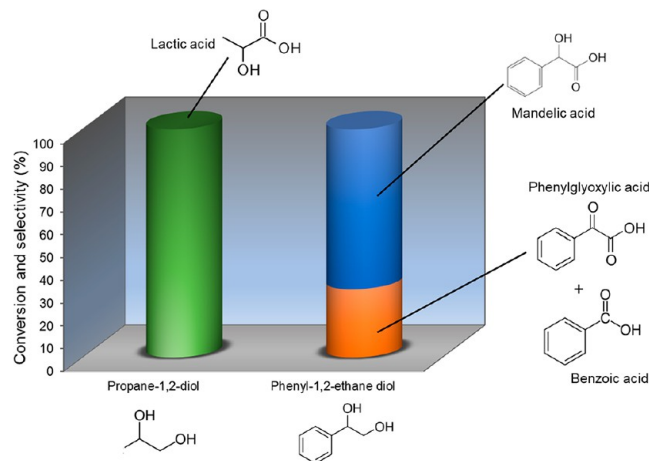
On the other hand, the presence of a carbonaceous protective layer may cause shielding effects, limiting Au atom exposure. It could be then presumed that the optimal particle size for catalysis was also dependent on gold surface concentration. In fact, when ionic surfactants, such as polydiallyl ammonium chloride, poly(diallyldimethylammonium) chloride (PDDA),<sup>27</sup> poly[bis(chloroethyl)ether-*alt*-1,3-bis-[3-(dimethylamino)propyl]urea (PEU) and sulphobetaines, such as *N*-dodecyl-*N,N*-dimethyl-3-amino-1-propansulfonate, were employed as protecting agents the protective layer conformation and charge density could be influenced by external ions, resulting in a reduced shielding effect and higher exposure of Au atoms.<sup>28</sup> As a consequence, when sulfobetaine-protected Au NPs with lower mean diameter (4.8–5.1 nm) than PVA-protected sol (7 nm) were deposited on activated carbon, the resulting Au/C catalyst exhibited higher activity (3300–3400 h<sup>-1</sup> vs 800 h<sup>-1</sup>) in EG oxidation, due to the high atomic Au/C percentage at the surface.

The sol immobilization procedure for the preparation of supported gold catalysts was then further optimized by Prof. Hutchings and co-workers, with particular emphasis to the development of protocols for the removal of stabilizer ligands from supported Au NPs.<sup>29</sup>

If the selection and removal of the protecting agent represented a critical point, on the other hand, the nature of the support also was far from being a silent actor and played a crucial role in the immobilization process. First, depending on the iso-electric point and pH, the surface charge of support affects the interaction of metal NPs with the electrified interface in the immobilization step. In addition, the functionalization degree of the support determines the dispersion and particle size control since surface functionalities can act as anchoring sites for metal NPs and contribute to their stabilization. Furthermore, the occurrence of strong metal–support interactions can influence the electronic and structural properties of deposited Au NPs.<sup>30</sup> Therefore, even the simple label Au/C was demonstrated to be too generic. Actually, it encompassed a large variety of catalysts, where the different structure, porosity, and surface chemistry of the carbon scaffold

may have significant consequences on the size, shape, and properties of Au NPs and on their catalytic behavior.<sup>31</sup> As a matter of fact, carbon materials include activated carbons (AC), graphite, and low-dimensional carbon allotropes (carbon nanotubes, CNTs, carbon nanofibers, CNFs, graphene), which strongly differ for their intrinsic textural, electronic, and surface properties. Moreover, as a further complication, activated carbons can possess different properties, depending on their source or the preparation procedure. When the same preformed metallic sol (Au–PVA protected NPs) was deposited on different activated carbons (from coconut and wood), the reactivity and catalytic performances in the liquid phase oxidation of ethylene glycol were affected by the different microstructure and surface properties of support. In this case, the nature of support did not influence gold exposure or average Au particle, but rather the density of phenolic groups at the surface-modulated specific metal–support interactions with obvious consequences on the catalytic behavior.<sup>32</sup>

Then, the selectivity of diol oxidation appeared to be the result of a delicate balance between the nature and structure of the catalysts (particle size, protecting agent, support, surface Au coverage), reaction conditions and the molecular structure of the substrate. As regard the latter point, the oxidation of aliphatic diols on Au/C catalysts demonstrated to be highly regioselective toward the primary alcoholic group (the oxidation of propan-1,2-diol proceeded with 100% selectivity to lactic acid), while the presence of a phenyl residue in phenyl-1,2-ethane diol activated the secondary position (Figure 2).<sup>33</sup>



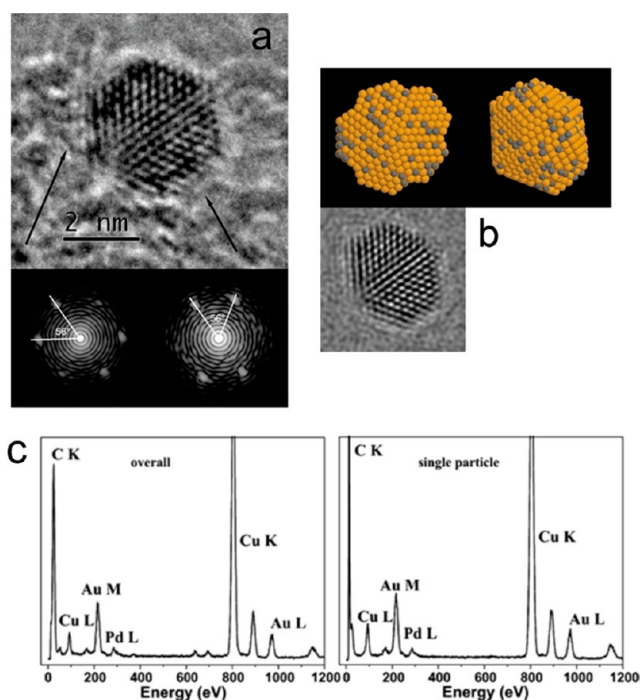
**Figure 2.** Catalytic performance of Au/C catalysts in the liquid-phase oxidation of propan-1,2-diol and phenyl-1,2-ethane diol. Reaction conditions:  $T$  = 90 °C, NaOH/propan-1,2-diol = 1; diol/M = 1000;  $p_{O_2}$  = 300 kPa;  $t$  = 1 h.

The great experience gained on liquid-phase oxidation of diols together with the promising results in the oxidation of more-complex substrates, such as glucose,<sup>34</sup> and aldehydes<sup>35</sup> opened stimulating growth scenarios for Au-based catalysis.<sup>36</sup> Actually, Laura's work inspired several researchers, such as Prof. Haruta's team,<sup>37,38</sup> Prof. Corma's group,<sup>39–41</sup> and Prof. Christensen,<sup>42–46</sup> who further investigated Au-based catalysts for the oxidation of alcohols and glucose. Gold catalysts were also successfully tested for the aerobic oxidation of primary amines both in homogeneous and heterogeneous cataly-

sis.<sup>47–49</sup> The international impact of Laura's pioneering work in the development of gold catalysts for liquid-phase processes was sublimated by her role as the Referent of the research topic concerning with liquid-phase gold-catalyzed oxidations from 2002 to 2006, inside the European project AURICAT (No. HPRNN-CT-2002–00174).

The lower activity, compared to Pt/C and Pd/C, together with the need for a basic environment still represented two drawbacks of Au/C catalysts calling for further improvement. Once again, Laura and her co-workers were demonstrated to be keen to find a practical and sustainable solution: merging the unique properties of gold (resistance to poisoning) with those of Pd or Pt (high activity even in the absence of a base), by preparing bimetallic Au–Pd and Au–Pt catalysts.<sup>50</sup> First attempts to prepare carbon-supported Au–Pd (Au: Pd = 1:1, molar ratio) nanoparticles consisted in a successive reduction of the two metals, followed by immobilization of the bimetallic sol on carbon. Preformed particles of the first metal acted as nucleation centers for the second metal reduced in the presence of poly(vinyl alcohol) (PVA) as the protective agent and NaBH<sub>4</sub> as the reducing agent. This two-step procedure led to bimetallic nanoparticles with an average diameter of 3.5 nm, which possessed an alloy structure with a partial segregation of Pd. The method was then optimized by replacing NaBH<sub>4</sub> with H<sub>2</sub> as the reducing agent.<sup>51</sup> In this way, the reduction rate of Pd ions was slowed and the increased time of the diffusion and the growth of Pd on Au allowed the segregation of Pd to be minimized. Random alloyed bimetallic nanoparticles with multi-ply twinned structure and coherent crystalline structure were obtained according to characterization by high-resolution transmission electron microscopy (HRTEM) coupled with energy-dispersive X-ray spectroscopy (EDX) (Figure 3). Uniform structure and homogeneous composition (Au–Pd atomic ratio close to 6:4) was observed independent of particle size without any segregation of metal phase Au NP solid solutions. Such a compositional and structural homogeneity was maintained even at different Au:Pd atomic ratios (Au:Pd = 9.5:0.5, 9:1, 8:2, 6:4, 2:8).<sup>52,53</sup> Once again, the protecting agent played an active role. Well-alloyed nanoparticles with uniform compositions were obtained when PVA was used as the stabilizer. Conversely, significant segregation and significant compositional discrepancies characterized bimetallic nanoparticles prepared in the absence of protecting agent or using an electrostatic stabilizer (e.g., THPC).<sup>54</sup> Interestingly, geometric and electronic effects induced by the altered interatomic distance on the surface of bimetallic catalysts can operate on opposite sides or can converge. In the latter case, the catalytic behavior of random alloyed PVA-protected Au–Pd NPs was found to benefit from synergistic effects.

The time had come to merge all the acquired knowledge on monometallic and bimetallic Au-containing catalysts and to move toward a critical design of Au-based catalysts for relevant industrial applications, such as oxidation and hydrogenation of biomass-derived products.<sup>55–57</sup> Such an ambitious goal required a progressive parallel advancement in the characterization of Au-based catalysts via techniques such as electron microscopies, X-ray spectroscopy techniques, vibrational spectroscopies, and chemisorption methods using ex situ and in situ methodologies (Scheme 3).<sup>58</sup> Laura's expertise in the preparation of noble-metal catalysts was recognized in 2017 by the TOTAL Company, which granted the Project Catalyst for the future, aimed to design efficient metal-based catalysts for emerging catalytic processes.

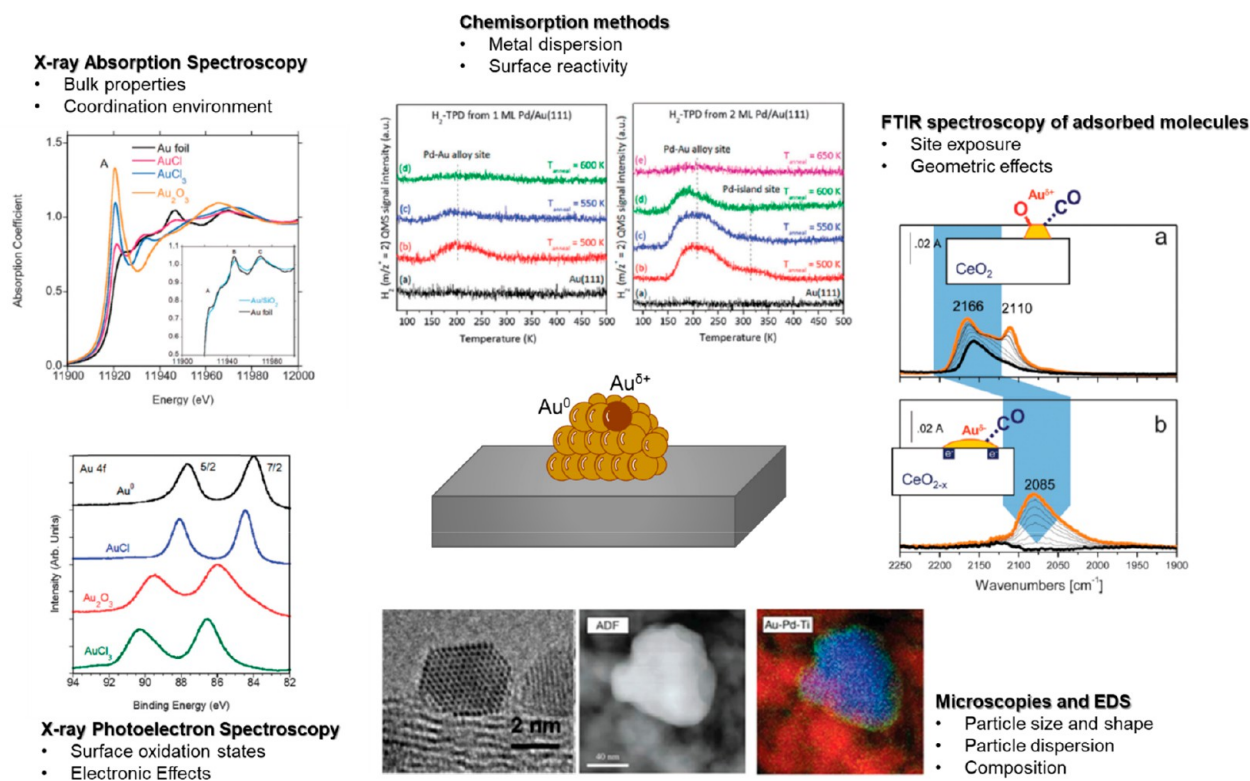


**Figure 3.** (a) Representative HRTEM microscopy of a multi-ply twinned particle in the form of truncated decahedron configuration with insets showing fast Fourier transforms (FFTs) from both sides of the visible twin boundary; (b) the modeled truncated decahedron particle viewed along the 5-fold axis (top left) and orientation that is analogue to the projection of the HRTEM image (top right); (c) the overall EDX spectrum (left) and the representative spectra taken from an individual single particle (right). The Au–Pd ratio is similar for each particle. [Reprinted with permission from ref 53. Copyright 2008, American Chemical Society, Washington, DC.]

