

Catalytic Oxidation of Methoxy Substituted Benzyl Alcohols as Model for Lignin Derivatives Valorisation.

Marta Stucchi¹, Stefano Cattaneo¹, Andrea Cappella¹, Wu Wang², Di Wang², Alberto Villa¹ and Laura Prati^{1,*}.

¹ Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi 19, 20133, Milano, Italy.

² Institute of Nanotechnology and Karlsruhe Nano Micro Facility, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

Abstract

Lignin contains around 50 wt% of aromatic hydrocarbons, which can be transformed in fuels and chemicals. Many processes convert lignin in phenols and alcohols, needing further oxidation to be converted in high-value products. This work reports a study on the catalytic oxidation of some model alcohols derived from lignin by bimetallic Au/Pd catalysts. The already proved beneficial synergistic effect between Au and Pd was investigated considering different Au:Pd ratios in the oxidation of benzyl alcohol, 4-methoxybenzyl alcohol and 3,4-dimethoxybenzyl alcohol, due to the importance of methoxy-substituents in lignin derivatives. The synergistic effect between Au and Pd on activated carbon was confirmed, being both the monometallic Au and Pd supported catalysts inactive for the oxidation of these alcohols under base-free conditions. Moreover, we proved that the position of the methoxy group on the aromatic ring played a crucial role, influencing the catalytic activity depending on the specific Au:Pd ratio. Results showed that Au-rich catalysts were not influenced by the substrate effect, on the contrary to the Pd-rich ones, where the specific Au:Pd ratio was crucial in determining the catalytic activity.

1. Introduction

Lignin is the second most abundant polymer after cellulose, and constitutes 30 % of lignocellulosic biomass [1]. In the last fifteen years the pulp and paper industry produced 50 million tons of extracted lignin [2], among which only approximately 2 wt% have been commercially valorised [1]. Large-scale industrial processes that use plant polysaccharides usually burn lignin to generate the power needed to productively transform biomass. However, biorefineries that convert cellulosic biomass into fuels generate more lignin than necessary to power the operation. Overall, lignin is underutilized, with about 60 % more lignin generated than is needed [3]. On the other hand, lignin extraction is rather efficient due to the flexibility in lignin monomer composition, which also gives to the lignin feedstock unique properties for coproduct development [4]. In particular, lignin is the only large-volume renewable feedstock that is composed of aromatics [5]. Structural studies of lignin revealed that 50 % of its components are aromatic hydrocarbons, and for this reason, lignin has major potential to serve as a renewable source or aromatic chemicals [6]. The transformation of lignocellulose beyond paper pulp to fine chemicals, polymer precursors, and fuels is the one of most realistic alternative to current refining

of fossil fuels as a carbon feedstock [7]. In particular, lignin consists of highly branched methoxylated phenylpropane units, composed of three primary monomers, namely, p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [8]. Despite many high-value products can be recovered from lignin, such as carbon fibers, plastic and thermoplastic elastomers, or polymeric foams, some lignin fractions from a biorefinery are not suitable for material applications, whereas they can be converted into fuels and chemicals. The key advantage is that they would be low cost and they completely replace the petroleum-derived ones. However, the production of each product has its own challenges. In particular, for fuels and chemicals, their production or enhancement by heterogeneous catalyst is an emerging strategy that requires a targeted scientific research. Processes such as oxidation, acid or base catalysed depolymerisation, gasification and pyrolysis, convert lignin in phenols, lignin monomers, alcohols or olefins [9]. Chemists have investigated different oxidation routes over the past several years, united by the need to find innovative strategies favouring mild reaction conditions [10].

However, many of the target products from lignin oxidation are compounds with small market volumes [4]. Overall, one of the largest challenges associated with lignin valorisation is whether there are economic pathways for its conversion to value-added fuels and chemicals.

Thring et al. [11] published a comprehensive study, reporting a list of phenols from lignin depolymerisation. Most of alcohols gain economic value when oxidised to aldehydes, either because aldehydes are known intermediates to high-value components, or because they have a very high market value themselves, being widely used in perfume, cosmetics and food industry [12]. However, the high presence of methoxy-substituents in lignin-derived alcohols requires a fine selection of model molecules in order to study their conversion and catalytic valorisation. Veratryl alcohol is regarded as a proper model substrate of lignin; its oxidation to veratryl aldehyde, in fact, represent a typical valorisation of a β -O-4 model compound of lignin [13,14]. Moreover, veratryl aldehyde, presents interest per se being used as flavouring agent, and finding application as pharmaceutical intermediate as well, particularly in the synthesis of angiocardiotherapy drugs [15].

The effective catalytic conversion of lignin-derivatives requires the study of the relation between the substrate features and the catalytic behaviour at molecular level. The correlation between the catalyst structural chemistry and the characteristics of the reactant in a specific environment allows to establish rules for a successful catalysts design. Indeed, among the factors that strongly influenced the catalytic activity, the substrate effect can play a crucial role.

Au nano-crystals are an environmental-friendly alternative for the oxidation of alcohols in base-medium, although the main product is often the corresponding monoacid and not the desired aldehyde [16-19]. On the other hand, Pd is a well-known effective metal for the selective oxidation of primary

alcohols to aldehydes. Kaneda et al. [20], for example, showed that hydroxyapatite-supported Pd nanoclusters are active for the oxidation of phenylethanol and benzyl alcohol to the corresponding aldehydes, while Pillai et al. [13] performed the aerobic oxidation of many primary and secondary alcohols into the corresponding aldehydes over a recyclable Pd/MgO catalyst. Prati et al. [21] recently reported a study on the liquid-phase oxidation of benzyl alcohol over Pd nanoparticles, suggesting that the reaction selectivity is influenced by the side reaction of oxygen scavenging surface hydrogen.

