

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

A Career in Catalysis: Laura Prati

Journal:	<i>ACS Catalysis</i>
Manuscript ID	Draft
Manuscript Type:	Account
Date Submitted by the Author:	n/a
Complete List of Authors:	Campisi, Sebastiano; Universita degli Studi di Milano, Dipartimento di Chimica Stucchi, Marta; Universita degli Studi di Milano, Department of Chemistry Dimitratos, Nikolaos; Universita degli Studi di Bologna Dipartimento di Chimica Industriale Toso Montanari, Villa, Alberto; Universita degli Studi di Milano, Department of Chemistry

SCHOLARONE™
Manuscripts

A career in catalysis: Laura Prati

Sebastiano Campisi,¹ Marta Stucchi,¹ Nikolaos Dimitratos,² and Alberto Villa^{1,}*

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

² Dipartimento di Chimica Industriale “Toso Montanari”, Alma Mater Studiorum Università di
Bologna, I-40136 Bologna, Italy

KEYWORDS gold catalysis; oxidation; hydrogenation; alcohols; polyols; metal colloids;

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 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 new strategies for preparing catalysts until laying the foundations of the colloidal synthesis of metal

1
2
3 nanoparticles, with particular interest in gold. Her investigations in colloids for catalysis had a
4
5
6
7 natural outcome on catalysts synthesis and optimization. In her career she dealt with liquid phase
8
9
10 oxidation reactions, with particular attention to biomass valorization processes. According to this,
11
12
13 she could not help to deal also with hydrogenation and hydrogenolysis reactions, to which she
14
15
16 dedicated herself especially in the more recent years. Her discoveries has influenced many
17
18
19
20 researchers in the area of heterogeneous catalysis and design of materials.
21
22
23
24
25
26
27

28 **1. Introduction**

29
30
31 Laura was born in 1959 in Milan, Italy. She graduated in Chemistry (1983) at University of Milan,
32
33
34 and received her specialisation in “Tecniche Analitiche per la Chimica Organica Fine” from the
35
36
37 Politecnico of Milano in 1985 and was awarded a PhD in Industrial Chemistry in 1988. Since the
38
39
40 beginning of her scientific career she was involved in the field of the heterogeneous materials
41
42
43 particularly applied to catalysis, being awarded by a MONTEDIPE S.r.l. fellowship, concerning
44
45
46 with the project “Substitutive catalysts of noble metals”. In 1989 she became Researcher, in 1999
47
48
49 Associate Professor of General Chemistry and in 2017 Full Professor. Since this year she was
50
51
52
53
54
55 elected as Head of the Department of Chemistry. She is applying from several years to low impact
56
57
58
59
60

1
2
3 environmental catalytic methodologies as alternative processes of the stoichiometric ones based
4
5
6
7 on organic synthesis. She introduced the use of gold as active metal in the aerobic selective
8
9
10 oxidation of organic compounds, contributing to the developing of the unusual gold catalytic
11
12
13 properties, the main one being the resistance to the poisoning due to the overoxidation in the liquid
14
15
16 phase oxidation. Her skills include the preparation and the functionalization of materials for
17
18
19 obtaining high metallic dispersed catalysts on oxides, active carbons and mesoporous systems. The
20
21
22 scientific results are reported in more than 150 publications on qualified international journals, h
23
24
25 index 46, two patents and more than 100 communications at national and international Congresses
26
27
28 (7 invited). From 2002 to 2006 she was the Referent of the research topic concerning with liquid
29
30
31 phase gold catalysed oxidations, inside the European project AURICAT (HPRNN-CT-2002-
32
33
34 00174). In 2007 she was funded by Fondazione Cariplo on “Metal based nanostructures materials
35
36
37 for catalysis” and in 2009 on the project “Metallic nanoparticles: the issue of stability for their
38
39
40 application”. She received a grant from CNR bilateral project Italy-Hungaria on the project:
41
42
43 Supported bimetallic AuCu and AuAg catalysts in selective alcohol (benzyl alcohol, glycerol)
44
45
46 oxidation reactions: Au/Cu(Ag) atomic ratio, Au/Cu(Ag) structure and support effect”. In 2017
47
48
49 she was granted by TOTAL on the project Catalyst for future. She was Visiting Professor at
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 Université Pierre et Marie Curie (Paris) [June – July 2015] and at Centro de Ciencias Aplicadas y
5
6
7 Desarrollo Tecnológico, Universidad Nacional Autónoma de México (Mexico City) [November
8
9
10 2015 and 2017]
11
12
13
14
15
16



43
44
45 **Figure 1.** Laura during a conference, showing the importance of Au in heterogeneous
46
47 catalysis.
48
49

- 50
51
52 **2. The origins of a “golden career”: gold catalysis for reactions in liquid phase from monometallic**
53
54 **to bimetallic systems**
55
56
57
58
59
60

1
2
3
4 At the core of the modern catalysis science is the fundamental awareness that a multidisciplinary
5
6
7 approach has to be implemented to tackle future challenges and opportunities. This paradigm is
8
9
10 well reflected by the above-summarized scientific career of Laura Prati, where material science
11
12
13 and inorganic chemistry were combined with organic, physical and analytical chemistry methods
14
15
16
17 in shaping a knowledge-based design of heterogeneous catalysts.
18
19

20 In the early 1990's Laura began her research on heterogeneous catalysis for the chemo-selective
21
22
23 oxidation of diols and phenols by using molecular oxygen. The attention was initially focused on
24
25
26
27 copper-based catalysts.¹⁻⁴ Meanwhile, a few years earlier, the research team of Prof. Haruta had
28
29
30 demonstrated that nanostructured gold was able to oxidize carbon monoxide even at low
31
32
33
34 temperatures,⁵ while Prof. Hutchings team had reported the unique activity of cationic gold in
35
36
37 acetylene hydrochlorination.⁶
38
39

40 Gold was considered as a poorly active metal until then. The possibility to finely disperse gold in
41
42
43
44 the form of small nanoparticles (2-6 nm) on a support imposed a reconsideration of the catalytic
45
46
47 potential of gold.
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 The fascinating seminal studies of Prof. Haruta and Prof. Hutchings stimulated Laura's interest in
5
6
7 catalysis by gold and drove her to perform research devoted to the investigation of the catalytic
8
9
10 activity of gold in the oxidation of diols in liquid phase.

11
12
13 At that stage, literature investigations had dealt with the catalytic oxidation of polyols and C2/C3
14
15
16 diols using palladium on carbon or platinum on carbon as catalysts. Despite their high activity,
17
18
19 these catalysts promoted overoxidation and C – C bond cleavage, resulting in poor selectivity,
20
21
22 which, together with poisoning effect of O₂, limited the large-scale application of Pd/C and Pt/C
23
24
25
26
27 catalysts. In this view, the unique capability of gold to favor molecular adsorption of O₂ over the
28
29
30 dissociative one was promising insofar as it could prevent subsurface oxygen diffusion and then
31
32
33
34 minimise the poisoning effect of oxygen.

35
36
37 Starting from these premises, in the first studies activated carbon was selected as the reference
38
39
40 support for gold-based catalysts and ethane-1,2-diol and propane-1,2-diol were studied as model
41
42
43 substrates. Surprisingly, 1% Au supported on activated carbon proven to be an effective catalyst
44
45
46
47 able to convert ethane-1,2-diol in alkaline solution and under mild conditions (70°C, 2 atm O₂,
48
49
50 substrate/metal ratio of 1000, NaOH/substrate molar ratio of 3) with remarkable selectivity toward
51
52
53
54 monooxygenation (90% selectivity in glycolate at very high conversion 94%) and improved

1
2
3 stability.⁷ When tested under similar conditions, Pd/C and Pt/C were more active but less selective,
4
5
6 Cu/C promoted C – C bond cleavage and Ir/C was inactive. In addition, gold catalyst was less
7
8
9
10 sensitive to poisoning, being recyclable up to 10 times without loss of activity neither significant
11
12
13 decrease in selectivity.⁷ The detected high activity and superior stability of Au/C catalyst in the
14
15
16 liquid phase oxidation of diols set a new important milestone in the rising “golden age” of
17
18
19 heterogeneous catalysis, especially in the area of heterogeneous liquid phase catalysis and later on
20
21
22
23 in gas phase catalysis.
24

25
26
27
28 However, right from these first studies it was clear that the catalytic behavior of gold catalysts was
29
30
31 influenced by the particle size, the type of support, the metal-support interaction, the different
32
33
34 preparation methods and the reaction conditions.⁸ The development of gold-based catalysts for
35
36
37 liquid phase reactions thereby demanded actions on several fronts.⁹ Firstly, a pre-requisite for an
38
39
40 optimal design of gold-based catalyst was the setting-up of a synthetic procedure to deposit gold
41
42
43
44 nanoparticles with controlled particle size and high dispersion, independently on the used support.
45
46
47
48 So far co-precipitation, deposition-precipitation and chemical vapor deposition (CVD) were the
49
50
51 most often used methods for the deposition of gold nanoparticles onto oxidic supports to produce
52
53
54 Au-based catalysts for gas-phase reactions. However, all these methods failed in producing small
55
56
57
58
59
60

1
2
3 and highly dispersed Au aggregates on activated carbon, which on the other hand had demonstrated
4
5
6
7 to be the most suitable support for Au catalysts to be used in liquid-phase.⁸ A major breakthrough
8
9
10 was made by Prof. Prati and Prof. Martra,¹⁰ when they prepared size-controlled gold nanoparticles
11
12
13 supported on activated carbon through immobilization of a pre-reduced gold sol (sol
14
15
16 immobilization method), by adopting a protocol proposed by Grunwaldt et al. for the preparation
17
18
19 of Au/TiO₂ and Au/ZrO₂ catalysts for the low temperature oxidation of CO.¹¹ The sol
20
21
22 immobilization method consisted in the chemical reduction of gold precursor (NaAuCl₄ or
23
24
25 HAuCl₄) in the presence of a protecting agent (polymer, surfactant, polar molecule, etc.) and the
26
27
28 subsequent immobilization of gold nanoparticles on a support. Interestingly, the activity of Au/C
29
30
31 catalyst prepared by the sol immobilization in the oxidation of ethane-1,2-diol was at least two-
32
33
34 fold higher (ca. 80% conversion) than that of analogous catalysts prepared by more conventional
35
36
37 methods (43% and 22% conversion for Au/C catalysts prepared by deposition precipitation and
38
39
40 impregnation, respectively). The unique activity of Au/C catalyst prepared by the sol
41
42
43 immobilization derived by two concomitant effects: the enhanced dispersion of gold NPs on the
44
45
46 support surface and the controlled particle size of Au. Specifically, Au NPs having mean particle
47
48
49 size of 7-8 nm were obtained by depositing preformed Au NPs on activated carbon, and these NPs
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 resulted to be more active and selective than those with larger or smaller particle sizes. These
5
6
7 effects were essentially governed by the interaction between metal NPs and support and their
8
9
10 extent depends on the nature of the support, on the molecular size and structure of the protecting
11
12
13 agent, on the protecting agent/Au weight ratio (w/w).¹² The protecting agent emerged as an
14
15
16 essential ingredient in sol immobilization method and its role deserved to be thoroughly
17
18
19 investigated. It foremost forms an organo-shell which provides stabilization and prevents
20
21
22 aggregation of metal NPs in the sol. Moreover, protecting agent molecules confer additional
23
24
25 functionalities and modify the surface charge of gold NPs. Typically, the surface of Au NPs is
26
27
28 negatively charged, due to the presence of adsorbed anions. Embedding polar or ionic character,
29
30
31 the protecting agent molecules adsorbed on the metal surface can alter its surface charge. By this
32
33
34 way, they may mediate the anchoring of gold nanoparticles on the support, resulting in a more
35
36
37 effective interaction with the support and allowing to preserve the original particle size and
38
39
40 morphology during the immobilization step. Among the most employed protecting agents,
41
42
43 tetrakis(hydroxymethyl-)phosphonium chloride (THPC, which acts also as a reducing agent and
44
45
46 provides electrostatic stabilization) produced small, monodispersed gold nanoparticles (2-4 nm).
47
48
49
50
51
52
53
54 However, high THPC/Au ratio was necessary to keep the original particle after immobilization on
55
56
57
58
59
60