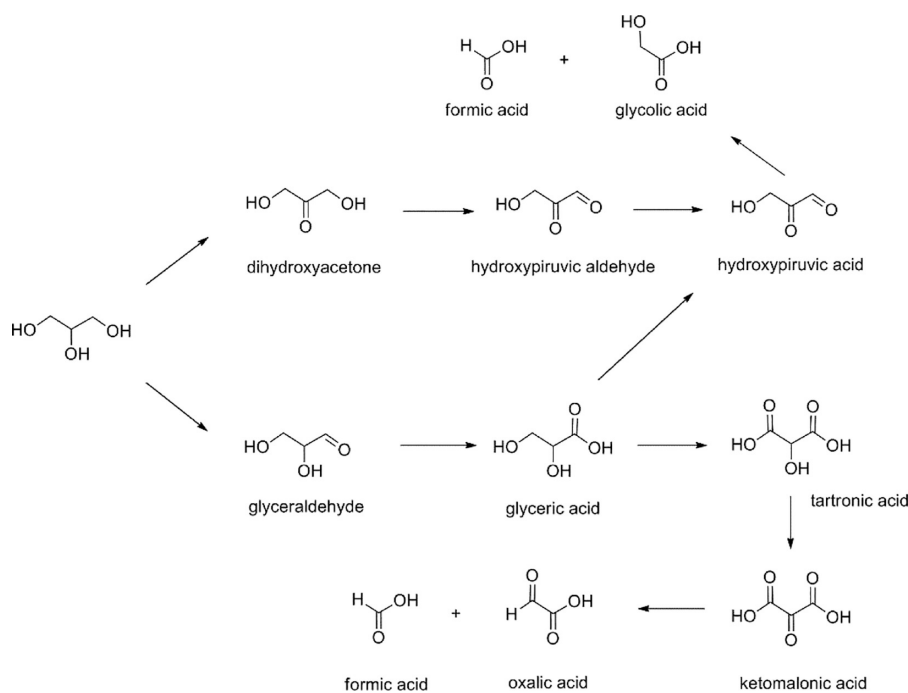
### 3. LIQUID-PHASE OXIDATION REACTIONS

**3.1. Optimization of Gold-Based Catalysts for Glycerol Oxidation.** Under the desire for a transition from fossil-based production/consumption to biomass-based industry, a range of important biomass-derived platform chemicals have been proposed for the concept of biorefinery. Glycerol has been proposed as one of the most important platform chemicals due to the fact that it is a primary byproduct in biodiesel production; therefore, it can be used as a potential source of producing fine chemicals and fuels and it is the subject of an ongoing intensive research for the last 20 years. In this view, the selective oxidation of glycerol could offer added-value in a variety of products through catalytic technologies. Several C3 compounds (glyceraldehyde, dihydroxyacetone, glyceric acid, hydroxyacetic acid, tartronic acid, mesoxalic acid), C2 compounds (oxalic acid, glycolic acid), and C1 compounds (formic acid) can be produced from glycerol oxidation according to Scheme 4. Nowadays, these chemicals are produced using expensive biotechnological technologies or by highly polluting oxidative processes using stoichiometric oxidants. Therefore, there is a significant interest in replacing these processes with environmentally friendly alternatives, such as the catalytic oxidation with dioxygen or air in the presence of heterogeneous catalysts. Because of the high functionality of glycerol molecule with the presence of three hydroxyl groups, the challenge remains to direct the selectivity to the desired product along such a complex reaction network.<sup>59</sup> For this reason, the development of effective, stable catalysts for the

## Scheme 3. Multi-technique Approach for the Characterization of Supported Au NPs



## Scheme 4. Glycerol Oxidation Reaction Network



selective oxidation of glycerol has represented a fertile testing ground for the design of selective and active gold-based catalysts.

Inspired by the encouraging results obtained by Laura's team in the oxidation of diols and polyols in the presence of Au/C catalysts, in 2002, Prof. Hutchings and co-workers successfully proposed Au/graphite catalysts for the liquid-phase oxidation of glycerol (80% selectivity to glycerate). The addition of

NaOH was necessary to promote the H-abstraction, the first step of the dehydrogenation pathway for glycerol oxidation.

In any case, the pH of the reaction medium is not the only parameter affecting the performances of supported noble metal nanoparticles. By precisely controlling the structure of the active sites and the microenvironment around it, the selectivity of the reaction can be controlled. This tunability arises from several features, such as particle size and shape, synergistic

alloying effects, addition of promoters, presence of protecting agent metal–support interactions, and cooperative effects. All these effects have been deeply investigated in the last decades by Laura's team.<sup>60</sup> The collected results by Laura and her co-workers, together with those from other research groups, such as the Prof. Claus group, who studied glycerol oxidation on Au/carbon and Au/ceria catalysts,<sup>61–63</sup> have constituted a solid starting point for the development of Au-based catalysts for glycerol and polyol oxidation.

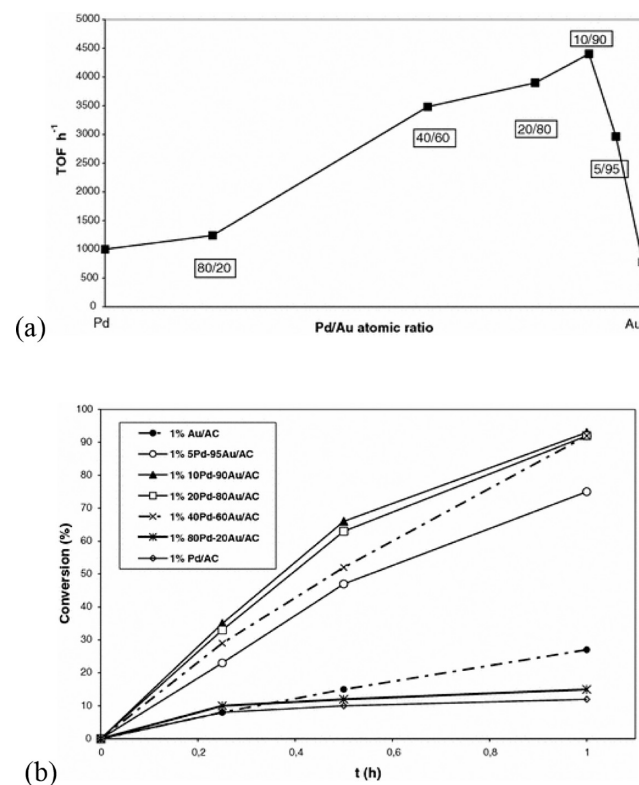
### 3.1.1. Effect of the Preparation Method and Particle Size.

The preparation method as well as the support can influence the Au mean particle size after deposition. Taking advantage from the previous experience on the Au-catalyzed oxidation of diols, the effect of different preparation methods (sol immobilization, incipient wetness, deposition precipitation, and conventional impregnation) was then investigated.<sup>64–66</sup> A variation of particle size (5–30 nm) could be obtained by depositing Au on activated carbon (AC) or TiO<sub>2</sub> as supports. The activity and the selectivity were strongly affected by gold particle size. Large Au NPs (10–30 nm) were less active than smaller ones (3–5 nm), even if the former were more selective to glyceric acid.

### 3.1.2. Synergistic and Compositional Effects in Bimetallic Catalysts.

The synergistic effects that are derived from alloying gold to a second metal (Pd, Pt) were investigated, by comparing the catalytic performance of AuPd/AC and AuPt/AC catalysts with those of the monometallic Au, Pd, and Pt/AC catalysts.<sup>53,67–70</sup> Monometallic and bimetallic catalysts were prepared using sol-immobilization procedures and tested in the glycerol oxidation under the same experimental conditions. Generally, bimetallic nanoparticles have been revealed to have similar activity, which, in any case, was higher than that of monometallic counterparts. Interesting differences between AuPt and AuPd emerged in terms of product distribution. The oxidation of the terminal hydroxyl groups was favored in the presence of supported AuPd nanoparticles, which preferentially produced glycerate and tartronate with selectivities over 90% at 90% conversion. Differently, an enhanced formation of glycolic acid was obtained using AuPt/AC catalysts. Interestingly, alloying gold to platinum and palladium conferred an improved stability and high resistance to deactivation. The catalytic performance of bimetallic nanoparticles was strongly dependent on the preparation method. One-step and two-step procedures were investigated, while NaBH<sub>4</sub> and H<sub>2</sub> were compared as the reducing agents. Best performances in glycerol oxidation were attained on supported single-phase Au–Pd nanoparticles prepared via a two-step procedure using H<sub>2</sub> as the reductant. These catalysts proved to possess improved resistance to poisoning, being stable after 11 recycles. The stability of Au–Pd catalysts was corroborated by electron microscopy characterization of the used catalysts, which presented negligible segregation, a low degree of metal leaching, and no evidence for surface reconstruction after prolonged use in catalysis. Further studies were devoted to unravelling the effect of nanoparticle composition, in terms of internal Au:Pd ratio on the activity and selectivity. Bimetallic nanoparticles, with Au/Pd atomic ratio ranging from 9:1 to 1:4, were prepared by the consolidated two-step procedure. Despite the similar particle size distribution (2.9–3.7 nm) and uniform alloyed structure, relevant difference was detected in the catalytic performances, depending on the Au/Pd ratio. In particular, the activity increased with the increase of gold content in the alloy

composition, with the catalyst having a Au/Pd ratio of 9:1 being the most active of the studied series (Figure 4). This



**Figure 4.** (a) TOFs of Au<sub>x</sub>Pd<sub>y</sub> bimetallic catalysts in glycerol oxidation. (b) Glycerol oxidation using Au, Pd, and bimetallic AuPd catalysts. Reaction conditions: 0.3 M glycerol, glycerol/NaOH = 4 mol/mol, glycerol/metal = 1000,  $p_{O_2}$  = 3 atm,  $T$  = 50 °C. [Reprinted with permission from ref 52. Copyright 2007, Springer Nature.]

might be ascribed to the presence of isolated Pd monomers in contact with Au particles. Differently, the selectivity was less affected by the catalyst composition, with glycerate being the main product (70%–80%) at 90% glycerol conversion in all cases.

More recently, bimetallic Au–Ag NPs supported on TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> were also investigated as catalysts for glycerol oxidation.<sup>71,72</sup> Important consideration has been given to the factors that determine the activity and selectivity of these systems. For this purpose, different catalysts were synthesized by varying the preparation route (sol immobilization, deposition–precipitation with urea and solvated-metal atom dispersion (SMAD) methods), the metal composition (internal Au:Ag atomic ratio = 1:1 or 4:1) and postsynthesis treatment (drying, calcination in air at 300 °C, reduction at 550 °C under H<sub>2</sub> flow). Generally, metal exposure at the surface, oxidation state of the metal, and strong metal–support interactions arose as the main ruling factors. Gold-enriched surfaces showed enhanced activity and improved stabilization of silver in the reduced state. A different selectivity characterized bimetallic Au–Ag catalysts, compared to monometallic Au, insofar as the former oxidizes glycerol to tartronate to a larger extent under alkaline conditions.