Enache et al. [22] showed that TiO₂-supported Au-Pd alloy nanocrystals give significantly enhanced activity for alcohol oxidation, increased TOFs by a factor of ≈ 25 , comparing with monometallic supported Au [23] and Pd [21]. Moreover, TiO₂-supported Au-Pd nanoparticles converted benzyl alcohol to benzaldehyde with a selectivity of 96 %, whereas Pd/TiO₂ mostly produced toluene and benzene [24]. In a recent study, Prati et al. synthesised a carbon supported Au-Pd catalyst (6:4 mol %) by sol-immobilisation technique, disclosing the specific correlation between particle structure and catalytic activity/selectivity towards the benzyl alcohol oxidation reaction [25]. The internal AuPd ratio has been also shown to have a big impact on the catalytic activity especially regarding the substrate structure [26].

Therefore, in this study, Au/Pd catalysts with different Au:Pd ratios were synthesised and their catalytic performance compared in the oxidation of lignin-model substrate, veratryl alcohol. In particular, we focussed our attention on the **substrate effect, in term of influence** of methoxy-substituent on the aromatic ring, comparing veratryl alcohol oxidation with 4-methoxybenzyl alcohol and benzyl alcohol oxidation. **The final aim is to evaluate if there is a relationship between the different Au:Pd ratio and the catalytic activity, according to the presence of the methoxy groups on the aromatic ring. This will allow to design more specific catalysts for lignin conversion and valorisation.**

2. Experimental

2.1 Catalysts synthesis

Monometallic Au and Pd, and bimetallic Au-Pd nanoparticles were synthesised by sol-immobilisation and supported on activated carbon (Norit Carbon GSX, 933 m² g⁻¹, pore volume 0.26 mL g⁻¹) [27]. NaAuCl₄•2H₂O (99 %, Aldrich) and Na₂PdCl₄ (98 % Aldrich) were used as metal precursors, while NaBH₄ (> 98%, Ventron) and polyvinyl alcohol (PVA, MW = 9,000–10,000, 80 % hydrolysed, Aldrich) were used as reducing agent and protecting agent respectively. The metal loading was 1 % in weight for every catalyst. Monometallic samples were prepared starting from an aqueous solution (10 mg ml⁻¹

¹) of NaAuCl₄•2H₂O or Na₂PdCl₄, respectively for Au and Pd sols. Under vigorous stirring, 500 μL of a 1% w/w solution of PVA were added (0.5 PVA/metal w/w ratio), followed by 2.5 mL of a freshly prepared 0.1 M NaBH₄ solution of (metal-to-NaBH₄ molar ratio of 4:1). The resulting metallic sol was kept under stirring for 1 hour, then 1 g of carbon support was added. A small amount of H₂SO₄ (97 %, Aldrich) was introduced in order to maintain the pH of the suspension at 3. After 30 min, the resulting catalyst was filtered, washed with 1 L of deionised water and dried at 80 °C for 1 h. Bimetallic samples were prepared with a similar procedure mixing the metal precursors in order to obtain the desired Au:Pd molar ratio (1:2, 2:8, 6:4, 8:2 and 9:1 respectively). Monometallic catalysts were labelled as Au@AC and Pd@AC, while bimetallic catalysts were labelled as Au_xPd_y@AC, where x and y denote the molar ratio between metals.

2.2 Catalysts characterisation

The catalyst specimens were characterised by Transmission Electron Microscopy (TEM). The powder samples of the Au-Pd@AC catalysts were directly dispersed on copper grids covered with holey carbon film. Morphology of the catalysts was characterised by high angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and its composition information were acquired by EDAX S-UTW EDX detector in a FEI Titan 80-300 microscopy operating at 300 kV. Analysis of STEM-EDX spectrum imaging was carried out by using TEM Image & Analysis (TIA 4.7 SP3 version) software. Particle size of the specimens were measured on HAADF-STEM images by using the ImageJ software fitting the particles with ellipsoid shapes.

A PANalytical X'Pert Pro X-ray diffraction equipment, using monochromatic CuKα1 radiation ($\lambda=1.5406 \text{ \AA}$) at 45 kV and 40 mA recorded the X-ray diffractograms (2θ range of 5-80° at 0.017° intervals and with a scan step time of 110 s).

The gold and palladium concentrations were checked by ICP analysis on a Jobin Yvon JV24 carried out on the filtrate after impregnation of the support.

2.3 Catalytic reactions

The mono- and bimetallic Au-Pd catalysts were tested for the oxidation of benzyl alcohol, 4-methoxybenzyl alcohol and 3,4-dimethoxybenzyl alcohol. Oxidation reactions were carried out in a glass reactor maintained at 80 °C and in oxygen atmosphere (2 bar); the substrate (0.0015 mol) was added to 10 mL of p-xylene before sealing the reactor. The catalyst amount was calculated in order to have a metal-to-substrate ratio of 1:1000. The products of reactions were identified by GC-MS (Thermo Scientific ISQ QD equipped with an Agilent VF-5ms column). Conversions and quantification of

products were performed using a GC-FID equipped with a non-polar column (Agilent 7820A equipped with an Agilent CP-Sil 5 CB column), using dodecanol (for benzyl alcohol) or undecane (for veratryl alcohol and 4-methoxybenzyl alcohol) as external standard.

3. Results and discussion

3.1 Characterisation

All the catalyst produced have been characterized by STEM in order to determine particle size distribution, dispersion and (in the case of bimetallic catalysts) the distribution of each metal. In the case of monometallic Au and Pd we observed a good dispersion of metal nanoparticle on the support.