1
2
3 support.¹³ Improved stabilization could be achieved when both electrostatic and steric effects were
4
5
6 involved. This was the case of polymers, such as poly(ethylene glycol) (PEG), poly(vinyl
7
8 pyrrolidone) (PVP) and in particular poly(vinyl alcohol) (PVA), which provide double protection
9
10
11 and assure good stabilization. In particular, the use of PVA not only enabled the maintenance of
12
13
14 sol particle dimension even after the immobilization on carbon support, but it also generated highly
15
16
17 active Au NPs with mean Au diameter centered at 7 nm. The latter were able to quantitatively
18
19
20 oxidize ethylene glycol (EG) after 1 h (substrate/catalyst ratio = 1000 mol/mol, substrate/NaOH
21
22
23 molar ratio = 1, $pO_2 = 2$ atm, $T = 70^\circ C$).¹⁴ On the other hand, the presence of a carbonaceous
24
25
26 protective layer may cause shielding effects, limiting gold atom exposure. It could be then
27
28
29 presumed that the optimal particle size for catalysis depended also on gold surface concentration.
30
31
32
33
34 In fact, when ionic surfactants, such as polydiallyl ammonium chloride, poly-
35
36
37 (diallyldimethylammonium) chloride (PDDA),¹⁵ poly[bis(chloroethyl)ether-alt-1,3-bis-[3-
38
39
40 (dimethylamino)pro-*pyl*]urea (PEU) and sulphobetaines, such as N-dodecyl-N,N-dimethyl-3-
41
42
43 amino-1-propansulfonate, were employed as protecting agents the protective layer conformation
44
45
46 and charge density could be influenced by external ions, resulting in a reduced shielding effect and
47
48
49
50
51 higher exposure of gold atoms.¹⁶ As a consequence, when sulphobetaine-protected Au NPs with
52
53
54
55
56
57
58
59
60

1
2
3 lower mean diameter (4.8–5.1 nm) than PVA-protected sol (7 nm) were deposited on activated
4
5
6 carbon, the resulting Au/C catalyst exhibited higher activity (3300–3400 h⁻¹ vs. 800 h⁻¹) in EG
7
8
9 oxidation, thanks to the high atomic Au/C percentage at the surface.
10
11
12

13
14 If the selection of the protecting agent represented a critical point, on the other hand the nature of
15
16
17 support, as well, was far from being a silent actor and played a crucial role in the immobilization
18
19
20 process. First, depending on the iso-electric point and pH, the surface charge of support affects the
21
22
23 interaction of metal NPs with the electrified interface in the immobilization step. In addition, the
24
25
26 functionalization degree of the support determines the dispersion and particle size control since
27
28
29 surface functionalities can act as anchoring sites for metal NPs and contribute to their stabilization.
30
31
32

33
34 Furthermore, the occurrence of strong metal-support interactions can influence the electronic and
35
36
37 structural properties of deposited Au NPs.¹⁷ Therefore even the simple label Au/C demonstrated
38
39
40 to be too generic. Actually, it encompassed a large variety of catalysts, where the different
41
42
43 structure, porosity and surface chemistry of the carbon scaffold may have dramatical consequences
44
45
46 on the size, shape, and properties of Au NPs and on their catalytic behaviour.¹⁸ As a matter of fact,
47
48
49 carbon materials include activated carbons (AC), graphite and low-dimensional carbon allotropes
50
51
52 (carbon nanotubes, CNTs, carbon nanofibers, CNFs, graphene) which strongly differ for their
53
54
55
56
57
58
59
60

1
2
3
4 intrinsic textural, electronic and surface properties. Moreover, as a further complication, activated
5
6
7 carbons can possess different properties depending on their source or on the preparation procedure.
8
9

10 When the same preformed metallic sol (Au–PVA protected NPs) was deposited on different
11
12
13 activated carbons (from coconut and wood), the reactivity and catalytic performances in the liquid
14
15
16 phase oxidation of ethylene glycol were affected by the different microstructure and surface
17
18
19 properties of support. In this case, the nature of support did not influence gold exposure or particle
20
21
22 sizes, but rather the density of phenolic groups at the surface modulated specific metal–support
23
24
25 interactions with obvious consequences on the catalytic behavior.¹⁹
26
27
28
29
30

31 Then, the selectivity of diol oxidation appeared to be the result of a delicate balance between the
32
33
34 nature and structure of the catalysts (particle size, protecting agent, support, surface Au coverage),
35
36
37 reaction conditions and the molecular structure of the substrate. As regard the latter point, the
38
39
40 oxidation of aliphatic diols on Au/C catalysts demonstrated to be highly regioselective towards the
41
42
43 primary alcoholic group (the oxidation of propan-1,2-diol proceeded with 100% selectivity to
44
45
46 lactic acid), while the presence of a phenyl residue in phenyl-1,2-ethane diol activated the
47
48
49 secondary position.²⁰
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 The large experience gained on liquid phase oxidation of diols together with the collected
5
6
7 promising results in the oxidation of more complex substrates, such as glucose²¹, and aldehydes²²
8
9
10 opened stimulating growth scenarios for Au-based catalysis.²³
11

12
13
14 However, the lower activity compared to Pt/C and Pd/C together with the need for a basic
15
16
17 environment still represented two drawbacks of Au/C catalysts calling for further improvement.
18

19
20
21 Once again, Laura Prati and coworkers demonstrated to be keen to find a practical and sustainable
22
23
24 solution: merging the unique properties of gold (resistance to poisoning) with those of Pd or Pt
25
26
27 (high activity even in the absence of a base), by preparing bimetallic AuPd and AuPt catalysts.²⁴
28

29
30
31 First attempts to prepare carbon-supported AuPd (Au : Pd = 1 : 1, molar ratio) nanoparticles
32
33
34 consisted in a successive reduction of the two metals, followed by immobilization of the bimetallic
35
36
37 sol on carbon. Preformed particles of the first metal acted as nucleation centers for the second
38
39
40 metal reduced in the presence of polyvinyl alcohol (PVA) as the protective agent and NaBH₄ as
41
42
43 the reducing agent. This two-step procedure led to bimetallic nanoparticles with an average
44
45
46 diameter of 3.5 nm, which possessed an alloy structure with a partial segregation of Pd. The
47
48
49 method was then optimized by replacing NaBH₄ with H₂ as the reducing agent.²⁵ In this way, the
50
51
52 reduction rate of Pd ions was slowed down and the increased time of the diffusion and the growth
53
54
55
56
57
58
59
60

1
2
3 of Pd on Au allowed to minimize the segregation of Pd. Random alloyed bimetallic nanoparticles
4
5
6
7 with multiply twinned structure and coherent crystalline structure were obtained according to
8
9
10 characterization by High Resolution Transmission Electron Microscopy (HRTEM) coupled with
11
12
13 Energy Dispersive X-ray Spectroscopy (EDX) (Figure 2). Uniform structure and homogeneous
14
15
16 composition (Au–Pd atomic ratio close to 6:4) was observed independently on particle size
17
18
19 without any segregation of metal phases. Such a compositional and structural homogeneity was
20
21
22 maintained even at different Au:Pd atomic ratios (Au : Pd; 9.5 : 0.5, 9 : 1, 8 : 2, 6 : 4, 2 : 8).^{26,27}
23
24
25
26
27 Once again, the protecting agent played an active role. Well-alloyed nanoparticles with uniform
28
29
30 composition were obtained when PVA was used as the stabilizer. Conversely, significant
31
32
33 segregation and remarkable compositional discrepancies characterized bimetallic nanoparticles
34
35
36 prepared in the absence of protecting agent or using an electrostatic stabilizer (e.g. THPC).²⁸
37
38
39
40 Interestingly, geometric and electronic effects induced by the altered interatomic distance on the
41
42
43 surface of bimetallic catalysts can operate on opposite sides or can converge. In the latter case the
44
45
46 catalytic behavior of random alloyed PVA-protected AuPd NPs was found to benefit from
47
48
49 synergistic effects.
50
51
52
53
54
55
56
57
58
59
60

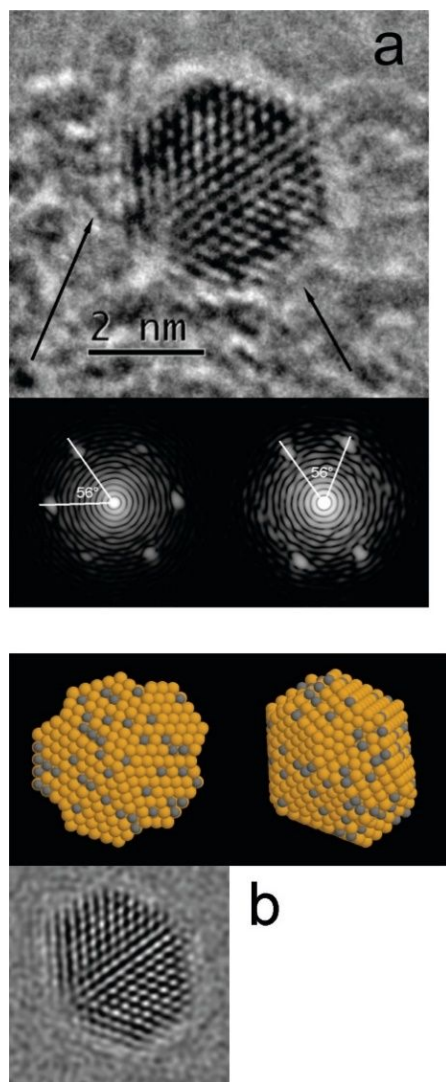


Figure 2. (a) Representative HRTEM microscopy of a multiply twinned particle in the form of truncated decahedron configuration with insets showing FFTs from both sides of the visible twin boundary; (b) the modeled truncated decahedron particle viewed along the 5-fold axis (top left) and orientation that is analogue to the projection of the HRTEM image (top right). Reprinted with permission from Ref. 27, Copyright 2008 American Chemical Society.