### 3.1.3. Effect of the Reaction Conditions.

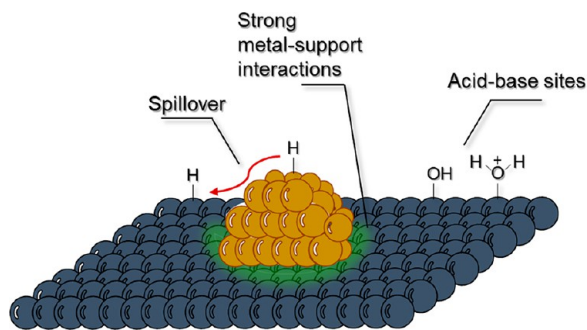
The catalytic activity and selectivity of single-phase AuPd/AC catalyst with small particle size ( $d$  = 3.4 nm) were investigated as a function of the reaction parameters.<sup>73</sup>

The amount of catalyst and, in particular, the glycerol/metal ratio had an impact on the mass transport phenomena and on the product distribution. When glycerol/metal ratios between 13 000 and 3500 were chosen, it was demonstrated that the reaction proceeded in a kinetic regime. Otherwise, minor deviation from kinetic regime was observed for glycerol/metal ratios between 3500 and 850 mol/mol. Additionally, a decrease in the glycerol/metal ratio had a detrimental effect in the product distribution, with a reduced selectivity to glycerate. The reaction resulted to be of zero order, with respect to oxygen at the specific range of oxygen pressure, since the oxygen pressure had no effect on the activity, which, in turn, was affected by the amount of base. In particular, the activity was enhanced by the addition of a base up to a threshold value of 2 mol/mol, after which any further addition of base produced negligible improvement.

The selectivity was influenced by the oxygen pressure and base concentration: glycerate formation was favored by high oxygen pressure and in the presence of a base.

**3.1.4. Insights on the Complex Role of the Support.** As mentioned in the previous section, the support is essential to providing anchoring sites and improved stabilization of metal nanoparticles. In many cases, the support also influences the catalytic performance of the deposited metal nanoparticles through metal–support interactions. In addition, the support can play an active role in the catalytic process, by intervening in some crucial steps (cooperative catalysis; see Scheme 5).

#### Scheme 5. Cooperative Effects in Supported Catalysts



Au-catalyzed oxidation of glycerol was studied as a function of the surface features of the support, with particular emphasis on acid–base properties and hydrophilicity of carbon-based materials.

In some cases, the different surface functionalization is a consequence of the different source of the carbon material. Three activated mesoporous carbon materials were prepared starting from the waste fractions of saw industries, namely, birch, pine, and spruce sawdust. The carbon materials differed in terms of surface functionalities, being aromatic groups predominant in spruce-derived carbons while the surface of birch-derived carbon was enriched by carboxylic groups. The latter had a beneficial effect on the catalytic performance of supported AuPt NPs in the glycerol oxidation reaction.<sup>74</sup>

More often, the nature and distribution of surface functionalities can be finely tuned by proper post-synthesis functionalization treatment. In the case of carbon nanofibers (CNFs), oxygen-containing acid functionalities were introduced through acid treatment with HNO<sub>3</sub>. On the other hand, basic N-groups were inserted on CNFs by heat treatment in the presence of ammonia. Gold-based catalysts were prepared

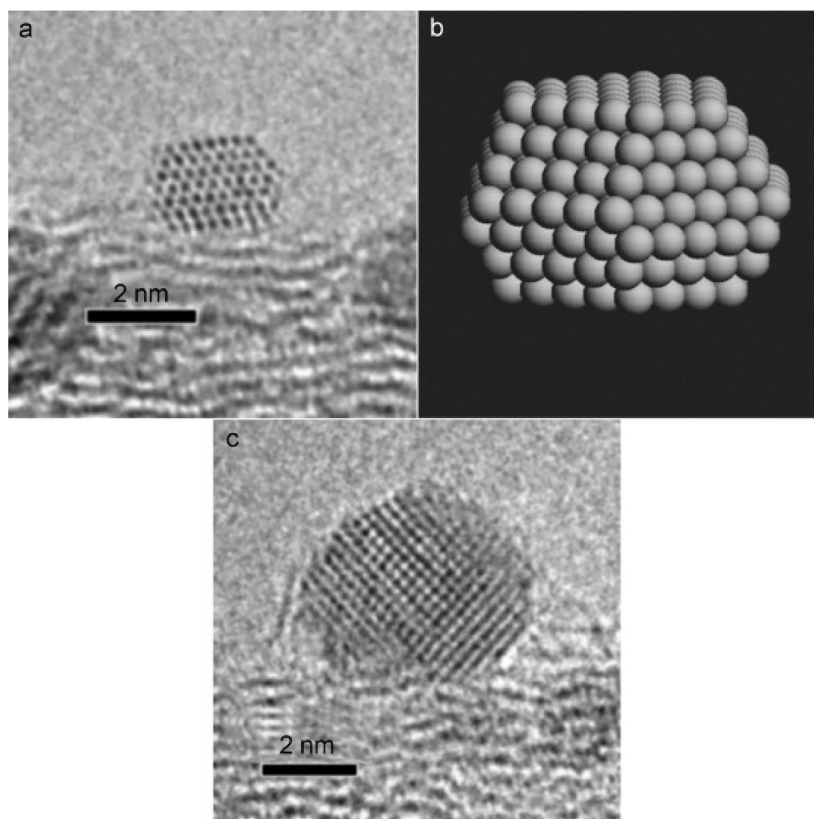
either by sol immobilization or by impregnation on as-modified substrates. The activity of the catalysts increased as the basic character of the support increased. The basic functionalities of the support, in fact, promote dehydrogenation with the formation of alkoxide and the subsequent dissociation of the C–H bond. On the other hand, the hydrophobicity affected the selectivity of the reaction, by increasing the quantity of C3 products from 65% to 82% to 90% as hydrophobic character increased.<sup>75</sup> The improved selectivity to C3 could be related to suppressed formation of H<sub>2</sub>O<sub>2</sub>, which was assumed to be involved in C–C bond cleavage reactions.<sup>76</sup> In addition, the peculiar tubular morphology of N-CNFs offered two different locations for Au NPs, the deposition of Au NPs either inside or outside the N-CNF channel. A specific confinement effect was observed, affecting activity and selectivity. Au NPs located within N-functionalized carbon nanofibers showed higher activity in glycerol oxidation and enhanced selectivity toward dicarboxylic acids. Conversely, C–C bond cleavage seemed to be promoted on Au NPs deposited on the external surface of N-CNFs.<sup>77</sup> A similar confinement effect was observed for PdH<sub>x</sub> entrapped in a covalent triazine framework.<sup>78</sup>

The presence of surface functionalities on the support can influence metal surface exposure, particle size, and shape. In some cases, these factors can have opposite effects on the catalytic performances. In particular, it has been reported that the higher the content of O-functionalities, the higher the Au exposure at the surface and the larger the metal particle size. These two effects have conflicting consequences in the activity in glycerol oxidation. In fact, high metal exposure enhances catalytic activity while the presence of large Au particles has a detrimental effect on the activity. Then the outcome depends on the relative predominance of the two effects.<sup>79</sup>

Alongside the possibility to introduce additional functional groups, in the case of carbon materials, the selectivity in glycerol oxidation also could be tuned by varying the degree of surface graphitization of carbon nanofibers. In fact, depending on the choice of heat treatment, CNF exposed surface with different order of graphitic layers. The different graphitization degree did not affect the Au particle size, but it influenced the shape of supported Au NPs, which is another factor to consider, except size, for structure–activity relationships.<sup>80</sup> Specifically, more-ordered graphitic surfaces favored a preferential immobilization of Au on their {111} plane (Figure 5). Differently, a random orientation of supported particles was detected in the case of disordered carbon nanofiber surfaces. The different facet exposure did not impact on the activity of Au NPs, whereas the product distribution changed depending on the orientation of Au NPs. Specifically, when bonded through their {111} planes, Au NPs exposed more facet area and this promoted the occurrence of C–C bond cleavage, likely to a higher production of H<sub>2</sub>O<sub>2</sub>, resulting in an increased amount of C1 and C2 products at the expense of C3 compounds.

The support can also influence the surface amount of metal. THPC-protected Au NPs immobilized on the commercial weak base resin Dowex M-43 were characterized by a higher Au surface concentration, compared to Au/AC catalysts; thus, as a result, the former was more active, despite the fact that it possessed larger particle sizes. Moreover, the intrinsic microporosity of Dowex M-43 might facilitate the desorption of products, thus minimizing the occurrence of consecutive reactions.<sup>81</sup>





**Figure 5.** Aberration-corrected HRTEM images of Au particles supported on PR24-LHT. (a) A representative 2–4 nm particle with (1 1 1) surface epitaxially parallel to the graphitic layer of CNF. (b) Structure model derived from the image in panel (a). (c) A larger particle with spherical shape showing carbon binding to the CNF surface. [Reprinted with permission from ref 80. Copyright 2012, John Wiley and Sons.]

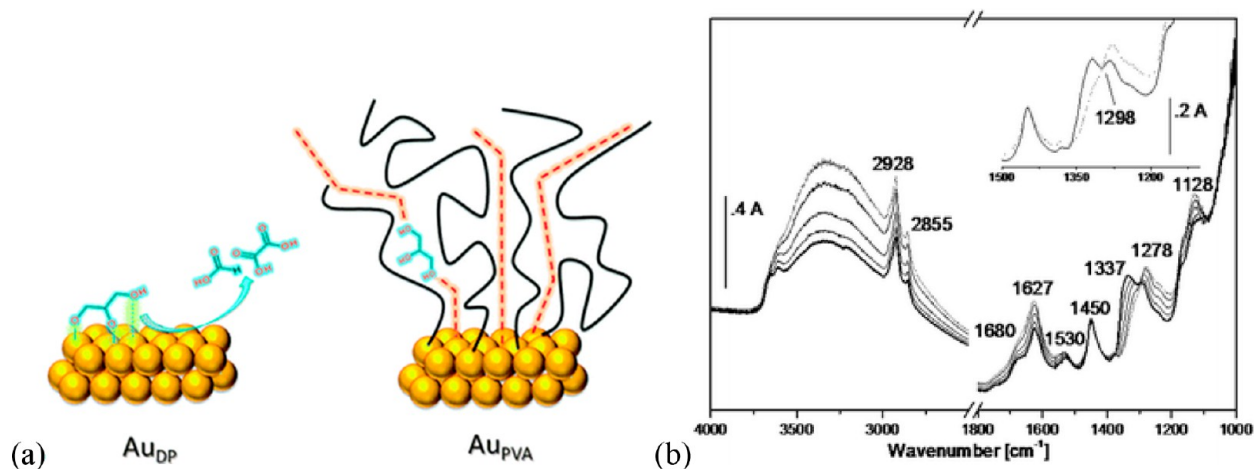
Not just the shape and size of Au NPs, but, in many cases, even their electronic structure can be affected by metal–support interactions, in particular when metal oxides were used as supports. This was clearly evident when nanostructured nickel oxide (nNiO) was used as a support for Au nanoparticles in comparison with TiO<sub>2</sub> and a mixture of Au/NiO–TiO<sub>2</sub> catalysts with different relative ratios of NiO to TiO<sub>2</sub>.<sup>82</sup> Au/nNiO catalysts showed high activity in glycerol oxidation but low selectivity to glycerate (55% selectivity at 90% conversion). The activity enhancement observed in the case of Au/nNiO was ascribed to the strong metal–support interactions between Au NPs and the support, as corroborated using CO as a probe molecule.

Besides mediating the interactions with deposited metal NPs, the surface properties of the supports can be directly involved in the catalytic process and assist metal nanoparticles. The surface Al/Mg ratio was a key factor, ruling the selectivity of Au/MgAl<sub>2</sub>O<sub>4</sub> in glycerol oxidation, where Al-rich surfaces promoted the dissociation of the C–C bond.<sup>83</sup>

Hence, the acid and basic features of supports can help in favoring the H abstraction and alkoxide formation, thus allowing one to avoid the addition of a base in the reaction medium, with remarkable practical advantages in terms of costs, including purification and safety. Laura and her co-workers reported that, by alloying Au with Pt, it was possible to combine the main advantages of the two metal components thus obtaining an active and selective catalyst, even in the absence of a base, with additionally an increased lifetime. However, the support also greatly influenced the activity and the selectivity. In particular, using a zeolite, H-mordenite, as

the support resulted in an enhanced activity, compared to activated carbon (99% and 62% after 6 h for 1% AuPt/H-mordenite and 1% AuPt/AC, respectively).<sup>84</sup> Moreover, AuPt/H-mordenite exhibited a high selectivity (83%) to glyceric acid, thus suppressing C–C cleavage and consequently the formation of C1 and C2 products. These interesting results encouraged further studies on the effect of the support. Therefore, Au–Pt nanoparticles were deposited on various metal oxides exhibiting different numbers, natures, and strengths of acid and basic sites and were tested as catalysts in base-free glycerol oxidation.<sup>85</sup> At 80 °C, high activity was associated with Au–Pt NPs deposited on basic supports (MgO, NiO). However, a pronounced occurrence of C–C bond cleavage reactions limited the selectivity of these catalysts. In contrast, the use of acidic supports (MCM41, SiO<sub>2</sub>, H-mordenite and sulfated-ZrO<sub>2</sub>) improved the selectivity to C3 oxidation products. In addition, according to spectroscopic and microcalorimetric analyses, a high number of acid sites (Brønsted sites or silanols) favored the oxidation of glyceraldehyde to glyceric acid, which involved an acid-catalyzed geminal diol formation and its dehydrogenation to carboxylic acid.