The investigation of bimetallic samples is more complex as the distribution of the different metals within the individual particle modifies the structural configuration and electronic properties, as they can form alloys, core-shell structure or segregations. STEM images indicate the morphology of catalysts, illustrated in Figure 1. We found higher nanoparticles aggregation in Pd-rich samples ($\text{Au}_1\text{Pd}_9@AC$ and $\text{Au}_2\text{Pd}_8@AC$, Figure 1 a and b), while a more homogeneous dispersion was obtained with Au-rich catalysts (Figure 1 c-e). The more homogeneous dispersion for Au-rich samples might be due to the fact that Au is found to act as nucleation seeds for further Pd immobilisation, as already reported by Wang et al. in a previous work [28]. The particle size distribution measured on STEM images are shown in Figure 2. The nanoparticle sizes of $\text{Au}_2\text{Pd}_8@AC$, $\text{Au}_6\text{Pd}_4@AC$, $\text{Au}_8\text{Pd}_2@AC$ and $\text{Au}_9\text{Pd}_1@AC$ catalysts are similar, around 3.1-3.5 nm in average with a similar size distribution. While the nanoparticle size of the $\text{Au}_1\text{Pd}_9@AC$ catalyst, with highest Pd concentration, slightly increased to 3.8 nm in average because of the high nanoparticles aggregation observed in STEM image. STEM-EDX spectrum imaging was performed on single nanoparticles to map the interior metal compositions (Figure 3). Both Pd and Au signals were found in the nanoparticles and the corresponding element maps show that Pd and Au have similar distribution in all investigated catalysts, indicating the alloy formation of nanoparticle in the Au-Pd@AC bimetallic catalysts. Moreover, composition of individual nanoparticle was quantified by integrated all EDX spectrums in the region of STEM-EDX imaging. Table 1 summaries the quantification compositions of three nanoparticles for each Au-Pd@AC catalyst. The results demonstrate that the composition of individual particles in these catalysts are fit to the nominal composition of Au-Pd.

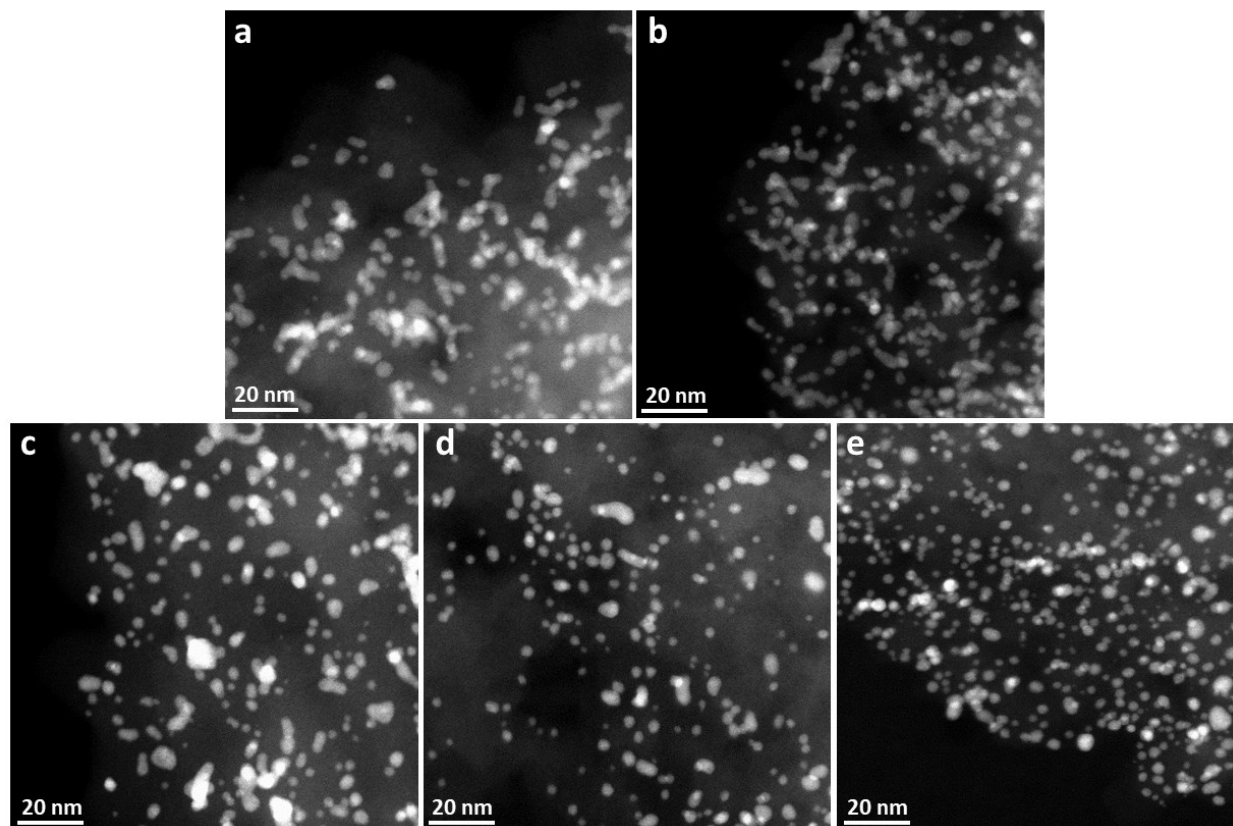


Figure 1. Typical STEM images of (a) $\text{Au}_1\text{Pd}_9@\text{AC}$, (b) $\text{Au}_2\text{Pd}_8@\text{AC}$, (c) $\text{Au}_6\text{Pd}_4@\text{AC}$, (d) $\text{Au}_8\text{Pd}_2@\text{AC}$ and (e) $\text{Au}_9\text{Pd}_1@\text{AC}$ catalysts.