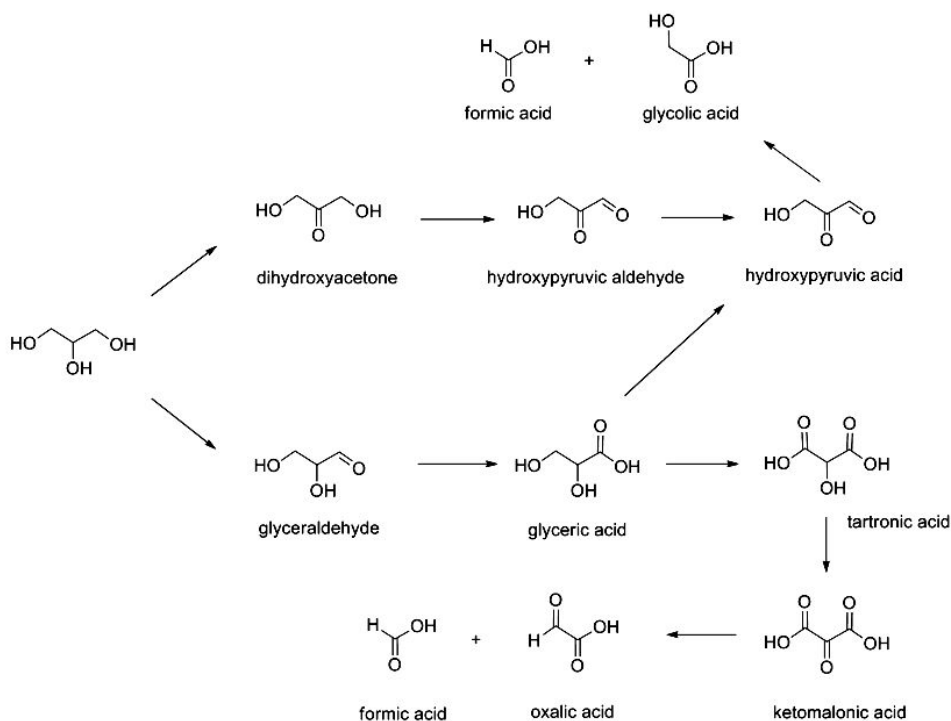
1
2
3
4 The time had come to merge all the acquired knowledge on monometallic and bimetallic Au-
5
6
7 containing catalysts and to move towards a critical design of Au-based catalysts for relevant
8
9
10 industrial applications, such as oxidation and hydrogenation of biomass-derived products.^{29–31}
11
12
13 Such an ambitious goal required a progressive parallel advancement in the characterization of Au-
14
15
16 based catalysts by techniques as electron microscopies, X-ray spectroscopy techniques, vibrational
17
18
19 spectroscopies and chemisorption methods.³²
20
21
22
23
24

25 3. Liquid phase oxidation reactions

26 27 28 3.1. Optimization of gold-based catalysts for glycerol oxidation

29
30
31
32 Under the impulse of a transition from fossil-based production/consumption to biomass-based
33
34
35 industry, the value chain generable from the valorisation of glycerol - from being a primary by-
36
37
38 product in biodiesel production to being a potential source of fine chemicals - is the subject of an
39
40
41 ongoing research. In this view the oxidative transformation of glycerol could offer added-value in
42
43
44 a variety of products through catalytic technologies. Several C₃ (glyceraldehyde,
45
46
47 dihydroxyacetone, glyceric acid, hydroxypiruvic acid, tartronic acid, mesoxalic acid), C₂ (oxalic
48
49
50 acid, glycolic acid) and C₁ (formic acid) compounds can be produced from glycerol oxidation
51
52
53 according to Scheme 1. Nowadays these chemicals are produced by expensive biotechnological
54
55
56
57
58
59
60

1
2
3 technologies or by highly polluting oxidative processes using stoichiometric oxidants. There is,
4
5
6
7 therefore, a significant interest in replacing these processes with environmentally friendly
8
9
10 alternatives, such as the catalytic oxidation with dioxygen or air in the presence of heterogeneous
11
12
13 catalysts. Due to the high functionality of glycerol molecule, the challenge remains to direct the
14
15
16 selectivity to the desired product along such a complex reaction route.³³ For this reason, the
17
18
19 development of effective, stable catalysts for the selective oxidation of glycerol has represented a
20
21
22
23
24 fertile testing ground for the design of selective and active gold-based catalysts.



Scheme 1. Glycerol oxidation reaction network.

1
2
3
4 Inspired by the encouraging results obtained by Laura Prati team in the oxidation of diols and
5
6
7 polyols in the presence of Au/C catalysts, in 2002 Prof. Hutchings and co-workers successfully
8
9
10 proposed Au/graphite catalysts for the liquid phase oxidation of glycerol (80% selectivity to
11
12
13 glycerate). The addition of NaOH was necessary to promote the H-abstraction, the first step of the
14
15
16
17 dehydrogenation pathway for glycerol oxidation.
18
19
20

21 In any case, the pH of the reaction medium is not the only parameter affecting the performances
22
23
24 of supported noble metal nanoparticles. By precisely controlling the structure of the active sites
25
26
27 and the microenvironment around it, the selectivity of the reaction can be controlled. This
28
29
30 tunability arises from several features, such as particle size and shape, synergistic alloying effects,
31
32
33 addition of promoters, presence of protecting agent metal-support interactions, and cooperative
34
35
36
37 effects. All these effects have been deeply investigated in the last decades by Prof. Laura Prati
38
39
40
41 team.³⁴
42
43
44
45

46 *3.1.1. Effect of the preparation method and particle size*

47
48
49

50 The preparation method as well as the support can influence the Au mean particle sizes after
51
52
53 deposition. Taking advantage from the previous experience on the Au-catalyzed oxidation of diols,
54
55
56
57
58
59
60

1
2
3 the effect of different preparation methods (sol immobilization, incipient wetness, deposition
4
5
6 precipitation, and conventional impregnation) was then investigated.^{35–37} A variation of particle
7
8 size (5–30 nm) could be obtained depositing Au on activated carbon (AC) or TiO₂ as supports.
9
10
11
12
13 The activity and the selectivity were strongly affected by gold particle size. Large Au nanoparticles
14
15
16 (10–30 nm) were less active than smaller ones (3–5 nm), even if the former were more selective
17
18
19 to glyceric acid.
20
21
22
23
24

25 *3.1.2. Synergistic and compositional effects in bimetallic catalysts*

26
27
28

29 The synergistic effects deriving from alloying gold to a second metal (Pd, Pt) were investigated,
30
31
32 by comparing the catalytic performance of AuPd/AC and AuPt/AC catalysts with those of the
33
34
35 monometallic Au, Pd, and Pt/AC catalysts.^{27,38–41} Monometallic and bimetallic catalysts were
36
37
38 prepared by sol-immobilisation procedure and tested in the glycerol oxidation under the same
39
40
41 experimental conditions. In general, bimetallic nanoparticles revealed to have similar activity,
42
43
44
45 which was in any case higher than that of monometallic counterparts. Interesting differences
46
47
48 between AuPt and AuPd emerged in terms of product distribution. The oxidation of the terminal
49
50
51 hydroxyl groups was favored in the presence of supported AuPd nanoparticles, which
52
53
54 preferentially produced glycerate and tartronate with selectivities over 90% at 90% conversion.
55
56
57
58
59
60

1
2
3
4 Differently, an enhanced formation of glycolic acid was obtained using AuPt/AC catalyst.
5
6
7 Interestingly, alloying gold to platinum and palladium conferred an improved stability and high
8
9
10 resistance to deactivation. The catalytic performance of bimetallic nanoparticles strongly depended
11
12
13 on the preparation method. One-step and two-step procedures were investigated, while NaBH₄ and
14
15
16 H₂ were compared as the reducing agents. Best performances in glycerol oxidation were attained
17
18
19 on supported single-phase Au–Pd nanoparticles prepared by two step procedure using H₂ as the
20
21
22 reductant. These catalysts proved to possess unique resistance to poisoning, being stable after 11
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

of gold content in the alloy composition, being the catalyst with Au/Pd ratio of 9:1 the most active

of the studied series (Figure 3). This 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, being in all cases glycerate the main product (70-80%) at 90% glycerol conversion.

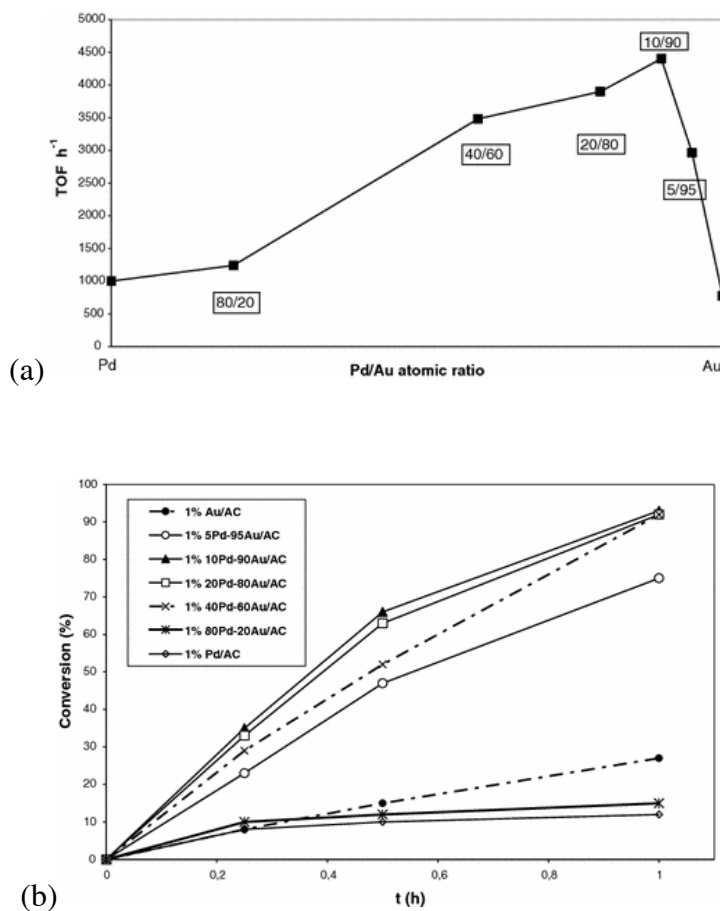


Figure 3. (a) TOFs of Au_xPd_y bimetallic catalysts in glycerol oxidation. (b) Reaction conditions:

glycerol 0.3 M, glycerol/NaOH = 4 mol/mol, glycerol/metal = 1000, pO₂ = 3 atm, T = 50 °C.

Reprinted with permission from Ref. ²⁶ Copyright 2007 Springer Nature.