**3.1.5. On the Role of Modifiers: The Case of Bismuth.** The addition of transition metals as modifiers to noble-metal-based catalysts has been intensively studied, and it is still debated in the literature.<sup>86–89</sup> The introduction of promoters in platinum-based catalysts for glycerol oxidation had resulted in a significant increase of the catalytic activity and a significant enhancement of the selectivity to dihydroxyacetone (DHA). In particular, according to the literature, the best catalytic



**Figure 6.** (a) Model for glycerol adsorption in the presence of PVA and on the free surface; (b) FTIR absorbance spectra of  $\text{Au}_{\text{PVA}}(1,1)/\text{TiO}_2$  before (bold curve) and after interaction with 0.01 mbar, 0.1 mbar, 0.15 mbar (fine curves), and 0.25 mbar (dotted curve) of glycerol at room temperature (rt). Inset shows FTIR absorbance spectra of  $\text{Au}_{\text{PVA}}/\text{TiO}_2$  with 0.25 mbar of adsorbed glycerol (dotted curve) and after prolonged outgassing at rt (30 min, solid curve). [Reproduced with permission from ref 96. Copyright 2013, Royal Society of Chemistry, London.]

performances, in terms of activity and DHA yield, were exhibited by the Pt–Bi system.<sup>90</sup>

Starting from these considerations, Laura and her co-workers studied Bi-modified Au–Pd and AuPt catalysts. In the former case, trimetallic Au–Pd–Bi catalysts were prepared according to two different routes: immobilization of Au–Pd sol on Bi-loaded carbon support or post-immobilization Bi modification of supported AuPd NPs on carbon.<sup>91</sup>

The introduction of Bi (0.1–3 wt %) onto the support prior to the immobilization of Au–Pd NPs did not affect the final particle size; nevertheless, the presence of Bi hindered the growth of alloyed nanoparticles with homogeneous composition. Conversely, the addition of Bi to preformed Au–Pd NPs supported on carbon allowed one to maintain the alloy composition. From a catalytic point of view, the addition of Bi resulted in an enhanced production of tartronate (34% yield).<sup>91</sup>

When Bi (0.1–1 wt %) was added to Au–Pt/AC catalysts, no modification of particle size and alloy composition was observed. Interestingly, the deposition of a low amount of Bi (0.1%) promoted dihydroxyacetone formation (stable selectivity of ~65% with the conversion) in the base-free glycerol oxidation and suffered from limited leaching.<sup>92</sup> These promising results encouraged to explore the performance of Au–Pt–Bi NPs supported on granular carbon in a continuous flow fixed-bed reactor under optimized reaction parameters (contact time, temperature, and  $\text{O}_2$  flow). Although a maximum of selectivity to DHA (48.1%) was obtained, the catalyst underwent significant structural modification after 80 h of time on stream.<sup>93</sup>

**3.1.6. Impact of the Protecting Agent on Activity, Selectivity, and Stability for the Liquid-Phase Oxidation of Glycerol.** When sol immobilization is used to prepare metal-based catalysts, the presence of a protecting agent is a component that cannot be ignored. The primary goal of the protecting agent is to provide stabilization to the metal sol before and during the immobilization on the support. During these stages, the protecting agents also mediate the interactions between metal nanoparticles and the supports, and it is partially responsible for particle size control and metal dispersion. The removal of the protecting agent can cause

coarsening or a tendency toward leaching. The effect of the protective agent removal has been investigated by Laura and her co-workers by gradually removing PVA through washing with water at room temperature and at 60 °C.<sup>94</sup> These studies demonstrated that the structural and textural properties of the support play a pivotal role in influencing metal particle sizes and in stabilizing nanoparticle under protective agent removal. Specifically activated carbon proved to be more effective in stabilizing Au NPs under PVA removal, compared to graphite, likely thanks to its highly functionalized surface, which exposes numerous anchoring sites.

Despite purification treatments by proper washing or removal protocols, in some cases, a residual amount of protecting agent remains in contact with the metal nanoparticle surface. In these cases, a direct influence on the catalytic performance may be expected. A shielding effect that limits surface accessibility can be proposed at first, leading to a decreased activity. It has been well evidenced by comparing the activity of Au NPs, stabilized by poly(vinyl alcohol) (PVA, 715  $\text{h}^{-1}$ ), tetrakis(hydroxymethyl)phosphonium chloride (THPC, 2478  $\text{h}^{-1}$ ), and citrate (160  $\text{h}^{-1}$ ).<sup>95</sup> However, often, a more complex situation emerges, wherever the protecting agent establishes positive electronic interactions with metal surfaces or mediates the interaction with the reagents and products. Consequently, promotional effects as well as selectivity control could be derived from the presence of a protecting agent. This appeared evident in the case of PVA-protected Au NPs immobilized on  $\text{TiO}_2$  and tested as catalysts in glycerol oxidation. In fact, the comparison of catalytic performances of Au/ $\text{TiO}_2$  prepared by sol immobilization and by deposition–precipitation highlighted interesting differences, in terms of activity and selectivity.<sup>96</sup> The presence of a protective PVA layer lowered the activity, increased the stability and favored the formation of glycerate, by suppressing C–C bond cleavage. The interaction between glycerol and PVA chains at the catalyst surface was studied by glycerol adsorption experiments in liquid phase followed by Fourier transform infrared (FT-IR) spectroscopy. FT-IR spectra were recorded at increasing glycerol coverages (from 0.01 mbar to 0.25 mbar) at room temperature and the evolution of the main IR bands (i.e., the peaks of  $\text{CH}_2$  stretching between 2928 and 2855  $\text{cm}^{-1}$ , C–OH

deformation in 1337–1289  $\text{cm}^{-1}$  region and C–O stretching at 1100–1200  $\text{cm}^{-1}$ ) was monitored. According to FT-IR characterization, the unique selectivity of PVA-protected Au NPs could be derived from direct interaction between C–OH groups of PVA and the glycerol molecule, which directs the adsorption configuration of the substrate (Figure 6).

**3.2. Liquid-Phase Oxidation of Alcohols.** Alcohol oxidation to carbonyl or carboxyl compounds represents a key reaction in modern industrial chemistry. Consequently, the implementation of heterogeneously catalyzed processes, which use atmospheric oxygen under mild conditions, is potentially attractive in a sustainability-driven perspective. The design of effective heterogeneous catalysts plays a pivotal role in the development of environmentally friendly approaches competitive with conventional oxidative routes based on homogeneous catalysts or on stoichiometric oxidation processes, which make use of toxic inorganic (Cr- and Mn-based compounds) or organic oxidants. Supported noble metals, namely Pt and Pd NPs, are well-studied heterogeneous catalysts for the oxidation of alcohols, although the above-mentioned drawbacks (over-oxidation of substrates, deactivation) have limited their practical application. With the aim to overcome these limitations, the acquired knowledge regarding the effective catalysts design of monometallic and bimetallic gold-based catalysts for the oxidation of diols and polyols was successfully transferred by Laura in the oxidation of alcohols and amino alcohols.<sup>97,98</sup> Among the numerous studied substrates, in the following, the attention will be focused on the oxidation of benzyl alcohol, cinnamyl alcohol, and long-chain alcohols, due to the relevance of these reactions from academic as well as industrial points of view.

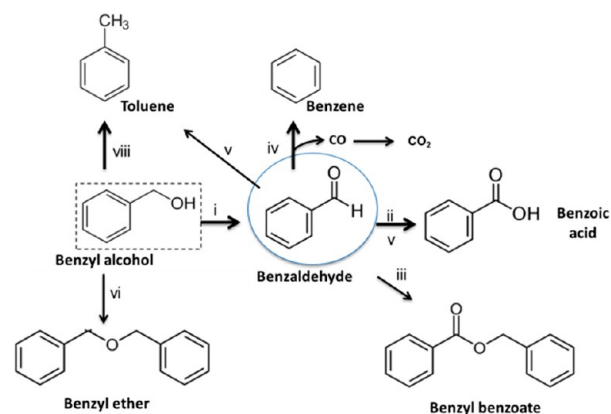
**3.2.1. Benzyl Alcohol Oxidation.** Benzyl alcohol is one of the most studied substrates for the selective aerobic oxidation of alcohols. The activating effect of the aromatic ring facilitates the oxidation of the alcohol functionality, with the formation of benzaldehyde as the main product, while benzoic acid, toluene, benzyl benzoate, and benzene are often observed as secondary products.

The industrial interest in the oxidation of benzyl alcohol is associated with the high market value of these products, primarily benzaldehyde, which is widely employed in the food and cosmetic industries as an additive for artificial bitter almond aroma. Additionally, benzyl alcohol oxidation has become a benchmark reaction to assess the mechanism of alcohol oxidation on supported noble-metal nanoparticles. In fact, depending on (1) the operative conditions and (2) the presence of specific active sites, benzyl alcohol can undergo several reactions (Scheme 6): (i) oxidative dehydrogenation to benzaldehyde, (ii) oxidation to benzoic acid, (iii) formation of benzyl benzoate, (iv) decarbonylation of benzaldehyde to benzene, (v) disproportionation to equimolar toluene and benzoic acid, (vi) dehydration to dibenzylether, (vii) condensation (benzylation) to anthracene and stilbene, and (viii) reduction of benzyl alcohol by metal hydride.

The transformation of benzyl alcohol to benzaldehyde proceeds according to a well-accepted dehydrogenation mechanism, which involves two elementary steps: (1) adsorption through oxygen-assisted homolytic dissociation to form an alkoxy intermediate and (2)  $\beta$ -H elimination of the alkoxy to produce benzaldehyde (rate-determining step).

Otherwise, the identification of mechanisms for the other consecutive and side reactions, which lead to the undesired byproducts (toluene, benzoic acid, and benzyl benzoate), is

**Scheme 6. Benzyl Alcohol Oxidation Reaction Network**



still controversial. Two different reaction pathways have been proposed for toluene formation: (1) the hydrogenolysis of benzyl alcohol by the hydride generated during the dehydrogenation of benzyl alcohol to benzaldehyde or (2) the disproportionation reaction of benzyl alcohol. Benzoic acid might be produced from benzaldehyde via direct oxidation in the presence of oxygen or by hydration via a geminal diol, followed by a dehydrogenation or the Cannizzaro reaction in the presence of basic sites on the support or via the formation of a dioxy or carboxyloxy intermediate. The same carboxyloxy intermediate also has been proposed to be a source of benzyl benzoate.

The study of the reaction mechanism and the optimization of product distribution in benzyl alcohol oxidation has represented a central target for Laura's research in gold-based catalysis.