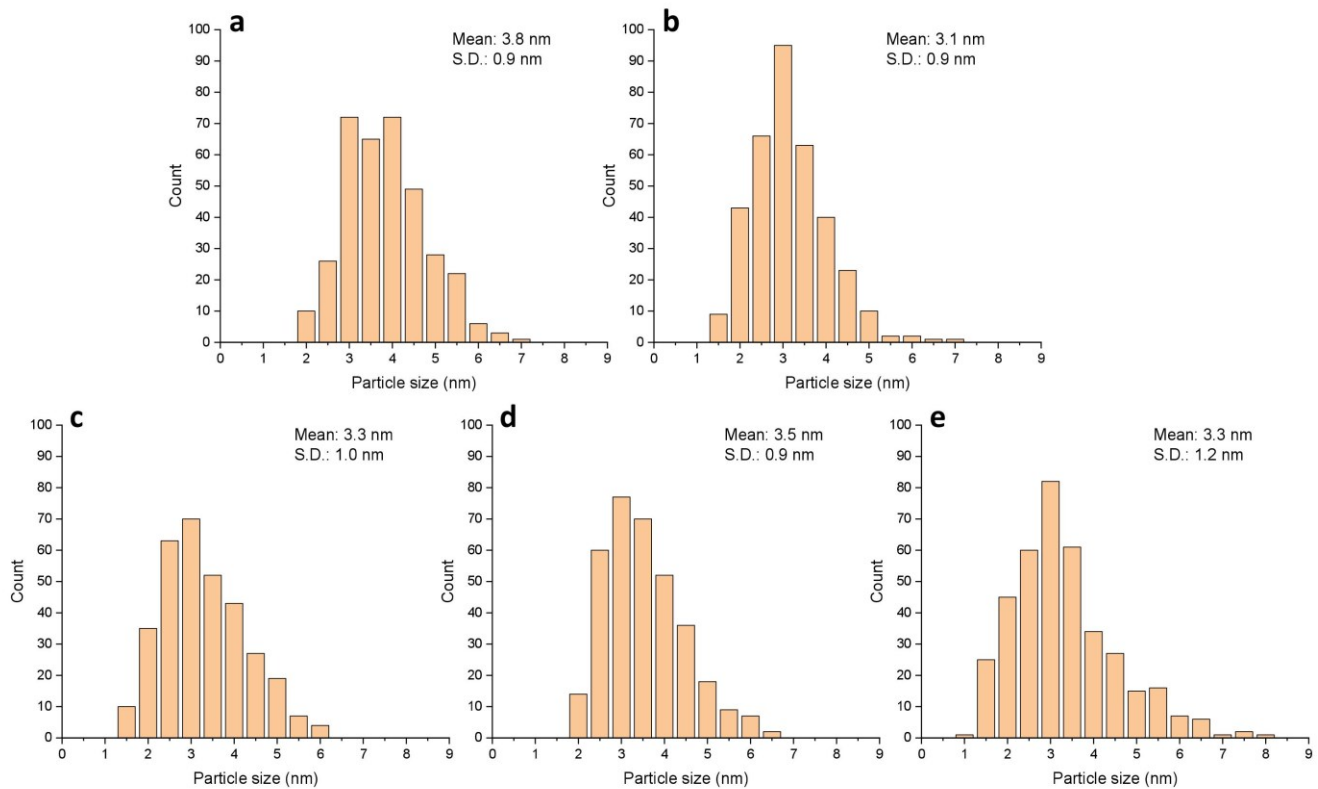


Figure 2. Particle size distribution of (a) Au₁Pd₉@AC, (b) Au₂Pd₈@AC, (c) Au₆Pd₄@AC, (d) Au₈Pd₂@AC and (e) Au₉Pd₁@AC catalysts.