1
2
3
4 More recently, bimetallic AuAg NPs supported on TiO₂ or Al₂O₃ were also investigated as
5
6
7 catalysts for glycerol oxidation.^{42,43} Important consideration has been given to the factors which
8
9
10 determine the activity and selectivity of these systems. For this purpose, preparation method (sol
11
12
13 immobilization, deposition-precipitation with urea and solvated metal atom dispersion – SMAD
14
15
16 methods), internal Au:Ag ratio (1:1 and 4:1) and post-synthesis treatment (drying, calcination in air
17
18
19 at 300°C, reduction at 550°C under H₂ flow) were varied. In general, metal exposure at the surface,
20
21
22
23 oxidation state of the metal and strong metal-support interactions arose as the main ruling factors.
24
25
26
27 Gold-enriched surfaces showed enhanced activity and improved stabilization of silver in the
28
29
30 reduced state. A different selectivity characterized bimetallic AuAg catalysts compared to
31
32
33 monometallic Au insofar as the former oxidize glycerol to tartronate to a larger extent.
34
35
36
37

38 *3.1.3. Effect of the reaction conditions*

39
40
41

42 The catalytic activity and selectivity of single-phase AuPd/AC catalyst with small particle size
43
44
45 (d=3.4 nm) were investigated as a function of reaction parameters.⁴⁴
46
47
48

49 The amount of catalyst and in particular the glycerol/metal ratio impacted on the mass transport
50
51
52 phenomena and on the product distribution. When glycerol/metal ratios between 13,000 and 3,500
53
54
55 were realized, it was demonstrated that the reaction proceeded in kinetic regime. Otherwise, minor
56
57
58
59
60

1
2
3 deviation from kinetic regime was observed for glycerol/metal ratios between 3,500 and 850
4
5
6 mol/mol. Additionally, a decrease in the glycerol/metal ratio had a detrimental effect in the product
7
8
9
10 distribution, with a reduced selectivity to glycerate. The reaction resulted to be of zero order with
11
12
13 respect to oxygen, since the oxygen pressure had no effect on the activity, which in turn was
14
15
16 affected by the amount of base. In particular, the activity was enhanced by the addition of a base
17
18
19
20 up to a threshold value of 2 mol/mol, after which any further addition of base produced negligible
21
22
23
24 improvement.

25
26
27
28 The selectivity was influenced by the oxygen pressure and base concentration: glycerate formation
29
30
31 was favored by high oxygen pressure and in the presence of a base.
32
33

34 35 36 *3.1.4. Insights on the complex role of the support* 37

38
39
40 As mentioned in the previous section, the support is essential to providing anchoring sites and
41
42
43 stabilization to metal nanoparticles. In many cases, the support also influences the catalytic
44
45
46 performance of the deposited metal nanoparticles through metal-support interactions. In addition,
47
48
49
50 the support can play an active role in the catalytic process, by intervening in some crucial steps
51
52
53 (cooperative catalysis).
54
55
56
57
58
59
60

1
2
3
4 Au-catalyzed oxidation of glycerol was studied as a function of the surface features of the support,
5
6
7 with particular emphasis on acid-base properties and hydrophilicity of carbon-based materials.
8
9

10 In some cases, the different surface functionalization is a consequence of the different source of
11
12
13 the carbon material. Three activated mesoporous carbon materials were prepared starting from the
14
15
16 waste fractions of saw industries namely birch, pine and spruce sawdust. The carbon materials
17
18
19 differed in terms of surface functionalities, being aromatic group predominant in Spruce-derived
20
21
22
23 carbons while the surface of Birch-derived carbon was enriched by carboxylic groups. The latter
24
25
26 had a beneficial effect on the catalytic performance of supported AuPt NPs in the glycerol
27
28
29
30 oxidation reaction.⁴⁵
31
32

33
34 More often, the nature and distribution of surface functionalities can be finely tuned by proper
35
36
37 post-synthesis functionalization treatment. In the case of carbon nanofibers (CNFs), oxygen-
38
39
40 containing acid functionalities were introduced through acid treatment with HNO₃. On the other
41
42
43 hand, basic N-groups were inserted on CNFs by heat treatment in the presence of ammonia. Gold-
44
45
46 based catalysts were prepared by sol immobilization or by impregnation on as-modified substrates.
47
48
49
50 The activity of the catalysts increased as the basic character of the support increased. The basic
51
52
53
54 functionalities of the support, in fact, promote dehydrogenation with formation of alkoxide and
55
56
57
58
59
60

1
2
3 the subsequent dissociation of the C – H bond. On the other hand, the hydrophobicity affected the
4
5
6
7 selectivity of the reaction, by increasing the quantity of C3 products from 65% to 82% to 90% as
8
9
10 hydrophobic character increased.⁴⁶ The improved selectivity to C3 could be related to suppressed
11
12
13 formation of H₂O₂, which was assumed to be involved in C - C bond cleavage reactions.⁴⁷ In
14
15
16
17 addition, the peculiar tubular morphology of N-CNFs offered two different locations for Au NPs:
18
19
20 inside or outside the N-CNF channel. A triggering confinement effect was then observed. Gold
21
22
23 nanoparticles located within N-functionalized carbon nanofibers showed higher activity in
24
25
26
27 glycerol oxidation and enhanced selectivity towards dicarboxylic acids. Conversely, C – C bond
28
29
30 cleavage seemed to be promoted on Au NPs deposited on the external surface of N-CNFs. ⁴⁸ A
31
32
33
34 similar confinement effect was observed for PdH_x entrapped in a Covalent Triazine Framework.⁴⁹
35
36
37 The presence of surface functionalities on the support can influence metal exposure, particle size
38
39
40 and shape. In some cases, these factors can have opposite effects on the catalytic performances. In
41
42
43
44 particular, it has been reported that the higher the content of O-functionalities the higher is the Au
45
46
47 exposure at the surface and the larger the metal particle size. These two effects have conflicting
48
49
50
51 consequences in the activity in glycerol oxidation. In fact, high metal exposure enhances catalytic
52
53
54
55
56
57
58
59
60

1
2
3 activity while the presence of large particles has a detrimental effect on the activity. Then the
4
5
6
7 outcome depends on the relative predominance of the two effects.⁵⁰
8
9

10
11 Alongside the possibility to introduce additional functional groups, in the case of carbon materials,
12
13
14 the selectivity in glycerol oxidation could be tuned also by changing the degree of surface
15
16
17 graphitization of carbon nanofibers. In fact, depending on the undergone heat treatment, CNF
18
19
20 exposed surface with different order of graphitic layers. The different graphitization degree did
21
22
23
24 not affect the Au particle size, but it influenced the shape of supported Au NPs, which is another
25
26
27 factor to consider except size for structure-activity relationships.⁵¹ Specifically, more ordered
28
29
30 graphitic surfaces favored a preferential immobilization of Au on their {111} plane (Figure 4).
31
32
33
34 Differently, a random orientation of supported particles was detected in the case of disordered
35
36
37 carbon nanofiber surfaces. The different facet exposure did not impact on the activity of Au NPs,
38
39
40
41 whereas the product distribution changed depending on the orientation of Au NPs. Specifically,
42
43
44 when bonded through their {111} planes, Au NPs exposed more facet area and this promoted the
45
46
47 occurrence of C – C bond cleavage, likely to a higher production of H₂O₂, resulting in an increased
48
49
50
51 amount of C1 and C2 products at the expense of C3 compounds.
52
53
54
55
56
57
58
59
60

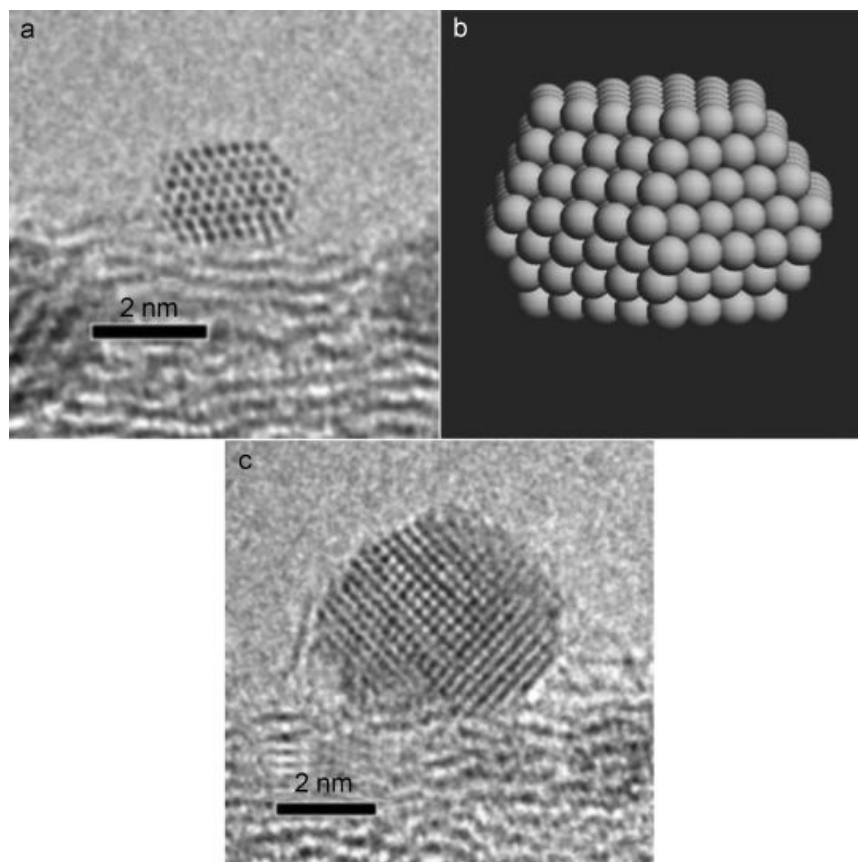


Figure 4. Aberration-corrected HRTEM images of Au particles supported on PR24-LHT. a) A representative 2–4 nm particle with (1 1 1) surface epitaxially parallel to the graphitic layer of CNF. b) Structure model derived from the image in part a. c) A larger particle with spherical shape showing carbon binding to the CNF surface. Reprinted with permission from Ref. ⁵¹ Copyright 2012 John Wiley and Sons.

1
2
3
4 The support can also influence the surface amount of metal. THPC-protected Au NPs immobilized
5
6
7 on the commercial weak base resin Dowex M-43 were characterized by a higher Au surface
8
9
10 concentration compared to Au/AC catalysts and thus the former resulted to be more active despite
11
12
13 it possessed larger particle sizes. Moreover, the intrinsic microporosity of Dowex M-43 might
14
15
16 facilitate the desorption of products, thus minimizing the occurrence of consecutive reactions.⁵²
17
18

19
20 Not just the shape and size of Au NPs, in many cases even their electronic structure can be affected
21
22
23 by metal-support interactions, in particular when metal oxides were used as supports. This was
24
25
26 clearly evident when nanostructured nickel oxide (nNiO) was used as support for Au nanoparticles
27
28
29 in comparison with TiO₂ and a of Au/NiO–TiO₂ catalysts with different relative ratio of NiO to
30
31
32 TiO₂.⁵³ Au/nNiO catalysts showed high activity in glycerol oxidation but low selectivity to
33
34
35 glycerate (55% selectivity at 90% conversion). The activity enhancement observed in the case of
36
37
38 Au/nNiO was ascribed to the strong metal-support interactions between Au NPs and the support,
39
40
41 as corroborated using CO as a probe molecule.
42
43
44
45
46

47 Beside mediating the interactions with deposited metal NPs, the surface properties of the supports
48
49
50 can be directly involved in the catalytic process and assist metal nanoparticles. The surface Al/Mg
51
52
53
54
55
56
57
58
59
60

1
2
3
4 ratio was a key factor, ruling the selectivity of Au/MgAl₂O₄ in glycerol oxidation, where Al-rich
5
6
7 surfaces promoted the dissociation of C–C bond.⁵⁴
8
9