Initially, the catalytic performance of monometallic (Au, Pd, Pt) and bimetallic (Au–Pd and Au–Pt) nanoparticles supported on activated carbon were compared in the conversion of benzyl alcohol under mild conditions (0.3 M benzyl alcohol, benzyl alcohol/metal = 1/500 mol/mol,  $T = 60\text{ }^{\circ}\text{C}$ ,  $p_{\text{O}_2} = 1.5\text{ atm}$ ) in two different solvents (toluene and water). Generally, better performance was observed in water than in toluene. In both solvents, monometallic Au/AC catalysts were not active, while Pt/AC was more active than Pd/AC. The addition of Au to Pd had a promotional effect in terms of activity, which was not evident in the case of bimetallic Au–Pt catalysts. This could be explained by invoking a different interaction between geometrical and electronic effects in Au–Pd and Au–Pt catalysts. It could be assumed that, in the former catalyst, the two effects synergistically converge resulting in an enhanced activity, while they negatively interfere in the case of AuPt catalysts. The activity trend in toluene was Au–Pd/AC ( $54\text{ h}^{-1}$ ) > 5% Pt/C > 1% Pt/AC = 0.4% Pt/AC ( $30\text{ h}^{-1}$ ) > Au–Pt/AC ( $15\text{ h}^{-1}$ ) > 5% Pd/C = 1% Pd/AC = 0.3% Pd/AC ( $5\text{ h}^{-1}$ ) > Au/AC ( $0\text{ h}^{-1}$ ). A similar trend was detected in water: Au–Pd/AC ( $160\text{ h}^{-1}$ ) > 1% Pt/AC = 0.4% Pt/AC ( $98\text{ h}^{-1}$ ) > 5% Pt/C ( $72\text{ h}^{-1}$ ) > AuPt/AC ( $55\text{ h}^{-1}$ ) > 5% Pd/C = 1% Pd/AC = 0.3% Pd/AC ( $33\text{ h}^{-1}$ ) > Au/AC ( $0\text{ h}^{-1}$ ).<sup>99</sup>

Noteworthy results were collected by experiments that were performed on physically mixed Au/AC and Pd/AC as catalysts for benzyl alcohol oxidation. By following the evolution of the physically mixed catalyst structures at different stages of the catalytic reaction by aberration-corrected HRTEM and spatially resolved element mapping techniques, it was possible

to prove the in situ formation of Au–Pd bimetallic active sites for the first time. These alloyed bimetallic systems were formed by leaching of Pd cationic species and redeposition on the surface of Au NPs.<sup>100</sup>

Considering the positive performance of Au–Pd/AC catalyst, further studies were performed for the purpose of disclosing the effects of alloy composition and reaction parameters on catalytic activity and selectivity in benzyl alcohol oxidation. According to TEM characterization and catalytic tests, uniform alloyed bimetallic nanoparticles with high activity were obtained only in the range from 90:10 to 60:40 of Au–Pd composition. The activity was enhanced by the addition of a base and the positive effect was more pronounced as the gold content in the alloy composition increased. The presence of a base also improved the durability of the catalysts, although a slight decrease in benzaldehyde selectivity was observed. The latter inconvenience could be overpassed by increasing the initial benzyl alcohol concentration. Optimal conditions were then identified for the Au<sub>60</sub>Pd<sub>40</sub>/AC catalyst, for which an initial activity of 18 000 h<sup>-1</sup> with high selectivity to benzaldehyde ( $S_{90} = 89\%$ ) was achieved working with a biphasic system 1 M alcohol in cyclohexane/1 M aqueous NaOH and 20 000 mol/mol benzyl alcohol/metal ratio.<sup>101</sup>

Replacing activated carbon support by carbon nanotubes produced Pd and Au–Pd catalysts with poor metal dispersion, compared to analogous carbon-supported catalysts. Although the nonoptimal metal dispersion caused a slight decline in the activity, this effect was compensated by a high selectivity to benzaldehyde and an attenuation of metal leaching, compared to Pd/AC and Au–Pd/AC.<sup>102</sup> It followed from this that the support appeared as a key actor for tuning surface features (degree of functionalization, acid/base properties, hydrophobicity/hydrophilicity, porosity) and therefore the nature and choice of support could allow one to obtain catalysts with improved catalytic behavior. Therefore, the research efforts of Laura's team were focused on identifying the role of surface functionalization of carbon-based supports in the activity of noble-metal catalysts. One interesting approach to the modification of support surface properties consisted of the introduction of O-functionalities or Lewis base-type N heteroatoms.

The hydrophilicity of carbon nanotube surfaces was tuned by introducing O-functionalities through treatment by nitric acid–sulfuric mixtures with different volume ratios (3:1, 1:1, and 1:3, respectively). The effects on benzyl alcohol oxidation were studied in two different solvents: water and cyclohexane. In cyclohexane, the hydrophilicity of the surface had a direct impact only on the activity, while the selectivity was unaltered (in all cases, toluene was the main byproduct). A more hydrophobic surface facilitates the accessibility of surface active sites to a hydrophobic substrate, such as benzyl alcohol, resulting in an improved activity. A different scenario was depicted in water, where a triphasic system was generated. In this case, the presence of hydrophilic surfaces showed high activity and at the same time suppressed the toluene formation.<sup>103</sup> Hydrophilicity of carbon support could be modulated also by introducing N-functionalities. The introduction of N heteroatoms at the surface of carbon-based support can be pursued according to several strategies, which differ from functional form (pyridinic-N, pyrrolic-N, pyridone-N, quaternary-N, amino groups, nitro groups),

location, interaction strength and type of connectivity of the N-species on the surface.<sup>104</sup>

The treatment of commercial carbon nanotubes (CNTs) and carbon nanofibers (CNFs) with NH<sub>3</sub> at different temperatures (200, 400, and 600 °C) produced N-containing groups, which enhanced surface basicity and surface hydrophobicity. Basicity and hydrophobicity increased with the increasing temperature of the thermal treatment. When N-modified carbon materials were used as supports for Au NPs, different catalysts were obtained. The activity and selectivity of the synthesized catalysts in base-free benzyl alcohol oxidation were depended mainly on the surface properties of the support. In particular, the activity was enhanced significantly by an increase in the basicity and hydrophobicity of the support, while the selectivity to benzaldehyde decreased as a consequence of the favored consecutive oxidation to benzoic acid.<sup>75</sup>

The effect of N-functionalities was also dependent on the number of N-groups and on their location. When covalent triazine frameworks (CTFs) were used as support for Pd NPs, the higher number (9 at. %) and the nature of N-groups in the CTF conferred better stability and dispersion to Pd NPs than those created on carbon nanotubes (2 at. %) by NH<sub>3</sub>/high-temperature treatment.<sup>105</sup> A more pronounced effect was observed when another polymeric carbon–nitrogen material, i.e., carbon nitride (C<sub>3</sub>N<sub>4</sub>) materials with a nitrogen content up to 58 at. %, was used as a support. In this case, the promoting effect was derived from the increased Lewis basicity, but most probably from a stronger and more effective coordination of Pd NPs on N groups.<sup>106</sup> On the other hand, the simple presence of N-groups coordinating the Pd active centers cannot be considered to be the sole factor determining the enhanced activity of these systems. N-groups should be near to the Pd active sites to strongly interact with them but without limiting their accessibility. Thus, the coordination of polyvinylpyrrolidone to Pd NPs through the pyrrolic groups resulted in a shielding effect with detrimental consequences, in terms of activity. In contrast, the presence of pyridine molecules, weakly bound to the carbon surface in the proximity of Pd sites, did not impart enough stability and activity enhancement.<sup>107</sup> However, in some cases, a strong interaction between the functional groups of the protecting agent and specific sites on the surface of Pd NPs could have a positive effect, in terms of selectivity, despite its detrimental influence on the activity. This is the case of PVA-protected Pd NPs, where the selectivity to benzaldehyde benefited from the specific interactions of PVA with Pd(111) facets, which were active in the decarbonylation process of benzaldehyde during benzyl alcohol dehydrogenation.<sup>108</sup>

Beside carbon-based materials, metal oxides also were studied as supports for metal nanoparticles to be used as catalysts in benzyl alcohol oxidation. Nanometric nickel oxide (nNiO) has been demonstrated to increase the activity of supported Au NPs in the base-free liquid-phase oxidation of benzyl alcohol. The unique performances of Au/nNiO could be ascribed to the improved basic properties of the support and to cooperative effects between Au NPs and the supports which strongly modified the electronic properties of Au.<sup>109</sup> More recently, carbon-supported hybrid Au/CuO with a core–shell heterostructure has been demonstrated to be an effective catalyst in benzyl alcohol oxidation. In particular, high activity was observed when the CuO shell just partially covered the Au-rich core.<sup>110</sup> Synergistic effects between Au and Cu and

Au and Pd in bimetallic Au–Cu and Au–Pd nanoparticles supported on carbon and Al<sub>2</sub>O<sub>3</sub> produced effective catalysts in the oxidation of methoxy-substituted benzyl alcohols, studied as model substrates for lignin degradation products.<sup>111,112</sup>

Transition-metal carbides (Mo and W carbides) have been also studied as less-expensive alternatives to noble-metal catalysts for benzyl alcohol oxidation showing a new and sustainable direction for minimizing the use of noble metals.<sup>113</sup>

**3.2.2. Cinnamyl Alcohol Oxidation.** The target product of cinnamyl alcohol is cinnaldehyde, which is an interesting chemical that can find industrial application as a flavorant, insecticide, and corrosion inhibitor. However, similarly to benzyl alcohol, cinnamyl alcohol also can be oxidized through a complex reaction network, which includes selective oxidation, transfer hydrogenation, hydrogenolysis, and decarbonylation. Hence, this reaction has been extensively studied as a model reaction. Monometallic and bimetallic noble metal catalysts prepared by sol immobilization proved to be able to convert cinnamyl alcohol effectively and selectively to cinnamaldehyde. Differently from commercial catalysts (i.e., 5% Pd/C, from Engelhard), the performance of catalysts prepared by sol immobilization was sensitive to the reaction solvent.<sup>99</sup> In particular, higher activity was observed in water than in toluene or acetonitrile. When tested under similar conditions (0.3 M cinnamyl alcohol, cinnamyl alcohol/metal molar ratio = 1/500,  $T = 60\text{ }^{\circ}\text{C}$ ,  $p_{\text{O}_2} = 1.5\text{ atm}$ , water as the solvent) monometallic 1% Au/AC was almost unactive, while both 1% Pd/AC and 1% Pt/AC showed remarkable activity (ca. 90 and 65 h<sup>-1</sup>, respectively), which remained constant even at low loading (ca. 0.4 wt %). Interestingly, bimetallic Au–Pd/C catalyst was more active than monometallic counterparts, while alloying Au to Pt had a negative effect on the activity, which decreased from 67 h<sup>-1</sup> (Pt/AC) to 45 h<sup>-1</sup> (1% Au–Pt/AC), along the same trend as outlined above for benzyl alcohol. The activity of bimetallic Au–Pd/AC catalysts was dependent on the catalyst composition and specifically on the Au:Pd molar ratio.<sup>101</sup> The highest activity (630 h<sup>-1</sup>) was obtained on the catalysts having an Au:Pd molar ratio of 8:2. A significant enhancement of the catalytic activity, specifically on monometallic Au/AC catalyst, was observed when the reaction was performed in the presence of a basic environment (1 equiv NaOH).<sup>101</sup> Alternatively, the activity of Pd-based catalysts could be improved by introducing N-containing functionalities, in particular, pyridinic nitrogen species, in the carbon support.<sup>114</sup>

The selectivity of the reaction was not influenced by the solvent, while it was strongly depended on the pH and on the internal composition in the case of bimetallic Au–Pd/AC catalysts. The selectivity to cinnamaldehyde was increased by increasing the catalyst gold content (selectivity of 80% to cinnamaldehyde was attained on 1% Au/AC and in Au<sub>90</sub>Pd<sub>10</sub>/AC catalysts), while palladium-rich catalysts promoted the hydrogen transfer and the consequent 3-phenyl-propanol production (up to 28% selectivity to 3-P-P in the case of Pd/AC). In all cases, the selectivity was negatively affected by the addition of base, due to the preferential occurrence of overoxidation of cinnamaldehyde to carboxylates (ester or acid), which was more pronounced in gold-rich compositions and in monometallic Au/AC catalyst (63% selectivity to acid/ester).

**3.2.3. Long-Chain Alcohol Oxidation.** It is reasonable to expect the activity of Au-based catalysts to be very sensitive to the nature and structure of the substrate. For example,

compared to benzyl alcohol and cinnamyl alcohol or to diols, aliphatic alcohols have no electronic activation and that should impact on the reactivity of these compounds. In fact, small simple alcohols (butanol and propanol) were converted quite slowly over Au/AC catalyst under typical conditions ([alcohol] = 0.35 M; alcohol/M = 1000 (mol/mol); NaOH = 1 equiv;  $p_{\text{O}_2} = 3\text{ atm}$ ;  $T = 70\text{ }^{\circ}\text{C}$ ). A more pronounced tendency to deactivate was observed when propanol was used as the substrate.<sup>115</sup> The reactivity of aliphatic alcohols under oxidative conditions usually decreases by increasing the chain length. On the other hand, the oxidation of aliphatic alcohols with a long linear chain produces aldehydes (e.g., *n*-octanal, *n*-capraldehyde) with pleasing olfactive features, which is the reason for their applications in the industrial production of perfumes and essences. Although these aldehydes can be sourced from natural products (i.e., essential oils and fruits), the development of synthetic routes is required to satisfy a continuously rising market demand. Unfortunately, monometallic (Au, Pd, and Pt) and bimetallic Au–Pt and Au–Pd on carbon catalysts were characterized by poor activity (<12% conversion) when toluene or water were used as the solvent (0.3 M 1-octanol, 1-octanol/metal = 1/500 mol/mol,  $T = 60\text{ }^{\circ}\text{C}$ ,  $p_{\text{O}_2} = 1.5\text{ atm}$ ). In addition, low selectivity (ca. 30%) to 1-octanal was observed in water, with acid and ester being the main byproducts. The deactivating effect that is derived from the formation of carboxylic species, which strongly adsorb on catalyst surface, is one of the main causes of the poor catalytic activity in water, together with the limited contact between active sites and substrate of the four-phase system. From this point of view, the introduction of basic conditions had a positive effect on the catalytic behavior of Au-based catalysts with a 20-fold increase in the activity values. The beneficial role of the base may be ascribed to the minimization of deactivation phenomena because of the formation of carboxylates, which easily desorb from the catalyst surface.