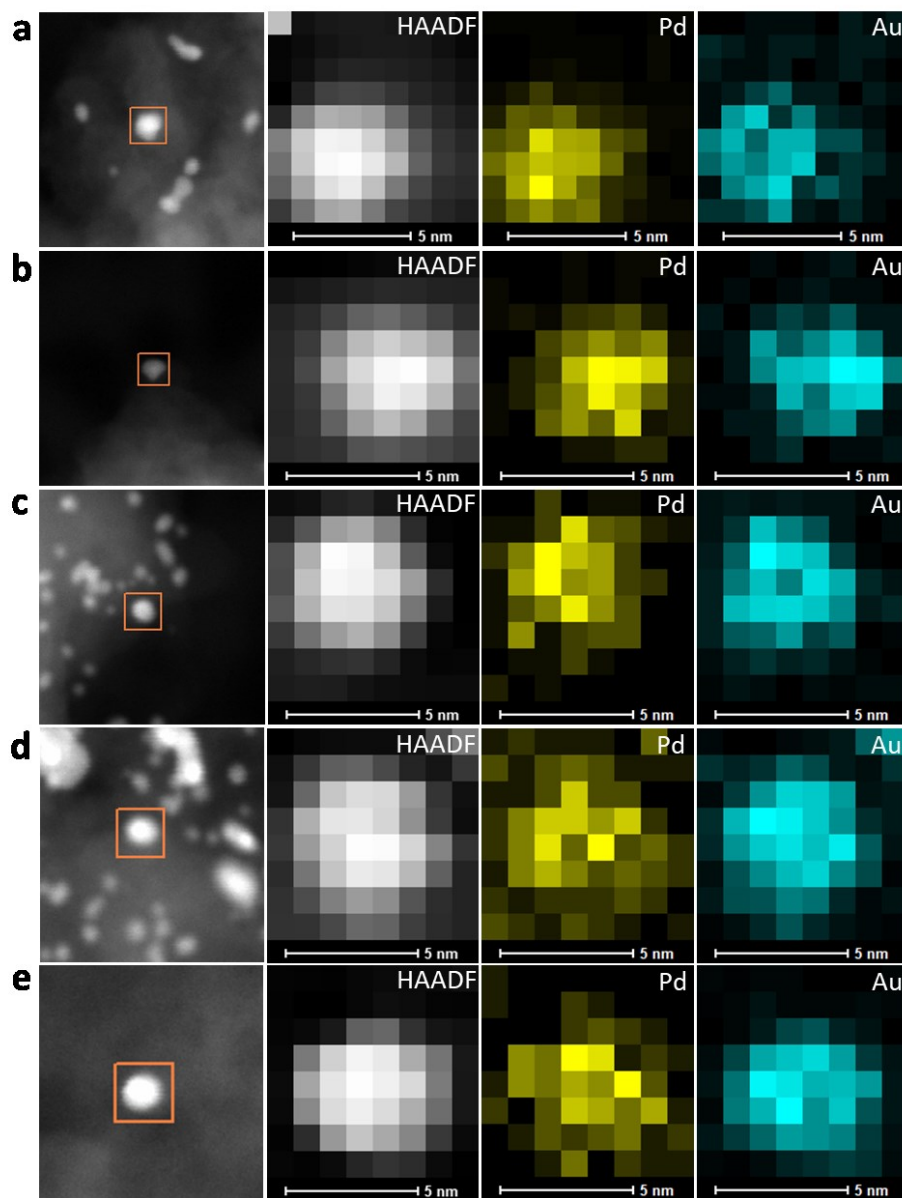


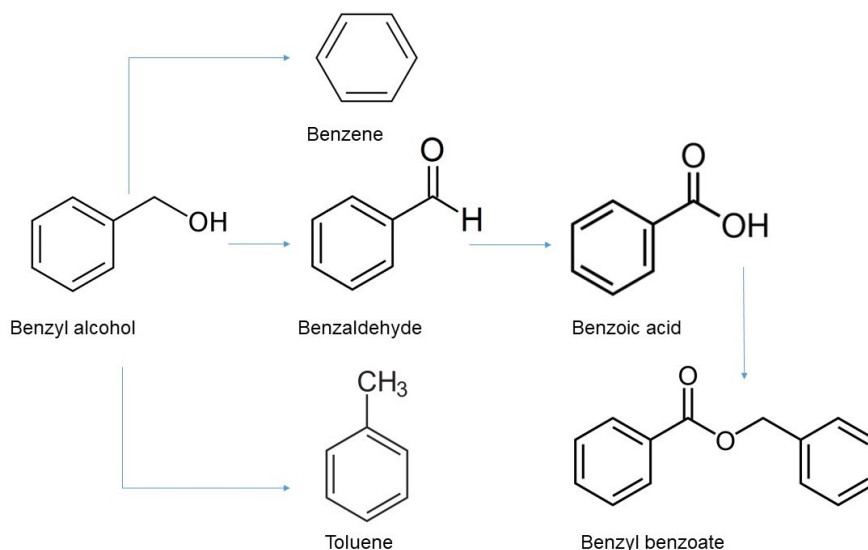
Figure 3. The element maps obtained from STEM-EDX spectrum imaging in the area marked box of (a) $\text{Au}_1\text{Pd}_9@AC$, (b) $\text{Au}_2\text{Pd}_8@AC$, (c) $\text{Au}_6\text{Pd}_4@AC$, (d) $\text{Au}_8\text{Pd}_2@AC$ and (e) $\text{Au}_9\text{Pd}_1@AC$ catalysts.

Table 1. Composition quantification from the integrated EDX spectra of individual nanoparticles in AuPd@AC catalysts.

Particle No.	Au/Pd (at.%/at.%)				
	Au ₁ Pd ₉ @AC	Au ₂ Pd ₈ @AC	Au ₆ Pd ₄ @AC	Au ₈ Pd ₂ @AC	Au ₉ Pd ₁ @AC
1	6/94	22/78	55/45	84/16	88/12
2	10/90	13/87	64/36	73/27	94/6
3	6/94	12/88	58/42	80/20	92/8

3.2 Catalytic activity

Benzyl alcohol oxidation is the model reaction for aromatic activated alcohols [29]. The main product is benzaldehyde, but other side-products such as, benzene, benzoic acid, benzyl benzoate, and toluene can be formed (Scheme 1).



Scheme 1. Reaction scheme for benzyl alcohol oxidation [30].

Here, Benzyl alcohol (BA) is selectively (selectivity > 99 %) oxidized to benzaldehyde in the presence of all the bimetallic catalysts tested whereas monometallic ones that were both almost inactive under base-free conditions (Figure 4).

The catalysts showed different catalytic performance in terms of BA conversion depending on the specific Au:Pd ratio. In particular, the most active catalyst was Au₂Pd₈@AC, with an initial activity (calculated as mol converted per mol of metal per hour) of 267 h⁻¹ followed by Au₆Pd₄@AC (150 h⁻¹), Au₁Pd₉@AC (140 h⁻¹) and Au₈Pd₂@AC (48 h⁻¹) (Figure 5). The synergistic effect between Au and Pd

in bimetallic structures was therefore confirmed. In particular, Pd-rich catalysts showed higher activities compared to Au-rich ones (Figure 5).

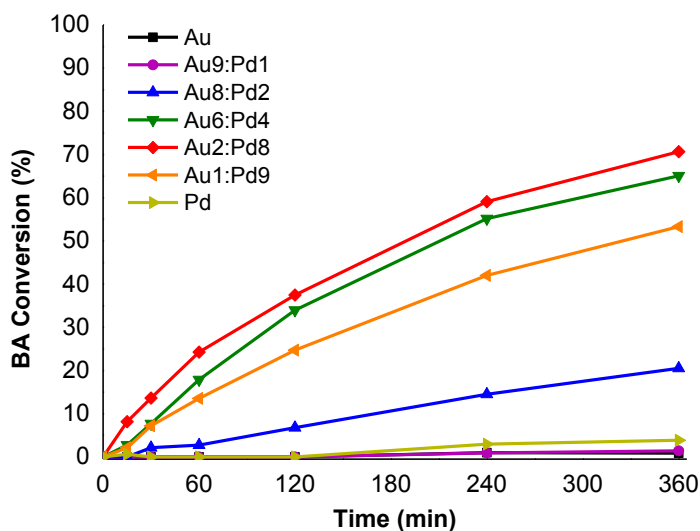
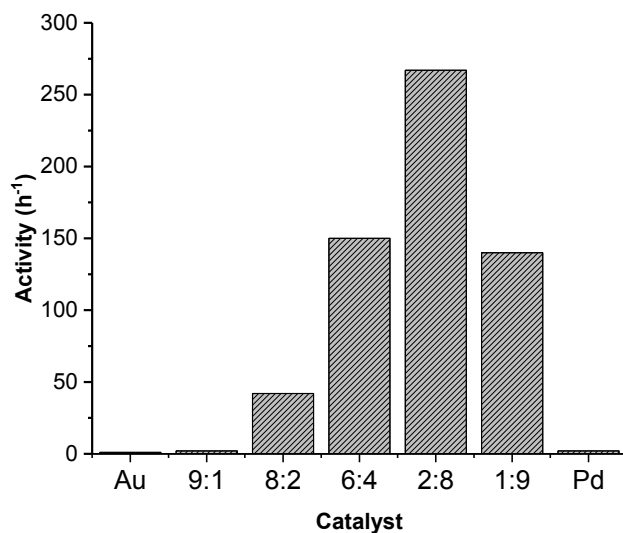