10 Hence, the acid and basic features of supports can help in favoring the H abstraction and alkoxide
11
12
13 formation, thus allowing to avoid the addition of a base in the reaction medium, with remarkable
14
15
16 practical advantages in terms of costs and safety. Laura Prati and coworkers reported that by
17
18
19 alloying Au with Pt, it was possible to combine the main advantages of the two metal components
20
21
22 thus obtaining an active and selective catalyst even in the absence of a base, with additionally an
23
24
25 increased lifetime. However, the support as well greatly influenced the activity and the selectivity.
26
27
28
29

30 In particular using a zeolite, H-mordenite, as the support resulted in an enhanced activity compared
31
32
33 to activated carbon (99% and 62% after 6 h for 1%AuPt/H-mordenite and 1%AuPt/AC,
34
35
36 respectively).⁵⁵ Moreover, AuPt/H-mordenite exhibited a high selectivity (83%) to glyceric acid,
37
38
39 thus suppressing C–C cleavage and consequently the formation of C1 and C2 products. These
40
41
42 interesting results encouraged further studies on the effect of the support. Various metal oxides
43
44
45 exhibiting different number, nature and strength of acid and basic sites were comparatively tested
46
47
48 as support for AuPt-based catalysts in base-free glycerol oxidation.⁵⁶ At 80°C, high activity was
49
50
51 associated with Au NPs deposited on basic supports (MgO, NiO). However, a pronounced
52
53
54
55
56
57
58
59
60

1
2
3
4 occurrence of C–C bond cleavage reactions limited the selectivity of these catalysts. On the
5
6
7 contrary, the use of acidic supports (MCM41, SiO₂, H-mordenite and sulfated-ZrO₂) improved the
8
9
10 selectivity to C3 oxidation products. In addition, according to spectroscopic and microcalorimetric
11
12
13 analyses, a high number of acid sites (Brønsted sites or silanols) favoured the oxidation of
14
15
16 glycerinaldehyde to glyceric acid, which involved an acid catalyzed geminal diol formation and its
17
18
19 dehydrogenation to carboxylic acid.
20
21
22
23
24
25
26

27 *3.1.5. On the role of modifiers: the case of bismuth*

28
29
30

31 The addition of transition metals as modifiers to noble metal-based catalysts has been largely
32
33
34 studied and it is still debated in the literature.^{57–60} The introduction of promoters in platinum based
35
36
37 catalysts for glycerol oxidation had resulted in a remarkable increase of the catalytic activity and
38
39
40 a significant enhancement of the selectivity to DHA. In particular, according to the literature, the
41
42
43 best catalytic performances, in terms of activity and DHA yield, were exhibited by Pt-Bi system.
44
45
46
47

48 61
49
50
51

52 Starting from these considerations, Laura Prati and coworkers studied Bi-modified Au–Pd and
53
54
55 AuPt catalysts. In the former case, trimetallic AuPdBi catalysts were prepared according to two
56
57
58
59
60

1
2
3 different routes: immobilization of AuPd sol on Bi-loaded carbon support or post-immobilization
4
5
6
7 Bi-modification of supported AuPd NPs on carbon.⁶²
8
9

10
11 The introduction of Bi (0.1-3 wt.%) onto the support prior the immobilization of AuPd NPs did
12
13
14 not affect the final particle size; nevertheless, the presence of Bi hindered the growth of alloyed
15
16
17 nanoparticles with homogeneous composition. Conversely, the addition of Bi to preformed AuPd
18
19
20 NPs supported on carbon allowed to maintain the alloy composition. From a catalytic point of
21
22
23 view, the addition of Bi resulted in an enhanced production of tartronate (34% yield).⁶²
24
25
26
27
28

29 When Bi (0.1-1 wt.%) was added to AuPt/AC catalysts no modification of particle size and alloy
30
31
32 composition was observed. Interestingly the deposition of low Bi amount (0.1%) promoted
33
34
35 dihydroxyacetone formation (stable selectivity around 65% with the conversion) in the base-free
36
37
38 glycerol oxidation and suffered from limited leaching.⁶³ These promising results encouraged to
39
40
41 explore the performance of AuPtBi NPs supported on granular carbon in a continuous flow fixed
42
43
44 bed reactor under optimized reaction parameters (contact time, temperature and O₂ flow).
45
46
47
48 Although a maximum of selectivity to DHA (48.1%) was obtained, the catalyst underwent
49
50
51 significant structural modification after 80 h of time on stream.⁶⁴
52
53
54
55
56
57
58
59
60

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 protecting agent is an component that cannot be ignored. The primary goal of the protecting agent is providing stabilization to the metal sol before and during the immobilization on the support. In these stages, the protecting agents also mediates the interactions between metal nanoparticles and the supports, and it is in part responsible for particle size control and metal dispersion. The removal of the protecting agent can cause coarsening or tendency to leaching. The effect of the protective agent removal has been investigated by Laura Prati et al. by gradually removing PVA through washing with water at room temperature and at 60°C.⁶⁵ These studies demonstrated that the structural and textural properties of the support plays 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, residual amount of protecting agent remains in contact with metal nanoparticle surface. In these cases, a

1
2
3 direct influence on the catalytic performance may be expected. A shielding effect limiting surface
4
5
6
7 accessibility can be proposed at first, leading to a decreased activity. It has been well evidenced
8
9
10 by comparing the activity of gold nanoparticles (Au NPs), stabilized by polyvinylalcohol (PVA,
11
12
13 715 h⁻¹), tetrakis(hydroxypropyl)phosphonium chloride (THPC, 2478 h⁻¹), and citrate (160 h⁻¹).⁶⁶
14
15
16
17 However, often a more complex situation emerges, wherever the protecting agent establishes
18
19
20 positive electronic interactions with metal surfaces or mediates the interaction with the reagents
21
22
23 and products. Consequently, promotional effects as well as selectivity control could derive from
24
25
26
27 the presence of protecting agent. This appeared evident in the case of PVA-protected Au NPs
28
29
30 immobilized on TiO₂ and tested as catalysts in glycerol oxidation. In fact, the comparison of
31
32
33 catalytic performances of Au/TiO₂ prepared by sol immobilization and by deposition-precipitation
34
35
36
37 highlighted interesting difference in terms of activity and selectivity.⁶⁷ The presence of a protective
38
39
40 PVA layer lowered the activity, increased the stability and favored the formation of glycerate, by
41
42
43
44 suppressing C – C bond cleavage. According to FT-IR characterization, the unique selectivity of
45
46
47 PVA-protected Au NPs could derive from direct interaction between PVA and the glycerol
48
49
50 molecule which direct the adsorption configuration of the substrate (Figure 5).
51
52
53
54
55
56
57
58
59
60

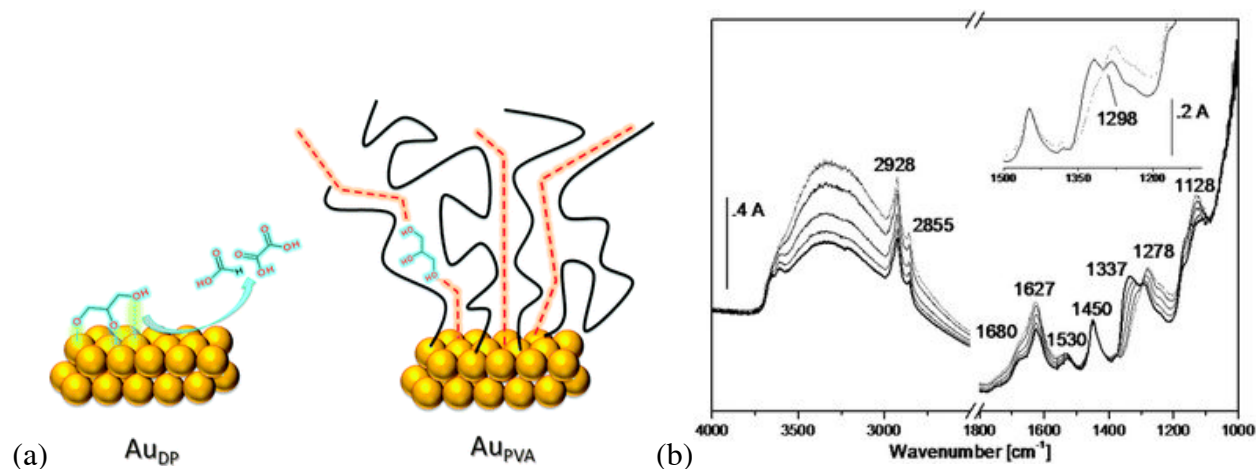


Figure 5. (a) Model for glycerol adsorption in the presence of PVA and on the free surface; (b)

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 r.t. Inset: 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 r.t. (30 min, solid curve). Reproduced with permissions, Copyright 2013

Royal Society of Chemistry from ref. ⁶⁷

3.2. Liquid phase oxidation of alcohols

Alcohol oxidation to carbonyl or carboxyl compounds represents a key-reaction in the modern

industrial chemistry. Consequently, the implementation of heterogeneously catalyzed processes,

which use atmospheric oxygen under mild conditions, is potentially attractive in a sustainability-

1
2
3 driven perspective. The design of effective heterogeneous catalysts plays a pivotal role in the
4
5
6 development of environmentally friendly approaches competitive with conventional oxidative
7
8
9 routes based on homogeneous catalysts or on stoichiometric oxidation processes, which make use
10
11
12 of toxic inorganic (Cr- and Mn-based compounds) or organic oxidants. Supported noble metals,
13
14
15 namely Pt and Pd NPs, are well-studied heterogeneous catalysts for the oxidation of alcohols,
16
17
18 although the above-mentioned drawbacks (overoxidation of substrates, deactivation) have limited
19
20
21 their practical application. With the aim to overcome these limitations, the acquired knowledge on
22
23
24 monometallic and bimetallic gold-based catalysts for the oxidation of diols and polyols was
25
26
27 successfully transferred by Laura Prati in the oxidation of alcohols and amino alcohols.^{68,69} Among
28
29
30 the numerous studied substrates, in the following the attention will be focused on the oxidation of
31
32
33 benzyl alcohol, cinnamyl alcohol, and long chain alcohols due to the relevance of these reactions
34
35
36 from academic as well as industrial point of view.
37
38
39
40
41
42
43
44

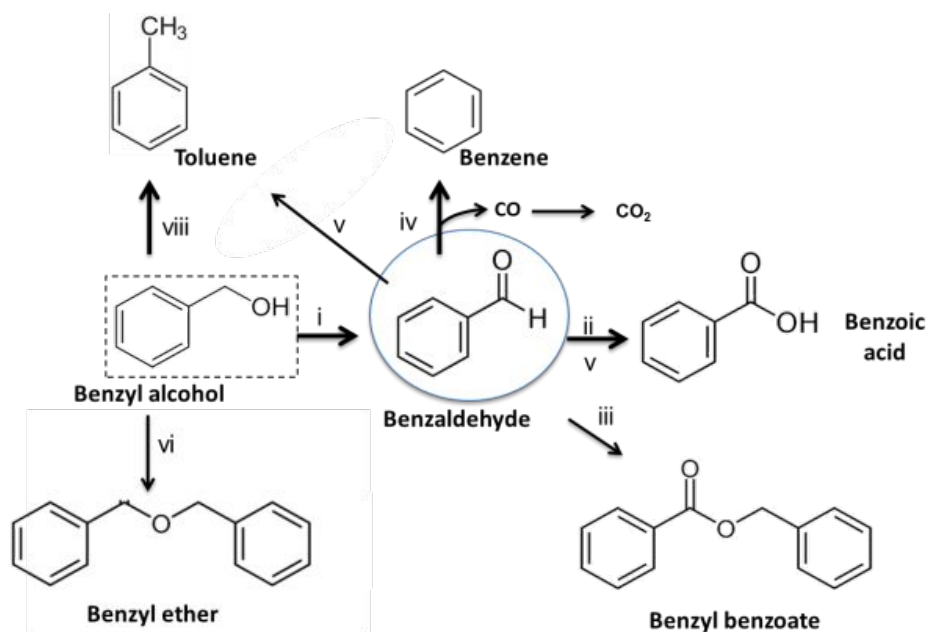
45 *3.2.1 Benzyl alcohol oxidation*

46
47
48

49 Benzyl alcohol is one of the most studied substrates for the selective aerobic oxidation of alcohols.
50
51
52 The activating effect of the aromatic ring facilitates the oxidation of the alcohol functionality, with
53
54
55
56
57
58
59
60