Among noble metals, supported Ru NPs have been demonstrated to be promising and active catalysts for octanol oxidation. Bimetallic Au–Ru nanoparticles were then deposited on activated carbon and tested as catalysts in octanol oxidation. Unfortunately, the presence of Au had a detrimental effect on the activity of Au–Ru bimetallic catalysts. However, when a physical mixture such as Au/AC and Ru/AC was tested, an unexpected enhancement of the activity was observed, compared to the monometallic Ru/AC catalyst.<sup>116</sup> This peculiar behavior could be ascribed to the leaching of Ru and successive deposition on Au NPs, as already observed for Au/AC and Pd/AC mixtures.<sup>100</sup>

Monometallic Ru/AC, Pt/AC, Au/AC and bimetallic Au–Ru/AC and Au–Pt/AC catalysts were tested in the oxidation of 1-octanol, 1-decanol, and 1-dodecanol, using toluene as a solvent (0.6 M, metal/alcohol ratio = 1/100 mol/mol,  $T = 100\text{ }^{\circ}\text{C}$ ,  $p_{\text{O}_2} = 2\text{ kPa}$ ).<sup>117</sup> The substrate reactivity was in inverse proportion to the length of the chain, since it decreased from C8 to C12. In the case of 1-octanol, the activity of monometallic catalysts increased in the following order: Au/AC (0 h<sup>-1</sup>) < Ru/AC (114 h<sup>-1</sup>) < Pt/AC (141 h<sup>-1</sup>). In contrast, Ru/AC was more active than Pt/AC in the oxidation of 1-decanol (84 vs 68 h<sup>-1</sup>, respectively) and 1-dodecanol (65 and 46 h<sup>-1</sup>) in the C12 oxidation, respectively. Aldehydes were the main products in the case of Ru/AC (selectivity values >95%), whereas carboxylic acids and esters were formed on Pt/AC catalysts (up to 54% selectivity to acid in the case of

dodecanol oxidation). Bimetallic catalysts were less active but more durable than the monometallic Ru/AC and Pt/AC. The addition of Au to Ru did not alter the selectivity, whereas, when Au was added to Pt, the main role of Au was to promote the formation of esters. The activity of the tested catalysts could be improved by using a water–dioxane mixture as the solvent, even if, in this case, acid was preferentially formed at the expense of the aldehyde.

#### 4. LIQUID-PHASE HYDROGENATION REACTIONS

The use of heterogeneous catalytic systems for the development of low environmental impact processes cannot ignore the vast field of hydrogenation reactions.

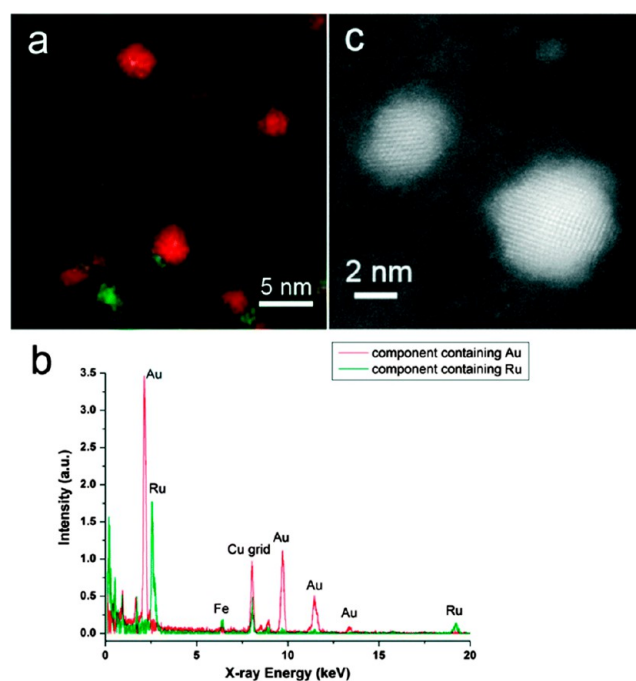
Hydrogenation reactions are among the pillars of the chemical industry and are particularly relevant in the field of biomass transformation, due to the high oxygen content present in the biomass, which must be removed to develop biomass-based processes.

Hydrogenation/hydrogenolysis catalytic processes represent the most considerable approach from an applicative point of view. The in-depth research work carried out by Laura has greatly improved the state of the art of research in this field.

**4.1. Au Catalysts for Hydrogenation Reactions.** Laura has devoted more attention on hydrogenation reactions quite recently, in particular when gold was beginning to be investigated as a catalyst for the liquid-phase hydrogenation of various molecules.<sup>118,119</sup> Before, indeed, gold has shown a more attractive behavior in the liquid-phase oxidation, showing high resistance to deactivation, compared to classical Pd or Pt catalysts,<sup>60</sup> while in hydrogen-mediated reactions, it had shown low catalytic activity, which is generally attributed to the less-effective activation/dissociation of dihydrogen.<sup>120</sup> However, the selectivity and stability of supported gold has continued to be higher than other metals,<sup>121</sup> as well gold-based bimetallic systems showed a great enhancement in their activity also in hydrogenations. For example, the addition of Au to Pd, or Ru, results in a great improvement in the catalytic activity and selectivity in the hydrogenation of cinnamaldehyde and glycerol.<sup>122</sup>

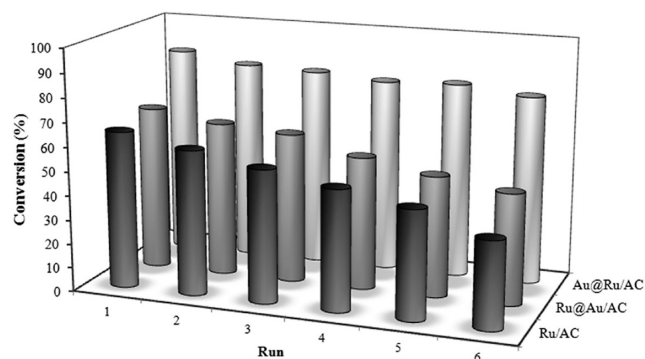
Laura focused first on the impact of Au–Ru nanoparticle structure in the hydrogenation/hydrogenolysis of two important compounds deriving from biomass, namely glycerol and levulinic acid.<sup>123</sup> Hydrogenolysis of glycerol can produce 1,2- and 1,3-propanediols, and lactic acid, as well as different alcohols, which are all important chemicals, whereas, from levulinic acid, the main product is  $\gamma$ -valerolactone (GVL) that can be transformed in pentanediol or pentanoic acid, both useful additives in biofuels.<sup>124</sup> Ru catalysts showed a high deactivation in the glycerol or levulinic acid hydrogenolysis, while a possible solution could be the addition of Au, as already reported in the oxidation of glycerol and aliphatic alcohols.<sup>125</sup> Au–Ru bimetallic catalysts have been prepared via the sequential deposition of Au on Ru or vice versa on activated carbon (AC), obtaining different nanostructures, i.e., Au<sub>core</sub>–Ru<sub>shell</sub> or a bimetallic phase with Ru enrichment on the surface (Figure 7).

One of the most important findings was that the selectivity and the stability are dependent on the structure of the bimetallic nanoparticles, where the Ru@Au/AC core–shell structure mostly behaved as the monometallic Ru, whereas the presence of bimetallic AuRu phase in Au@Ru/AC provides a great beneficial effect on both activity and stability. The synergistic effect showed by the Au@Ru/AC was also shown,



**Figure 7.** (a) Component maps and (b) component EDX spectra from multivariate analysis of STEM-EDX spectrum imaging for Ru@Au/AC catalyst. Red and green correspond to Au and Ru containing components, respectively; (c) HAADF-STEM image showing Ru clusters decorating on the surface of Au particles. [Reproduced with permission from ref 123. Copyright 2015, Royal Society of Chemistry, London.]

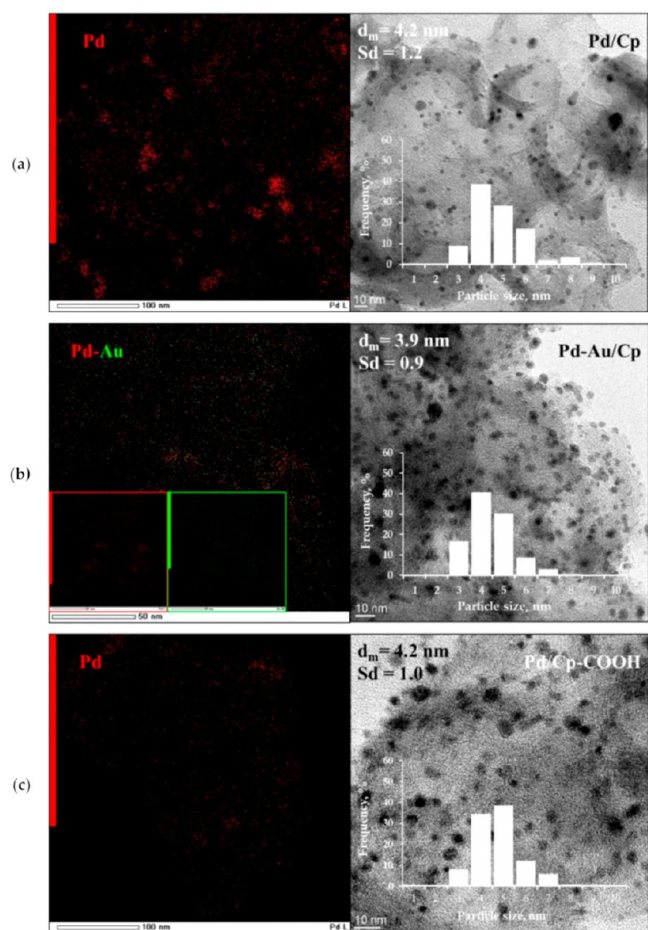
in terms of durability: recycling experiments showed that Au@Ru/AC reached the same substrate conversion after 6 runs with stable selectivity (Figure 8).



**Figure 8.** Recycling tests for the levulinic acid hydrogenolysis. [Reproduced with permission from ref 123. Copyright 2015, Royal Society of Chemistry, London.]

More recently, she was involved in a study on Au–Pd supported on carbon catalysts for furfural hydrogenation.<sup>126</sup>

Specifically, she investigated the effect of the carbon support modification with butyl, carboxyl, and amino groups, using corresponding diazonium salts (Figure 9). The results showed a crucial influence of surface chemistry on the catalytic behavior of the catalysts, especially regarding selectivity. Indeed, the modification of carbon with various functional groups leads to changes in the hydrophobic/hydrophilic and/or electrostatic properties of the surface, which influenced the selectivity of the process. The core idea was to show that the



**Figure 9.** TEM images and EDX maps of the studied catalysts, as well as Pd and Pd–Au NPs distribution: (a) Pd/Cp, (b) Pd–Au/Cp, (c) Pd/Cp–COOH, (d) Pd–Au/Cp–COOH, (e) Pd/Cp–butyl, (f) Pd–Au/Cp–butyl, (g) Pd/Cp–NH<sub>2</sub>, and (h) Pd–Au/Cp–NH<sub>2</sub>. [Reproduced with permission from ref 126. Copyright 2022, under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

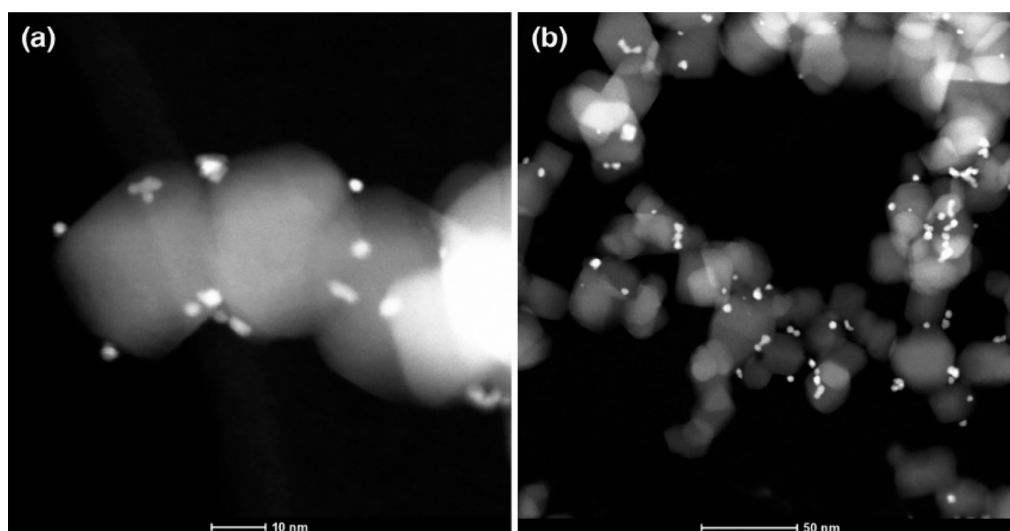
catalytic behavior (activity and selectivity) of furfural hydrogenation catalysts could be influenced not only by changing the reaction parameters or the content of supported metals, but also by changing the surface chemistry of the support if all other conditions are kept equal.