Figure 4. Benzyl alcohol (BA) conversion over time by Au:Pd catalysts in different ratio. Reaction conditions: 2 bar O₂, 80 °C, BA 0.15 M in p-xylene, metal:substrate ratio 1:1000.



	Au	9:1	8:2	6:4	2:8	1:9	Pd
Activity (h⁻¹)^a	0	0	42	150	267	140	0

Figure 5. Activity (mol converted per mol of metal per hour) at 30' of Au_xPd_y catalysts for the oxidation of benzyl alcohol (BA). Reaction conditions: 2 bar O₂, 80 °C, BA 0.15 M in p-xylene, metal:substrate ratio 1:1000.

The effect of methoxy group introduction in para-position has been studied comparing the latter results with the ones obtained using 4-methoxybenzyl alcohol (4-MBA) as the substrate. Firstly, a general decrease of the catalytic activity was found (Figure 6 and 7) in comparison to the case of BA oxidation. However, in this case, Au₆Pd₄@AC catalyst showed a higher activity (247 h⁻¹) than Au₂Pd₈@AC (149 h⁻¹) (Figure 7). To be noted that the selectivity was fully maintained to the corresponding aldehyde.

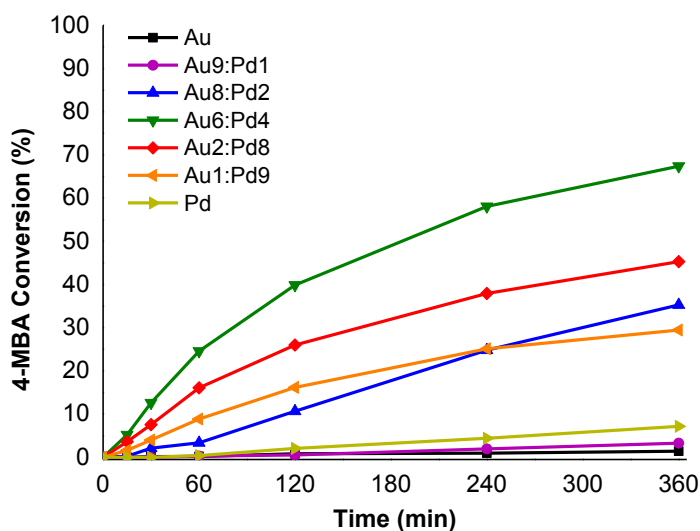
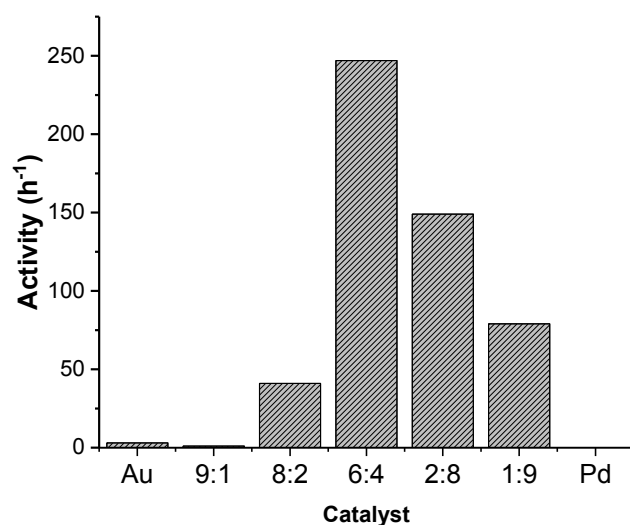


Figure 6. 4-Methoxybenzyl alcohol (4-MBA) conversion over time with different Au_xPd_y catalysts. Reaction conditions: 2 bar O₂, 80 °C, BA 0.15 M in p-xylene, metal:substrate ratio 1:1000.



	Au	9:1	8:2	6:4	2:8	1:9	Pd
Activity (h ⁻¹)	3	1	41	247	149	79	0

Figure 7. Activity (mol converted per mol of metal per hour) at 30' of Au_xPd_y catalysts for the oxidation of 4-methoxybenzyl alcohol (4-MBA). Reaction conditions: 2 bar O₂, 80 °C, BA 0.15 M in p-xylene, metal:substrate ratio 1:1000.

Considering the oxidation of 3,4-dimethoxybenzyl alcohol (veratryl alcohol, VA), we observed that the addition of another methoxy-group creates a general decrease of activity (Figure 8 and 9) but, more importantly, Au₆Pd₄@AC, Au₂Pd₈@AC and Au₁Pd₉@AC catalysts showed a very similar synergistic effect. Moreover, differently from the cases of the other two substrates, monometallic Au@AC showed a non-negligible activity (13 h⁻¹) (Figure 9).