1
2
3 formation of benzaldehyde as the main product, while benzoic acid, toluene, benzyl benzoate, and
4
5
6
7 benzene are often observed as secondary products.
8
9

10
11 The industrial interest in the oxidation of benzyl alcohol is associated with the high market value
12
13
14 of these products, benzaldehyde in the first place, which is widely employed in food and cosmetic
15
16
17 industries as an additive for artificial bitter almond aroma. Additionally, benzyl alcohol oxidation
18
19
20 has become a benchmark reaction to assess the mechanism of alcohol oxidation on supported noble
21
22
23 metal nanoparticles. In fact, depending on the operative conditions and on the presence of specific
24
25
26 active sites, benzyl alcohol can undergo several reactions (Scheme X): (i) oxidative
27
28
29 dehydrogenation to benzaldehyde, (ii) oxidation to benzoic acid, (iii) formation of benzyl
30
31
32 benzoate, (iv) decarbonylation of benzaldehyde to benzene, (v) disproportionation to equimolar
33
34
35 toluene and benzoic acid, (vi) dehydration to dibenzylether, (vii) condensation (benzylation) to
36
37
38 anthracene and stilbene, and (viii) reduction of benzyl alcohol by metal hydride.
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



Scheme 2. Benzyl alcohol oxidation reaction network.

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) β -H elimination of the alkoxide to produce benzaldehyde (rate-determining step).

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

1
2
3 controversial. Two different reaction pathways have been proposed for toluene formation: 1) the
4
5
6
7 hydrogenolysis of benzyl alcohol by the hydride generated during the dehydrogenation of benzyl
8
9
10 alcohol to benzaldehyde or 2) the disproportionation reaction of benzyl alcohol. Benzoic acid
11
12
13 might be produced from benzaldehyde by direct oxidation in the presence of oxygen or by
14
15
16 hydration via a geminal diol, followed by a dehydrogenation or by the Cannizaro reaction in the
17
18
19 presence of basic sites on the support or by formation of a dioxy or carbonyloxyl intermediate. The
20
21
22 same carbonyloxyl intermediate has been proposed also to be a source of benzyl benzoate.
23
24
25
26
27

28 The study of the reaction mechanism and the optimization of product distribution in benzyl alcohol
29
30
31 oxidation has represented a central target for Laura's research in gold-based catalysis.
32
33
34

35 Initially, the catalytic performance of monometallic (Au, Pd, Pt) and bimetallic (AuPd and AuPt)
36
37
38 nanoparticles supported on activated carbon were compared in the conversion of benzyl alcohol
39
40
41 under mild conditions (benzyl alcohol 0.3 M, benzyl alcohol/metal 1/500 mol/mol, $T = 60^{\circ}\text{C}$, $p\text{O}_2$
42
43
44 = 1.5 atm) in two different solvents (toluene and water). In general, better performance were
45
46
47 observed in water than in toluene. In both solvents, monometallic Au/AC catalysts was not active,
48
49
50 while Pt/AC was more active than Pd/AC. The addition of Au to Pd had a promotional effect in
51
52
53 terms of activity, which was not evident in the case of bimetallic AuPt catalysts. This could be
54
55
56
57
58
59
60

1
2
3 explained by invoking a different interaction between geometrical and electronic effects in AuPd
4
5
6 and AuPt catalysts. It could be assumed that in the former catalyst, the two effects synergistically
7
8
9 converge resulting in an enhanced activity, while they negatively interfere in the case of AuPt
10
11
12 catalysts. The activity trend in toluene was AuPd/AC (54 h^{-1}) > 5% Pt/C > 1%Pt/AC = 0.4% Pt/AC
13
14
15
16
17 (30 h^{-1}) > AuPt/AC (15 h^{-1}) > 5%Pd/C = 1%Pd/AC = 0.3% Pd/AC (5 h^{-1}) > Au/AC (0 h^{-1}). A
18
19
20 similar trend was detected in water: AuPd/AC (160 h^{-1}) > 1%Pt/AC = 0.4% Pt/AC (98 h^{-1}) > 5%
21
22
23 Pt/C (72 h^{-1}) > AuPt/AC (55 h^{-1}) > 5%Pd/C = 1%Pd/AC = 0.3% Pd/AC (33 h^{-1}) > Au/AC (0 h^{-1}).⁷⁰
24
25
26
27

28 Noteworthy results were collected by experiments carried out on physically mixed Au/AC and
29
30
31 Pd/AC as catalysts for benzyl alcohol oxidation. By following the evolution of the physically
32
33
34 mixed catalyst structures at different stages of the catalytic reaction by aberration-corrected
35
36
37 HRTEM and spatially resolved element mapping techniques, it was possible to prove the *in situ*
38
39
40 formation of Au–Pd bimetallic active sites for the first time. These alloyed bimetallic systems were
41
42
43
44 formed by leaching of Pd cationic species and re-deposition on the surface of Au NPs.⁷¹
45
46
47

48 Considering the positive performance of AuPd/AC catalyst, further studies were carried out aimed
49
50
51 to disclose the effects of alloy composition and reaction parameters on catalytic activity and
52
53
54 selectivity in benzyl alcohol oxidation. According to TEM characterization and catalytic tests,
55
56
57
58
59
60

1
2
3 uniform alloyed bimetallic nanoparticles with high activity were obtained only in the range 90:10
4
5
6
7 to 60:40 of Au–Pd composition. The activity was enhanced by the addition of a base and the
8
9
10 positive effect was more pronounced the higher the gold content in the alloy composition. The
11
12
13 presence of a base improved also the durability of the catalysts, although a slight decrease in
14
15
16 benzaldehyde selectivity was observed. The latter inconvenience could be overpassed by
17
18
19 increasing the initial benzyl alcohol concentration. Optimal conditions were then identified for the
20
21
22 Au₆₀Pd₄₀/AC catalyst, for which an initial activity of 18,000 h⁻¹ with high selectivity to
23
24
25 benzaldehyde (S₉₀ = 89%) was achieved working with a biphasic system 1 M alcohol in
26
27
28 cyclohexane/1 M aqueous NaOH and 20,000 mol/mol benzyl alcohol/metal ratio.⁷²
29
30
31

32
33
34 Replacing activated carbon support by carbon nanotubes produced Pd and AuPd catalysts with
35
36
37 poor metal dispersion compared to analogous carbon supported catalysts. Although the non-
38
39
40 optimal metal dispersion caused a slight decline in the activity, this effect was compensated by a
41
42
43 high selectivity to benzaldehyde and an attenuation of metal leaching compared to Pd/AC and
44
45
46 AuPd/AC.⁷³ It followed from this that the support appeared as a key actor and a fine tuning of
47
48
49 surface features (functionalization degree, acid/base properties, hydrophobicity/hydrophilicity,
50
51
52 porosity) could allow to obtain catalysts with improved catalytic behavior. Therefore, the research
53
54
55
56
57
58
59
60

1
2
3 efforts of Laura Prati's team were focused on identifying the role of surface functionalization of
4
5
6
7 carbon-based supports in the activity of noble metal catalysts. One interesting approach to the
8
9
10 modification of support surface properties consisted in the introduction of O-functionalities or
11
12
13 Lewis base-type N heteroatoms.
14
15

16
17
18 The hydrophilicity of carbon nanotube surfaces was tuned by introducing O-functionalities
19
20
21 through treatment by nitric acid-sulphuric mixtures with different volume-ratio (3:1, 1:1 and 1:3,
22
23
24 respectively). The effects on benzyl alcohol oxidation were studied in two different solvents, water
25
26
27 and cyclohexane. In cyclohexane the hydrophilicity of the surface had a direct impact only on the
28
29
30 activity, while the selectivity was unaltered (in all cases toluene was the main byproduct). A more
31
32
33 hydrophobic surface facilitates the accessibility of surface active sites to a hydrophobic substrate,
34
35
36 such as benzyl alcohol, resulting in an improved activity. A different scenario was depicted in
37
38
39 water, where a triphasic system was generated. In this case hydrophilic surfaces assured high
40
41
42 activity and at the same suppressed the toluene formation.⁷⁴ Hydrophilicity of carbon support could
43
44
45 be modulated also by introducing N-functionalities. The introduction of N heteroatoms at the
46
47
48 surface of carbon-based support can be pursued according to several strategies, which differ from
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 functional form (pyridinic-N, pyrrolic-N, pyridone-N, quaternary-N, amino groups, nitro groups),
4
5
6
7 location, interaction strength and type of connectivity of the N-species on the surface.⁷⁵
8
9

10
11 The treatment of commercial carbon nanotubes (CNTs) and carbon nanofibers (CNFs) with NH₃
12
13
14 at different temperatures (200, 400 and 600°C) produced N-containing groups which enhanced
15
16
17 surface basicity and surface hydrophobicity. Basicity and hydrophobicity increased with the
18
19
20 increasing temperature of the thermal treatment. When N-modified carbon materials were used as
21
22
23 supports for Au NPs, different catalysts were obtained, whose activity and selectivity in base-free
24
25
26 benzyl alcohol oxidation depended on the surface properties of the support. In particular the
27
28
29 activity was enhanced significantly by an increase in the basicity and hydrophobicity of the
30
31
32 support, while the selectivity to benzaldehyde decreased as a consequence of the favored
33
34
35 consecutive oxidation to benzoic acid.⁴⁶
36
37
38
39

40
41 The effect of N-functionalities depended also on the number of N-groups and on their location.
42
43
44 When covalent triazine frameworks (CTF) were used as support for Pd NPs, the higher number (9
45
46
47 at.%) and the nature of N-groups in the CTF conferred better stability and dispersion to Pd NPs
48
49
50 than those created on carbon nanotubes (2 at.%) by NH₃/high-temperature treatment.⁷⁶ A more
51
52
53 pronounced effect was observed when another polymeric carbon–nitrogen material, i.e. carbon
54
55
56
57
58
59
60