**4.2. Support Effect in Hydrogenation Reactions.** The support can, in fact, be very important to determine the activity, selectivity, and stability of a catalyst. To limit the deactivation often showed by monometallic Ru, Laura also investigated the use of ordered mesoporous carbons (OMCs) as supports.<sup>127</sup> P- and S-containing acid groups were introduced by post-synthetic functionalization before the addition of 1% Ru.

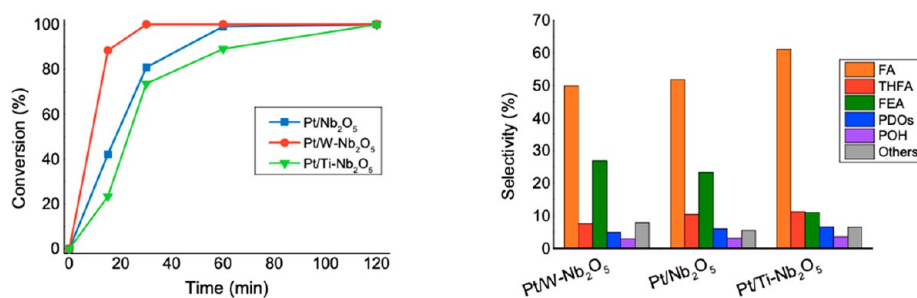
As a result, it was found that the functionalities mediate the activity and selectivity of the levulinic acid hydrogenation. In particular, the presence of S-containing groups deactivated the Ru catalysts, whereas the presence of P-containing groups (Ru/OMC-P) enhances the activity compared to that of pristine Ru/OMC. At 70 °C and 7 bar of H<sub>2</sub>, the Ru/OMC-P catalyst showed a selectivity of >95% to GVL and high stability on recycling. By changing the reaction conditions to 200 °C and 40 bar of H<sub>2</sub>, this catalyst was also able to promote the GVL ring opening and the consecutive hydrogenation to pentanoic acid.

Using the same substrate (levulinic acid), she also investigated other metal species, such as iridium.<sup>128</sup> Ir-based catalysts had been poorly investigated in this reaction, with only a few reports on Ir/SiO<sub>2</sub>, which showed low activity and selectivity; however, soluble Ir complexes have been reported to show a good activity in levulinic hydrogenation.<sup>129,130</sup> Laura investigated the use of TiO<sub>2</sub> as a support, supposing that a reducible oxide would have helped the activity of supported Ir, but also the influence of Au.

Comparing the activity of Ir/TiO<sub>2</sub>, Ru/TiO<sub>2</sub>, and bimetallic catalysts of Au–Ir/TiO<sub>2</sub> and Au–Ru/TiO<sub>2</sub> in the levulinic acid hydrogenation, it was found that the monometallic Ir was the most active catalyst, even more than Ru. However, different from the case of depositing Au on Ru, when depositing Au on Ir catalysts, a segregation of Ir atoms toward the TiO<sub>2</sub> surface occurred. As a result, the two catalysts showed very different



**Figure 10.** HAADF images of Au–Pt/TiO<sub>2</sub>. Images (a) and (b) show the presence of nanoparticles ca. 3.7 nm in size. [Reproduced with permission from ref 132, Copyright 2017, Springer Science Business Media, LLC.]



**Figure 11.** Furfural hydrogenation with different Nb<sub>2</sub>O<sub>5</sub> catalysts and product distribution at 90% conversion. [Reproduced with permission from ref 133. Copyright 2019, under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).]

catalytic behaviors, where the addition of Au to Ir/TiO<sub>2</sub> led to a drastic drop of the activity (12% of levulinic acid conversion after 6 h of reaction). A pretreatment of the catalyst with H<sub>2</sub> increased the conversion up to 38%, but it was always lower than the activity of Ir/TiO<sub>2</sub> (>99%). In this work, Laura and her co-workers demonstrated that Ir provided a stronger metal–support interaction with TiO<sub>2</sub>, compared to Ru, which was beneficial for the stabilization of the metals onto the support.

Studying the role of the support is a characterizing part of Laura's research in catalysis. After the work on levulinic acid hydrogenation with Ir-based catalysts, she focused her attention on Pt-based catalysts, with particular interest in the role of the support.<sup>131,132</sup> She studied the impact of the acidity of support oxide in Pt-catalyzed HMF hydrogenation,<sup>131</sup> as well as the role played by support acid sites in Pt-catalyzed glycerol hydrogenation.<sup>132</sup>

In the case of the catalytic hydrogenolysis of glycerol to diols and alcohols,<sup>132</sup> she investigated the activity of bimetallic AuPt NPs supported on acidic (TiO<sub>2</sub>, H-mordenite, SiO<sub>2</sub>, MCM-41, sulfated ZrO<sub>2</sub>), and basic (MgO) oxide supports (Figure 10).

The activity and the selectivity were significantly influenced by the acid–base properties of the support. The Au–Pt/TiO<sub>2</sub> showed an activity higher than AuPt/MgO and the other acidic oxides. Different from the others, this catalyst showed almost exclusively Lewis sites. No Lewis and Brønsted acidities were observed in the case of Au–Pt/MCM-41 and Au–Pt/SiO<sub>2</sub>, both Lewis and Brønsted acid sites were observed on AuPt/S-ZrO<sub>2</sub>, while Au–Pt/H-mordenite showed almost exclusively Brønsted acidity. Considering that the activity followed the order Au–Pt/TiO<sub>2</sub> > Au–Pt/MCM41 ≥ Au–Pt/SiO<sub>2</sub> > Au–Pt/H-mordenite > Au–Pt/S-ZrO<sub>2</sub>, it was supposed that the presence of Lewis acid sites is crucial for achieving good catalytic performances, but the higher the strength of the acidic sites, the lower the activity. Thus, the nature of the acidic sites plays an important role that can also be extended to the selectivity, where the intermediate acidic character of TiO<sub>2</sub> led to an improved selectivity toward 1,2-PD.

In the case of HMF hydrogenation, silica and three mixed silica oxides, i.e., silica–alumina, silica–niobia, and silica–zirconia (5 wt % of Al, Nb, and Zr, respectively) were used as supports for Pt NPs. The presence of the second oxide component changed the acidity of the samples. In particular, the Nb/SiO<sub>2</sub> showed a higher acidity in alcohol than that measured in cyclohexane, due to the presence of Lewis acid sites at the surface. Also, in this case, the acidic strength of the catalytic surface had relevant consequences in the activity and selectivity of the reaction. Moreover, the introduction of Pt

nanoparticles modified the surface properties of the bare oxide support. In that case, the catalyst behaved as bifunctional material and a different product distribution has been obtained. The results gave indication for the preparation of optimized catalysts for the hydrogenolysis of HMF, which follows various pathways, depending on the support acidity besides the activity of the metal phase. Niobia-supported Pt nanoparticles were also applied in the hydrogenation of furfural, but in this case, modifications in the surface acidity of the support have been obtained by the incorporation of W<sup>6+</sup> (increasing Lewis acid sites) and Ti<sup>4+</sup> (decreasing Lewis acid sites) as dopants in the Nb<sub>2</sub>O<sub>5</sub> structure.<sup>133</sup> The catalytic activity toward the hydrogenation of furfural was higher when the sample showed high surface acidity; in the opposite case, i.e., decreasing the Lewis acid sites, the activity was lower but the selectivity toward furfuryl alcohol increased (Figure 11).

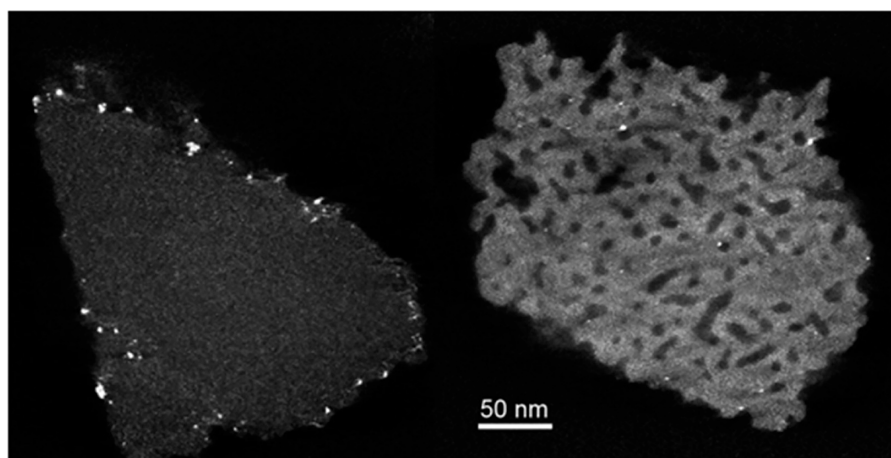
Considering all this, the experimental research from Laura proved that niobia represents an acidic support that can be fruitfully used as supporting material for Pt nanoparticles in hydrogenation reactions, creating a bifunctional catalyst. Acidity is one of the main ruling factors determining the activity and selectivity in the hydrogenation of furfural or HMF.

**4.2.1. Support Modification in Pt-Based Catalysts for Hydrogenation.** Considering that Pt is an active metal in hydrogenation and its activity can be ruled also by the characteristics of the support, Laura continued investigating the catalytic properties of platinum derived from its modification. Indeed, the major issue related to the use of platinum that should be considered is the high market price. Transition metals are available and inexpensive, and among them, Mo (in the form of MoO<sub>3</sub>) showed a promoting effect on the hydrogenation activity.<sup>134</sup> Bimetallic structures consisting of Mo and Pt already showed higher activity than monometallic ones in the hydrogenolysis of alkanes<sup>135</sup> and the dehydrogenation of cyclohexane.<sup>136</sup> Therefore, Laura investigated the properties of a new Mo supported on activated carbon (AC) as a support for platinum nanoparticles (Pt NPs).<sup>137</sup>

Mo-supported AC was prepared by incipient-wetness impregnation method using (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> as metal precursor to have a loading of 40 wt % Mo. Pt NPs were then supported on the 40% Mo@AC by impregnation.

Mo supported on activated carbon is active in furfural hydrogenation, which was addressed, with regard to the presence of the orthorhombic phase of Mo<sub>4</sub>O<sub>11</sub>. The addition of Pt to Mo/AC enhanced the activity, which was higher than that of the reference Pt-AC. From structural/morphological





**Figure 12.** Representative cross section slices from STEM tomogram of Ru/AC (left) and Ru/MC (right). [Reproduced with permission from ref 145. Copyright 2020, Elsevier.]

analyses, it was found that Pt NPs supported on Mo-AC have particle size distribution between 1 and 3 nm smaller than Pt/AC and more homogeneously dispersed, thus explaining the higher catalytic activity of the Pt/Mo system, with respect to Pt/AC. Moreover, this  $\text{Mo}_4\text{O}_{11}$  orthorhombic phase could have a central role interacting with Pt and promoting hydrogen spillover. As a conclusion, Mo supported on activated carbon is a promising material either as a precious-metal-free catalyst, or as a support, improving Pt nanoparticles distribution and the final catalytic activity in furfural hydrogenation.

Continuing this research line, novel Mo–Pt bimetallic catalysts have been synthesized from two different molybdenum precursors, i.e.,  $\text{Na}_2\text{MoO}_4$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ . Indeed, Mo-based catalysts synthesized by different approaches have been shown to present different activities; that is not a novelty in heterogeneous catalysis, but, to date, the reasons remain unclear. The effect of the two Mo salt precursors in this case was studied based on the catalytic activity showed by the two catalysts in the selective hydrogenation of cinnamaldehyde.<sup>138</sup> Hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to the corresponding unsaturated alcohols is often studied as a model reaction for discriminating the catalytic selectivity for  $\text{C}=\text{C}$  or  $\text{C}=\text{O}$  hydrogenation. Overall, the hydrogenation and hydrodeoxygenation of aldehydes are important industrial processes to produce a wide range of chemicals,<sup>139</sup> as well as aldehydes that can be found in several biomass-derived feedstocks. Thus, the conversion of aldehydes is playing a crucial role, as the value of biomass-derived compounds is a critical step toward the replacement of fossil fuel as a source of chemicals. This is another important chapter of Laura's research, which will be reported in the conclusion of this manuscript.

Concerning Pt–Mo supported on carbon catalysts, characterization by means of TEM analysis showed very homogeneously dispersed Pt NPs only when they were deposited on the heat-treated Mo/C supports.