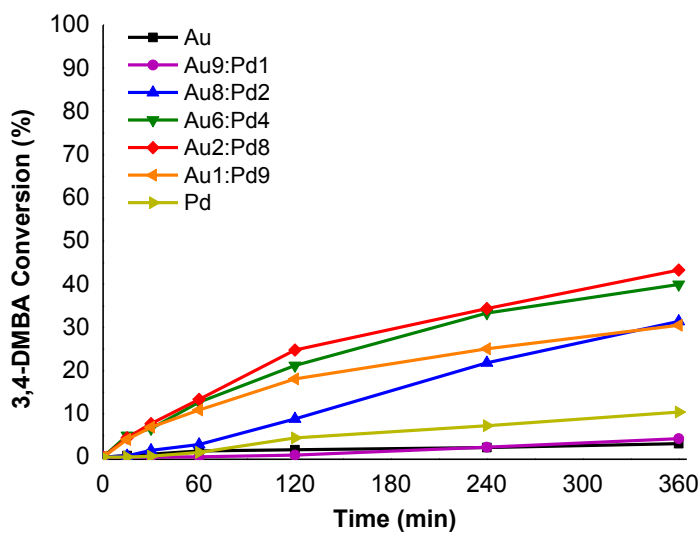
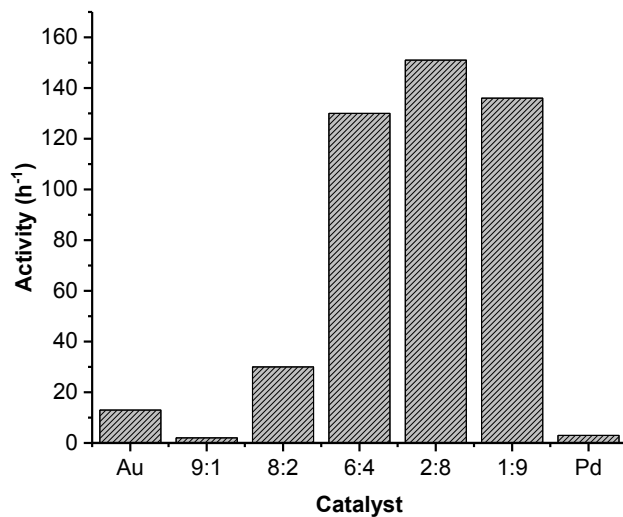


Figure 8. Veratryl alcohol (VA or 3,4-DMBA) conversion over time with different Au_xPd_y catalysts. Reaction conditions: 2 bar O_2 , 80 °C, BA 0.15 M in p-xylene, metal:substrate ratio 1:1000.



	Au	9:1	8:2	6:4	2:8	1:9	Pd
Activity (h⁻¹)^a	13	0	30	130	151	136	0

Figure 9. Activity (mol converted per mol of metal per hour) at 30' (h^{-1}) of Au_xPd_y catalysts for the oxidation of veratryl alcohol (VA). Reaction conditions: 2 bar O_2 , 80 °C, VA 0.15 M in p-xylene, metal:substrate ratio 1:1000.

Summing up we observed a strong effect of the substrate structure in determining the catalyst activity. In particular, the Au-rich catalysts appeared less sensible than the Pd-rich by the substrate structure (Figure 10). It seems the more the Pd content the more the methoxy substituent is effective in decreasing the catalyst activity. A possible explanation could be seen in the increasing of the activity of monometallic Au@AC observed in the case of veratryl alcohol. The methoxy-group can exert, through a mesomeric effect, an electronic enrichment on the alcoholic group thus improving its activity. On the other hand Au with respect of Pd is less sensible to an irreversible adsorption of the substrate on the metal active site increased by the methoxy-group.

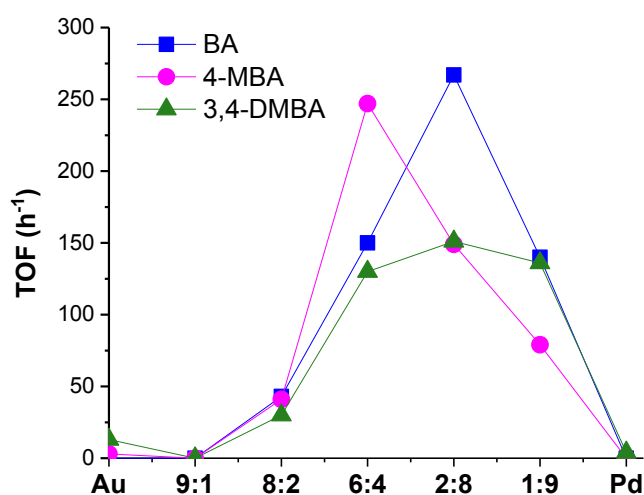


Figure 10. Initial activity calculated at 30' conversion. Comparison between benzyl alcohol (BA), 4-methoxybenzyl alcohol (4-MBA) and 3,4-dimethylbenzyl alcohol (3,4-DMBA) oxidation. Reaction conditions: 2 bar O₂, 80 °C, BA 0.15 M in p-xylene, metal:substrate ratio 1:1000.

4. Conclusions

AuPd on carbon catalysts appeared active under base-free conditions in the oxidation of benzyl alcohol, 4-methoxybenzyl alcohol and 3,4-dimethoxybenzyl alcohol (veratryl alcohol) to the corresponding aldehydes. The two metals presented a strong synergistic effect being the monometallic counterparts almost inactive. Moreover, we found the activity of the catalysts depended on the Au:Pd ratio and the substrate structures. In particular, Pd-rich catalysts were more sensible to the presence of functional groups on the benzene ring than Au-rich catalysts; the more the Pd content and the more effective was the methoxy group to inhibit the oxidation reaction. This effect was

attributed to a mesomeric effect exerted by the substituent group that caused electronic enrichment on the alcoholic group.

Acknowledgements

We acknowledge Karlsruhe Nano Micro Facility for using the TEM.