1
2
3
4 nitride (C_3N_4) materials with nitrogen content up to 58 at.% was used as support. In this case the
5
6
7 promoting effect did derive from the increased Lewis basicity, but most probably from a more
8
9
10 relevant coordination of Pd NPs on N groups.⁷⁷ On the other hand, the simple presence of N-
11
12
13 groups coordinating the Pd active centers cannot be considered the sole factor determining the
14
15
16 enhanced activity of these systems. Actually, N-groups should be near to the Pd active sites to
17
18
19 strongly interact with them but without limiting their accessibility. Thus, the coordination of
20
21
22 polyvinylpyrrolidone to Pd NPs through the pyrrolic groups resulted in a shielding effect with
23
24
25 detrimental consequences in terms of activity. On the contrary the presence of pyridine molecules,
26
27
28 weakly bound to the carbon surface in the close proximity of Pd sites, did not impart enough
29
30
31 stability and activity enhancement.⁷⁸ However, in some cases, a strong interaction between the
32
33
34 functional groups of the protecting agent and specific sites on the surface of Pd NPs, could have a
35
36
37 positive effect in terms of selectivity, despite its detrimental influence on the activity. This is the
38
39
40 case of PVA-protected Pd NPs, where the selectivity to benzaldehyde benefited from the specific
41
42
43 interactions of PVA with Pd(111) facets, which were active in the decarbonylation process of
44
45
46 benzaldehyde during benzyl alcohol dehydrogenation.⁷⁹
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 Beside carbon-based materials, also metal oxides were studied as supports for metal nanoparticles
4
5
6
7 to be used as catalysts in benzyl alcohol oxidation. In particular, nanometric nickel oxide (nNiO)
8
9
10 demonstrated to boost the activity of supported Au NPs in the base-free liquid phase oxidation of
11
12
13 benzyl alcohol. The unique performances of Au/nNiO could be ascribed to compared to the
14
15
16 improved basic properties of the support and to cooperative effects between Au NPs and the
17
18
19 supports which strongly modified the electronic properties of Au.⁸⁰ More recently, carbon-
20
21
22 supported hybrid Au/CuO with core-shell hetero structure demonstrated to be effective catalysts
23
24
25 in the benzyl alcohol oxidation. In particular, high activity was observed when CuO shell just
26
27
28 partially covered the Au-rich core.⁸¹ Synergistic effects between Au and Cu and Au and Pd in
29
30
31 bimetallic AuCu and AuPd nanoparticles supported on carbon and Al₂O₃ produced effective
32
33
34 catalysts in the oxidation of methoxy substituted benzyl alcohols, studied as model substrates for
35
36
37 lignin degradation products.^{82,83}

38
39
40
41
42
43 Transition metal carbides (Mo and W carbides) have been also studied as less expensive alternative
44
45
46 to noble metal catalysts for benzyl alcohol oxidation showing a new and sustainable direction for
47
48
49 minimizing the use of noble metals.⁸⁴
50
51
52
53
54
55
56
57
58
59
60

3.2.2. *Cinnamyl alcohol oxidation*

The target product of cinnamyl alcohol is cinnaldehyde, an interesting chemical that can find industrial application as flavorant, insecticide and corrosion inhibitor. However, similarly to benzyl alcohol, also cinnamyl alcohol 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 immobilisation 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 immobilisation was sensitive to the reaction solvent.⁷⁰ In particular higher activity was observed in water than in toluene or acetonitrile. When tested under similar conditions (cinnamyl alcohol 0.3 M, cinnamyl alcohol/metal molar ratio 1/500, T = 60 °C, pO₂ = 1.5 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⁻¹, respectively), which maintained constant even at low loading (ca. 0.4 wt.%). Interestingly, bimetallic AuPd/C catalyst was more active than monometallic counterparts, while alloying Au to Pt had a negative effect on the activity, which dropped from 67 h⁻¹ (Pt/AC) to 45h⁻¹

1
2
3
4 (1% AuPt/AC), along the same trend as outlined above for benzyl alcohol. The activity of
5
6
7 bimetallic AuPd/AC catalysts depended on the catalyst composition and specifically on the Au:Pd
8
9
10 molar ratio.⁷² Highest activity (630 h⁻¹) was obtained on the catalysts having an Au:Pd molar ratio
11
12
13 of 8:2. A significant enhancement of the catalytic activity, specifically on monometallic Au/AC
14
15
16 catalyst, was observed when the reaction was carried out in the presence of a basic environment (
17
18
19 1 equiv. NaOH).⁷² Alternatively, the activity of Pd-based catalysts could be improved by
20
21
22 introducing N-containing functionalities, in particular pyridinic nitrogen species, in the carbon
23
24
25
26
27 support.⁸⁵
28
29
30

31 The selectivity of the reaction was not influenced by the solvent, while it strongly depended on the
32
33
34 pH and on the internal composition in the case of bimetallic AuPd/AC catalysts. The selectivity
35
36
37 to cinnamaldehyde increased by increasing the catalyst gold content (selectivity of 80% to
38
39
40 cinnamaldehyde was attained on 1% Au/AC and in Au₉₀Pd₁₀/AC catalysts), while palladium-rich
41
42
43
44 catalysts promoted the hydrogen transfer and the consequent 3-phenyl-propanol production (up to
45
46
47 28% selectivity to 3-P-P in the case of Pd/AC). In all cases, the selectivity was negatively affected
48
49
50
51 by the addition of base, due to the preferential occurrence of overoxidation of cinnamaldehyde to
52
53
54
55
56
57
58
59
60

1
2
3
4 carboxylates (ester or acid), which was more pronounced in gold-rich compositions and in
5
6
7 monometallic Au/AC catalyst (63% selectivity to acid/ester).
8
9

10 11 *3.2.3. Long chain alcohol oxidation* 12 13

14
15 It is reasonable to expect the activity of Au-based catalysts to be very sensitive to the nature and
16
17
18 structure of the substrate. For example, compared to benzyl alcohol and cinnamyl alcohol or to
19
20
21 diols, aliphatic alcohols have no electronic activation and that should impact on the reactivity of
22
23
24 these compounds. In fact, small simple alcohols (butanol and propanol) were converted quite
25
26
27 slowly over Au/AC catalyst under typical conditions ([alcohol] = 0.35 M; alcohol/M = 1000
28
29
30 (mol/mol); NaOH = 1 eq; pO₂ = 3 atm; T= 70°C). In particular, a more pronounced tendency to
31
32
33 deactivate was observed when propanol was used as the substrate.⁸⁶ The reactivity of aliphatic
34
35
36 alcohols under oxidative conditions usually decreases by increasing the chain length. On the other
37
38
39 hand, the oxidation of aliphatic alcohols with a long linear chain produces aldehydes (e.g.
40
41
42 n-octanal, n-capraldehyde) with pleasing olfactive features, which are the reason of their
43
44
45 applications in the industrial production of perfumes and essences. Although these aldehydes can
46
47
48
49 be sourced from natural products (i.e. essential oils and fruits), the development of synthetic routes
50
51
52
53 is required to satisfy a continuously rising market demand. Unfortunately, monometallic (Au, Pd
54
55
56
57
58
59
60

1
2
3 and Pt) and bimetallic AuPt and AuPd on carbon catalysts were characterized by poor activity
4
5
6 (<12% conversion) when toluene or water were used as the solvent (1-octanol 0.3 M, 1-
7
8
9
10 octanol/metal 1/500 mol/mol, T = 60°C, pO₂ = 1.5 atm). In addition, low selectivity (ca. 30%) to
11
12
13 1-octanal was observed in water, being acid and ester the main by-products. The deactivating effect
14
15
16 deriving from the formation of carboxylic species, which strongly adsorb on catalyst surface, is
17
18
19 one of the main causes of the poor catalytic activity in water, together with the limited contact
20
21
22 between active sites and substrate of the four-phase system. From this point of view, the
23
24
25 introduction of basic conditions had a positive effect on the catalytic behavior of Au-based
26
27
28 catalysts with a 20-fold increase in the activity values. The beneficial role of the base may be
29
30
31 ascribed to the minimization of deactivation phenomena because of the formation of carboxylates,
32
33
34
35
36
37 which easily desorb from catalyst surface.
38
39
40

41 Among noble metals, supported Ru NPs had demonstrated to be promising and active catalysts for
42
43
44 octanol oxidation. Bimetallic AuRu nanoparticles were then deposited on activated carbon and
45
46
47 tested as catalysts in octanol oxidation. Unfortunately, the presence of Au had a detrimental effect
48
49
50 on the activity of AuRu bimetallic catalysts. However, when a physical mixture Au/AC and Ru/AC
51
52
53
54
55 was tested an unexpected enhancement of the activity was observed compared to the monometallic
56
57
58
59
60

1
2
3 Ru/AC catalyst.⁸⁷ This peculiar behaviour could be ascribed to the leaching of Ru and successive
4
5
6 deposition on Au NPs, as already observed for Au/AC and Pd/AC mixtures.⁷¹
7
8
9

10
11 Monometallic Ru/AC, Pt/AC, Au/AC and bimetallic AuRu/AC and AuPt/AC catalysts were tested
12
13
14 in the oxidation of 1-octanol, 1-decanol, and 1-dodecanol using toluene as solvent (0.6 M,
15
16
17 metal/alcohol ratio 1/100 mol/mol, T = 100 °C, p(O₂) = 2 kPa).⁸⁸ The substrate reactivity was
18
19
20
21 in inverse proportion to the length of the chain, since it decreased from C₈ to C₁₂. In the case of
22
23
24 1-octanol, the activity of monometallic catalysts increased in the order: Au/AC (0 h⁻¹) < Ru/AC
25
26
27 (114 h⁻¹) < Pt/AC (141 h⁻¹). On the contrary Ru/AC was more active than Pt/AC in the oxidation
28
29
30
31 of 1-decanol (84 vs. 68 h⁻¹, respectively) and 1-dodecanol (65 and 46 h⁻¹) in the C₁₂ oxidation,
32
33
34 respectively. Aldehydes were the main products in the case of Ru/AC (selectivity values >95%),
35
36
37 whereas carboxylic acids and esters were formed on Pt/AC catalysts (up to 54% selectivity to acid
38
39
40 in the case of dodecanol oxidation). Bimetallic catalysts were less active but more durable than the
41
42
43 monometallic Ru/AC and Pt/AC. The addition of Au to Ru did not alter the selectivity, whereas
44
45
46 when added to Pt, Au promoted the formation of esters. The activity of the tested catalysts could
47
48
49 be improved by using water-dioxane mixture as the solvent, even if in this case acid was
50
51
52 preferentially formed at the expense of the aldehyde.
53
54
55
56
57
58
59
60

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 particularly relevant in the field of biomass transformation, due to the high oxygen content present in the biomass which has to 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 Prof. Prati 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 Au was beginning to be investigated as catalyst for the liquid phase hydrogenation of various molecules.⁸⁹⁻⁹⁰ Before, indeed, gold has shown a more attractive behaviour in the liquid phase oxidation, showing high resistance to deactivation compared to classical Pd or Pt catalysts⁹¹, while

1
2
3
4 in hydrogen mediated reactions it had shown low catalytic activity generally attributed to the less
5
6
7 effective activation/dissociation of dihydrogen.⁹² However, the selectivity and stability of
8
9
10 supported gold continued to be higher than other metals,⁹³ as well gold based bimetallic systems
11
12
13 showed a great enhancement in their activity also in hydrogenations. For example, the addition of
14
15
16 Au to Pd, or Ru results in a great improvement in the catalytic activity and selectivity in the
17
18
19 hydrogenation of cinnamaldehyde and glycerol.⁹⁴
20
21
22
23