Moreover, Mo precursors direct the functionalization of C during the calcination step and form a different ratio of  $\text{MoO}_2$  and  $\text{MoO}_3$ . These different species have a different impact in the dispersion of Pt and in its final oxidation state, which, in turn, modify the catalytic activity. On the other hand, the explanation of the different selectivity was found in a different acidity, which played a decisive role in the hydrogenation rates of  $\text{C}=\text{C}/\text{C}=\text{O}$ . The sample prepared from  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  has stronger acid sites, compared to that synthesized from

$\text{Na}_2\text{MoO}_4$ ; such a decrease in acidity resulted in greater electron density on the metal particles,<sup>140</sup> which may cause a suppression in the  $\text{C}=\text{C}$  hydrogenation by enhancing the delocalization of electrons in the adsorbed conjugated substrate. In contrast, a more acidic Pt catalyst has poorer electron density, which reduces the electron repulsion related to the  $\text{C}=\text{C}$  adsorption, favoring the formation of hydrocinnamaldehyde.<sup>141</sup>

**4.2.2. Support Modification in Carbon-Based Catalysts.** After the study of platinum as an active metal, she studied ruthenium-based catalysts. In this case, one of the initial targets was the investigation of the possible role of different carbonaceous supports.<sup>142</sup> Carbons from second-generation biomass as sustainable supports for catalytic systems were in fact another crucial step of Laura's research.<sup>143</sup> For example, she studied the properties of activated carbons produced from wood using different wood species, as supports for Au–Pt nanoparticles, proving that the catalyst activity depends on the structural features of carbons (in particular, in LA hydrogenation, a higher content of aliphatic structure enhanced the stability and the activity of the catalyst). In the case study of HMF hydrogenation,<sup>142</sup> Ru was supported on activated carbon (AC) and carbon nanofibers (CNFs) for the selective production of liquid fuel dimethylfuran (DMF) and fuel additives such as alkoxymethyl furfural (AMF). The choice of different supports significantly affected the selectivity of the desired products, where DMF was mainly produced with AC as a support, while a high amount of AMF was produced using CNFs.

The next step was the functionalization of CNFs by introducing O-, N-, and P-containing groups to investigate the effect of support functionalization.<sup>144</sup> Ru was once again used as the desired metal and the HMF and levulinic acid (LA) hydrogenation were studied as model reactions. In the case of LA, despite all the catalysts produced selectively, such as  $\gamma$ -valerolactone (GVL), the functionalization strongly affected the activity of the reaction, where O-containing and N-containing supports showed higher activity than the bare support. In contrast, in HMF hydrogenation, functionalization had a detrimental effect on the activity and changed the selectivity, increasing the production of ethers. CNFs-N appeared as the best support in the Ru-catalyzed LA hydrogenation in water, not only due to the higher

hydrophilicity of the support but also to the strong interaction of N-groups with Ru particles.

Then, to overcome some limitations such as deactivation coming from Ru leaching and particles aggregation, Laura worked with Ru supported on activated (Ru/AC) or mesoporous carbon (Ru/MC), to determine if the spatial restriction on metal nanoparticles could limit aggregation, reducing performance losses.<sup>145</sup> In fact, electron tomography characterization showed preferential Ru location, depending on the material porosity (see Figure 12).

Looking at the catalytic behavior, Ru/MC reached the complete conversion of levulinic acid while Ru/AC converted only 83% (in both cases with a selectivity to  $\gamma$ -valerolactone of 96%). Moreover, the Ru/AC materials deactivated after 1 catalytic cycle; however, the Ru/MC maintained constant activity for multiple catalytic cycles.

**4.3. Aldehydes Hydrogenation for Valuing of Biomass-Derived Compounds.** Recently, Laura was awarded funding for an important project in collaboration with Total Energies about tailoring catalyst active sites in hydrogenation/hydrogenolysis reactions for biofuel production. The design of a catalytic material starts from the principle that the active site properties are derived from an ensemble of factors, as demonstrated in many of Laura's works described in the previous paragraphs. Hydrogenation reactions are among the pillars of the chemical industry and particularly relevant in the field of biomass transformation. Indeed, the use of biomass appears a good alternative for replacing fossil sources of energy, but the high oxygen content must be removed by hydrogenation and hydrogenolysis catalytic processes. Therefore, Laura concentrated her efforts of these last years on the study of a better understanding of catalyst structure–activity relationships in the hydrogenation/hydrogenolysis reactions of highly functionalized, oxygen-containing reactants, with the final goal to indicate requisites for the design of specific catalytic materials that minimize waste and energy consumption, thus reducing risks, hazards, and costs.

The hydrogenation and hydrodeoxygenation of aldehydes are important industrial processes for the production of a wide range of chemicals that find use as solvents, fuels, plasticizers, detergents, pharmaceutical precursors, and fine chemicals. Aldehydes, in fact, can be found in several biomass-derived feedstock.<sup>146</sup> First, Laura investigated one of the critical parameters that govern the reactivity of the carbonyl group toward hydrogenation and hydrodeoxygenation, that is the effect of the side chains of aldehydes.<sup>147</sup> In this work, she demonstrated that the presence of a p-electron conjugation on the side chains strongly affects the conversion of aldehydes to alcohols and hydrocarbons. Indeed, a Pd-supported carbon catalyst was tested and, while in the presence of a strong p-electron conjugation (aromatic ring), the catalyst was active toward the hydrogenation and further hydrodeoxygenation of the carbonyl group, it was inactive with molecules with no or weak p-electron conjugation (alkyl chains).

As a next step, she disclosed some still existing uncertainty with respect to the properties governing the catalyst activity of Pd/C, using the hydrogenation of benzaldehyde as a model reaction.<sup>148</sup> The research work demonstrated which are the main parameters that determine catalyst activity of Pd nanoparticles supported on a carbonaceous material, varying its physicochemical properties, such as nanoparticle size, Pd oxidation state, and Pd surface exposure. Indeed, a linear correlation between catalyst activity and the amount of surface

Pd(0) atoms was found, highlighting the nature of the active site of the Pd/GNP catalyst represented by exposed Pd(0) species.

Lastly, she started to investigate the possibility of understanding the phenomena responsible for catalytic performance not only looking at the structural properties of the catalytic material, but also considering the entire catalytic system, as complex interplay between the catalyst, reactant, and reaction medium. The extent of interaction between a reactant and a catalyst can, in fact, be evaluated through nuclear magnetic resonance (NMR) spectroscopy looking at the spin relaxation. This is considered a sensitive probe for molecular dynamics. Laura, once again, focused on Pd nanoparticles supported on an activated carbon for hydrogenation of aldehydes. What was shown in the previous work,<sup>149</sup> i.e., benzaldehyde could be readily hydrogenated by Pd/C catalyst while negligible activity was observed with octanal, as it was finally disclosed by using <sup>13</sup>C T1 NMR.<sup>150</sup> Two different T1 relaxation times were used: the T1<sub>ads</sub>, which is measured when the molecule adsorbed on the catalyst (in the presence of the catalyst in the reaction medium), and the T1<sub>bulk</sub>, which is for the free diffusing (bulk) molecule. The ratio (T1<sub>ads</sub>/T1<sub>bulk</sub>) can be used as an indicator of the relative strength of interaction between the reactant and the catalytic surface.

Comparing and correlating the different T1<sub>ads</sub>/T1<sub>bulk</sub> values, Laura was able to prove that the different catalytic results mainly depend on the contrasting adsorption behavior of substrates on the catalyst, and, in addition, by NMR, she found that the adsorption of the reactants depended on the choice of solvent, proving that T1<sub>ads</sub>/T1<sub>bulk</sub> measurements can provide a guide to the selection of appropriate reaction conditions for improving catalytic activity.

At this moment, she is still working on this technique in parallel with the catalytic studies of new materials. Her latest results in this field are reported in a very recent publication on Pt-WO<sub>x</sub> supported on carbon catalysts, used for the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes.<sup>151</sup> Pt supported on carbon catalysts have been modified by WO<sub>x</sub> species, differentiating the sequential addition of W precursors and Pt. Coupling Pt with WO<sub>x</sub> had a positive effect on the catalytic activity, which can be correlated to the W/Pt atomic ratio: the less active catalyst showed the lowest W/Pt ratio, while the most active catalyst showed the highest W/Pt atomic ratio.

Moreover, the catalysts showed a different selectivity toward C=C or C=O hydrogenation, which is explained by the different superficial amounts of WO<sub>2</sub> or WO<sub>3</sub>.

Using <sup>13</sup>C NMR relaxation times (T1<sub>bulk</sub>/T1<sub>ads</sub>), Laura still found a direct correlation between the strength of reactant interaction and the catalytic surface with the reaction selectivity.

In the field of aldehydes hydrogenation, one must also mention the work that Laura did on the reductive amination of halogenated aldehydes.<sup>152</sup> The chemoselective conversion of a specific functional group of a substrate is of great importance in the chemical industry, and indeed based on this work, Laura and her co-workers had also successfully filed a patent on the “preparation of compounds containing amino groups bound to a carbon skeleton by reductive alkylation of ammonia, amines or compounds having groups reducible to amino groups, with carbonyl compounds by reduction with hydrogen (ref. n. WO2016071410A1)”.

The research focuses in particular on the chemoselective amination of halogenated benzaldehyde with dimethyl amine

toward halogenated aromatic amines, which are important compounds used in the production of agrochemical active ingredients. The key point was the finding of a highly performing catalyst obtained combining palladium and copper. By depositing Cu onto Pd supported on carbon, the reaction yield increased from 66% (Pd/C) to 98% (PdCu/C). Moreover, this bimetallic catalyst showed suppressed dehalogenation side reactions, as well as in other chemical conversions, such as the hydrogenation of nitro functional groups and the hydrogenation of aldehydes.

For the experiments, precisely, the reductive amination of 2-chlorobenzaldehyde with dimethyl amine to the corresponding 2-chlorobenzyl *N,N*-dimethyl amine was selected as the model reaction. Monometallic Pd/C was compared with several different bimetallic palladium/copper catalysts on activated carbon and finally monometallic Cu/C. While a monometallic Pd on a carbon catalyst enhanced dehalogenation reactions, switching to a catalyst composed of a 1:1 Pd:Cu molar ratio suppressed the dehalogenation reactions. Then, by increasing the Cu amount, decreased the activity of the dehalogenation reaction, resulting in a yield of 99% toward the desired halogenated amine. When the applicability of the Pd–Cu catalytic system was further investigated for other hydrogenation reactions in the presence of a halogen atom (i.e., the hydrogenation of an aldehyde, the hydrogenation of a nitro group and the reductive amination of aldehydes with different amination agents), the positive effect of Cu on suppressing the dehalogenation reaction was confirmed in all cases.

Therefore, Laura contributed to developing an efficient method for the chemoselective reductive amination of halogenated benzaldehyde, by designing a new and efficient catalyst that combined Pd and Cu and reached conversions and selectivity as high as 99%. Comparing with others,<sup>153</sup> this process shows the highest potential for an industrial process due to the high yields and the low amount of solvents needed. In fact, the project came from an industrial collaboration with the Eastman Chemical Company.

## 5. CONCLUSION

During the last 35 years, Laura Prati has had an extraordinary career in catalysis, using colloidal Au based nanoparticles for several successful and important catalytic applications. Her work has inspired many research groups around the world for the use of Au NPs not only for catalytic applications but also biomedical and energy-related applications that are essential for our society and economy. Especially Laura was a pioneer and one of the first groups worldwide to show the high catalytic efficiency of mono and bimetallic Au-based preformed colloidal nanoparticles with well-defined structural design for sustainable catalytic processes, especially the selective liquid-phase oxidation of alcohols, sugars, for tuning the selectivity to desired products, as well as for improving catalyst's stability. A prominent example is the selective oxidation of glycerol, where the systematic control of specific experimental parameters led to the synthesis of novel and size- and shape-controlled supported nanoparticles and especially the deeper understanding of reaction pathways and identification of active sites using different characterization techniques including electron microscopy and infrared spectroscopy. She has also developed new synthesis approaches for the development of novel catalysts for hydrogenation reactions from biomass resources with Total Energies, especially the production of fine chemicals. Moreover, the nature and influence of support

was exploited in many cases, and the use of functionalized carbon materials showed new directions for improving not only catalytic efficiency but also emphasizing on the role of controlling the surface functionality of carbon-based materials and how it affects catalytic performance. Her approach was to investigate first the fundamental chemistry of functionalized colloidal metal nanoparticles and supports that have applicability for different catalytic model reactions and then try to develop better understanding between the morphology of the catalyst and the catalytic performance, using advanced characterization techniques. Then, the outcome of this knowledge especially can be used either for improving existing catalytic processes or to generate new catalytic applications and synthesizing highly efficient nanomaterials. We wish Laura to continue her wonderful academic success in the next years.

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### Notes

The authors declare no competing financial interest.

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