References

- [1] R.J.A. Gosselink, E. de Jong, B. Guran, A. Abächerli, Co-ordination network for lignin—standardisation, production and applications adapted to market requirements, *Ind. Crops Prod.* 20 (2004) 121–129.
- [2] J. Zakzeski, P.C.A. Bruijninx, A.L. Jongerius, B.M. Weckhuysen, The Catalytic Valorization of Lignin for the Production of Renewable Chemicals, *Chem. Rev.* 110 (2010) 3552–3599.
- [3] P. Sannigrahi, A. J. Ragauskas, Characterization of fermentation residues from the production of bio-ethanol from lignocellulosic feedstocks. *J. Biobased Mat. Bioeng.* 5 (2011) 514–519.
- [4] Ragauskas et al. Lignin valorization, *Science* 344 (2014) 1246843.
- [5] C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, Valorization of biomass: Deriving more value from waste, *Science* 337 (2012) 695–699.
- [6] M. Graglia, N. Kanna, D. Esposito, Lignin Refinery: Towards the Preparation of Renewable Aromatic Building Blocks, *ChemBioEng Rev.* 2 (2015) 377–392.
- [7] M. V. Galkin, J. S. M. Samec, Lignin Valorization through Catalytic Lignocellulose Fractionation: A Fundamental Platform for the Future Biorefinery, *ChemsusChem*, 9 (2016) 1544-1558.
- [8] M. Kleinert, T. Barth, Phenols from lignin, *Chem. Eng. Technol.* 31 (2008) 736–745.
- [9] C. Li, X. Zhao, A. Wang, G.W. Huber, T. Zhang, Catalytic Transformation of Lignin for the Production of Chemicals and Fuels, *Chem. Rev.* 115 (2015) 11559–11624.
- [10] R. Behling, S. Valangea, G. Chatel, Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends?, *Green Chem.* 18 (2016) 1839-1854.

- [11] R.W. Thring, E. Chornet, R.P. Overend, Analysis of phenols from lignin depolymerization by capillary gas chromatography, *J. Chromatogr. A.* 467 (1989) 441–446.
- [12] C. Xu, R.A.D. Arancon, J. Labidi, R. Luque, Lignin depolymerisation strategies: towards valuable chemicals and fuels, *Chem. Soc. Rev.* 43 (2014) 7485–7500.
- [13] U.R. Pillai, E. Sahle-Demessie, Oxidation of alcohols over Fe³⁺/montmorillonite-K10 using hydrogen peroxide, *Appl. Catal. A Gen.* 245 (2003) 103–109.
- [14] V.R. Mate, A. Jha, U.D. Joshi, K.R. Patil, M. Shirai, C. V Rode, Effect of preparation parameters on characterization and activity of Co₃O₄ catalyst in liquid phase oxidation of lignin model substrates, *Appl. Catal. A Gen.* 487 (2014) 130–138.
- [15] H. Lange, S. Decina, C. Crestini, Oxidative upgrade of lignin – Recent routes reviewed, *Eur. Polym. J.* 49 (2013) 1151–1173.
- [16] F. Porta, L. Prati, Selective oxidation of glycerol to sodium glycerate with gold-on-carbon catalyst: an insight into reaction selectivity, *J. Catal.* 224 (2004) 397–403.
- [17] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, Selective oxidation of glycerol to glyceric acid using a gold catalyst in aqueous sodium hydroxide, *Chem. Commun.* (2002) 696–697.
- [18] F. Porta, L. Prati, M. Rossi, G. Scari, New Au(0) Sols as Precursors for Heterogeneous Liquid-Phase Oxidation Catalysts, *J. Catal.* 211 (2002) 464–469.
- [19] L. Prati, M. Rossi, Gold on Carbon as a New Catalyst for Selective Liquid Phase Oxidation of Diols, *J. Catal.* 176 (1998) 552–560.
- [20] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, Hydroxyapatite-Supported Palladium Nanoclusters: A Highly Active Heterogeneous Catalyst for Selective Oxidation of Alcohols by Use of Molecular Oxygen, *J. Am. Chem. Soc.* 126 (2004) 10657–10666.
- [21] A. Savara, C.E. Chan-Thaw, I. Rossetti, A. Villa, L. Prati, Benzyl Alcohol Oxidation on Carbon-Supported Pd Nanoparticles: Elucidating the Reaction Mechanism, *ChemCatChem.* 6 (2014) 3464–3473.
- [22] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, Solvent-free oxidation of primary alcohols to aldehydes using Au-Pd/TiO₂ catalysts, *Science.* 311 (2006) 362–365.
- [23] A. Abad, P. Concepción, A. Corma, H. García, A collaborative effect between gold and a

support induces the selective oxidation of alcohols., *Angew. Chemie Int. Ed.* 44 (2005) 4066–4069.

- [24] L. Prati, A. Villa, A. Jouve, A. Beck, C. Evangelisti, A. Savara, Gold as a modifier of metal nanoparticles: effect on structure and catalysis, *Faraday Discuss.* 208 (2018) 395–407.
- [25] A. Villa, N. Janjic, P. Spontoni, D. Wang, D.S. Su, L. Prati, Au–Pd/AC as catalysts for alcohol oxidation: Effect of reaction parameters on catalytic activity and selectivity, *Appl. Catal. A Gen.* 364 (2009) 221–228.
- [26] N. Dimitratos, J.A. Lopez-Sanchez, D. Morgan, A.F. Carley, R. Tiruvalam, C.J. Kiely, D. Bethell, G.J. Hutchings, Solvent-free oxidation of benzyl alcohol using Au-Pd catalysts prepared by sol immobilisation., *Phys. Chem. Chem. Phys.* 11 (2009) 5142–5153.
- [27] L.L. Vasiliev, L.E. Kanonchik, A.G. Kulakov, D.A. Mishkins, Activated Carbon and Hydrogen Adsorption Storage in Hydrogen Materials Science and Chemistry of Carbon Nanomaterials, Springer Netherlands, Dordrecht, 2007.
- [28] D. Wang, A. Villa, F. Porta, L. Prati, D. Su, Bimetallic Gold/Palladium Catalysts: Correlation between Nanostructure and Synergistic Effects, *J. Phys. Chem. C.* 112 (2008) 8617–8622.
- [29] T. Mallat and A. Baiker, Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts, *Chem. Rev.* 104 (2004) 3037-3058.
- [30] A. Villa, D. Wang, D. Sheng Su, L. Prati, New challenges in gold catalysis: bimetallic systems, *Catal. Sci. Technol.* 5 (2015) 55-68.