24 Laura focused first on the impact of AuRu nanoparticle structure in the
25
26
27 hydrogenation/hydrogenolysis of two important compounds deriving from biomass, namely
28
29
30 glycerol and levulinic acid.⁹⁵ Hydrogenolysis of glycerol can produce 1,2- and 1,3-propanediols,
31
32
33
34 lactic acid as well as different alcohols which are all important chemicals, while from levulinic
35
36
37 acid the main product is gamma valerolactone (GVL) that can be transformed in pentanediol or
38
39
40 pentanoic acid, both useful additives in biofuels.⁹⁶ Ru catalysts showed a high deactivation in the
41
42
43 glycerol or levulinic acid hydrogenolysis, while a possible solution could be the addition of Au, as
44
45
46 already reported in the oxidation of glycerol and aliphatic alcohols.⁹⁷ AuRu bimetallic catalysts
47
48
49 have been prepared by sequential deposition of Au on Ru or vice versa on activated carbon (AC),
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 obtaining different nanostructures, i.e. Au_{core}-Ru_{shell} or a bimetallic phase with Ru enrichment on
5
6
7 the surface.
8
9

10
11 One of the most important findings was that the selectivity and the stability depend on the structure
12
13
14 of the bimetallic nanoparticles, where Ru@Au/AC core-shell structure mostly behaved as the
15
16
17 monometallic Ru, whereas the presence of bimetallic AuRu phase in Au@Ru/AC provides a great
18
19
20 beneficial effect on both activity and stability. The synergistic effect showed by the Au@Ru/AC
21
22
23 was showed also in terms of durability: recycling experiments showed that Au@Ru/AC reached
24
25
26
27
28 the same substrate conversion after 6 runs with stable selectivity.
29
30

31
32 More recently, she was involved in a study on Au-Pd supported on carbon catalysts for furfural
33
34
35 hydrogenation.⁹⁸
36
37
38
39

40 Precisely she investigated the effect of the carbon support modification with butyl, carboxyl and
41
42
43 amino groups using corresponding diazonium salts. The results showed a crucial influence of
44
45
46 surface chemistry on the catalytic behavior of the catalysts, especially regarding selectivity.
47
48
49

50 Indeed, the modification of carbon with various functional groups leads to changes in the
51
52
53 hydrophobic/hydrophilic and/or electrostatic properties of the surface, which influenced the
54
55
56
57
58
59
60

1
2
3
4 selectivity of the process. The core idea was to show that the catalytic behavior (activity and
5
6
7 selectivity) of furfural hydrogenation catalysts can be influenced not only by changing the reaction
8
9
10 parameters or the content of supported metals, but also by changing the surface chemistry of the
11
12
13 support if all other conditions are kept equal.
14
15

16 17 18 **4.2 Support effect in hydrogenation reactions** 19 20

21
22 The support can be in fact very important to determine the activity, selectivity and stability of a
23
24
25 catalyst. To limit the deactivation often showed by monometallic Ru, Laura investigated also the
26
27
28 use of ordered mesoporous carbons (OMCs) as support.⁹⁹ P- and S-containing acid groups were
29
30
31 introduced by post-synthetic functionalization before the addition of 1% Ru. As result, it was found
32
33
34 that the functionalities mediate the activity and selectivity of the levulinic acid hydrogenation. In
35
36
37 particular, the presence of S-containing groups deactivated the Ru catalysts, whereas the presence
38
39
40 of P-containing groups (Ru/OMC-P) enhances the activity compared to that of pristine Ru/OMC.
41
42
43
44
45 At 70 °C and 7 bar of H₂ the Ru/OMC-P catalyst showed a selectivity to GVL > 95 % and high
46
47
48 stability on recycling. Changing the reaction conditions to 200 °C and 40 bar of H₂ this catalyst
49
50
51 was also able to promote the GVL ring-opening and the consecutive hydrogenation to pentanoic
52
53
54
55
56 acid.
57
58
59
60

1
2
3
4 Using the same substrate (levulinic acid) she investigated also other metal species, such as
5
6
7 iridium.¹⁰⁰ Ir-based catalysts had been poorly investigated in this reaction with only few reports
8
9
10 on Ir/SiO₂ which showed low activity and selectivity, however soluble Ir complexes had been
11
12
13 reported to show a good activity in levulinic hydrogenation.¹⁰¹⁻¹⁰² Laura investigated the use of
14
15
16 TiO₂ as support, supposing that a reducible oxide would have helped the activity of supported Ir,
17
18
19 but also the influence of Au.
20
21
22
23

24 Comparing the activity of Ir/TiO₂, Ru/TiO₂ and bimetallic catalysts Au-Ir/TiO₂ and Au-Ru/TiO₂
25
26
27 in the levulinic acid hydrogenation, it was found that the monometallic Ir was the most active
28
29
30 catalyst, even more than Ru. However, differently from the case of depositing Au on Ru, when
31
32
33 depositing Au on Ir catalysts a segregation of Ir atoms toward the TiO₂ surface occurred. As result,
34
35
36 the two catalysts showed a very different catalytic behaviour, where the addition of Au to Ir/TiO₂
37
38
39 led to a drastic drop of the activity (12% of levulinic acid conversion after 6 h of reaction). A pre-
40
41
42 treatment of the catalyst with H₂ increased the conversion up to 38% but it was always lower than
43
44
45 the activity of Ir/TiO₂ (>99%). In this work Laura Prati et al. demonstrated that Ir provided a
46
47
48 stronger metal-support interaction with TiO₂ compared to Ru, which was beneficial for the
49
50
51 stabilization of the metals onto the support.
52
53
54
55
56
57
58
59
60

1
2
3
4 Studying the role of the support is a characterizing part of Laura's research in catalysis. After the
5
6
7 work on levulinic acid hydrogenation with Ir-based catalysts, she focused her attention on Pt-based
8
9
10 catalysts, with particular interest in the role of support.¹⁰³⁻¹⁰⁴ She studied the impact of the acidity
11
12
13 of support oxide in Pt-catalysed HMF hydrogenation,¹⁰³ as well as the role played by support acid
14
15
16 sites in Pt-catalysed glycerol hydrogenation.¹⁰⁴
17
18
19

20
21 In the case of the catalytic hydrogenolysis of glycerol to diols and alcohols,¹⁰⁴ she investigated the
22
23
24 activity of bimetallic AuPt NPs supported on acidic (TiO₂, H-Mordenite, SiO₂, MCM-41,
25
26
27 sulphated ZrO₂) and basic (MgO) oxide supports. The activity and the selectivity were
28
29
30 significantly influenced by the acid base properties of the support. The AuPt/TiO₂ showed an
31
32
33 activity higher than AuPt/MgO and the other acidic oxides. Differently from the others, this
34
35
36 catalyst showed almost exclusively Lewis sites. No Lewis and Brønsted acidity were observed in
37
38
39 the case of AuPt/MCM-41 and AuPt/SiO₂, both Lewis and Brønsted acid sites were observed on
40
41
42 AuPt/S-ZrO₂, while AuPt/H-Mordenite showed almost exclusively Brønsted acidity. Considering
43
44
45 that the activity followed the order AuPt/TiO₂ > AuPt/MCM41 ≥ AuPt/SiO₂ > AuPt/H-Mordenite
46
47
48 > AuPt/S-ZrO₂, it was supposed that the presence of Lewis acid sites is crucial for achieving good
49
50
51 catalytic performances, but the higher the strength of the acidic sites, the lower the activity. Thus,
52
53
54
55
56
57
58
59
60

1
2
3 the nature of the acidic sites plays an important role, that can be extended also to the selectivity,
4
5
6
7 where the intermediate acidic character of TiO_2 led to an improved selectivity towards 1,2-PD.
8
9

10
11 In the case of HMF hydrogenation, silica and three mixed silica oxides, i.e. silica–alumina, silica–
12
13
14 niobia, and silica–zirconia (5 wt% of Al, Nb and Zr respectively) were used as supports for Pt NPs.
15
16

17
18 The presence of the second oxide component changed the acidity of the samples: in particular, the
19
20
21 Nb/SiO₂ showed a higher acidity in alcohol than that measured in cyclohexane, due to the presence
22
23
24 of Lewis acid sites at the surface. Also in this case, the acidic strength of the catalytic surface had
25
26
27 relevant consequences in the activity and selectivity of the reaction. Moreover, the introduction of
28
29
30 Pt nanoparticles modified the surface properties of the bare oxide support: in that case the catalyst
31
32
33 behaved as bi-functional material and a different product distribution has been obtained. The
34
35
36 results gave indication for the preparation of optimized catalysts for the hydrogenolysis of HMF,
37
38
39 which follows various pathways depending on the support acidity besides the activity of the metal
40
41
42 phase. Niobia-supported Pt nanoparticles was also applied in the hydrogenation of furfural, but in
43
44
45 this case modifications in the surface acidity of the support have been obtained by the incorporation
46
47
48 of W^{6+} (increasing Lewis acid sites) and Ti^{4+} (decreasing Lewis acid sites) as dopants in the Nb_2O_5
49
50
51 structure.¹⁰⁵ The catalytic activity towards the hydrogenation of furfural was higher when the
52
53
54
55
56
57
58
59
60

sample showed high surface acidity; in the opposite case, i.e. decreasing the Lewis acid sites, the activity was lower but the selectivity towards furfuryl alcohol increased (Figure 6).

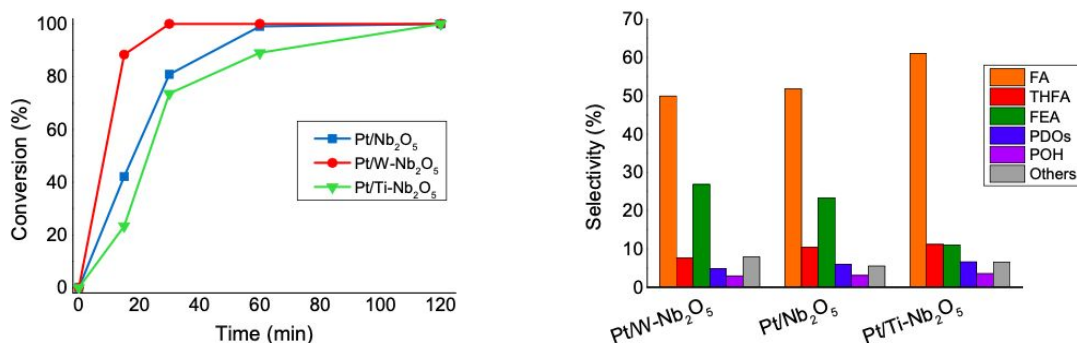


Figure 6. Furfural hydrogenation with different Nb₂O₅ catalysts and product distribution at 90% conversion.

As conclusion the experimental research from Laura proved that Niobia represents an acidic support which can be fruitfully used as supporting material for Pt nanoparticles in hydrogenation reactions, creating 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

Proved 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 Pt derived

1
2
3
4 from its modification. Indeed, the major issue related to the use of Pt that should be considered is
5
6
7 the high market price. Transition metals are available and cheap, and among them Mo in the form
8
9
10 of MoO_3 showed a promoting effect on the hydrogenation activity.¹⁰⁶ Bimetallic structures
11
12
13 consisting of Mo and Pt already showed higher activity than monometallic ones in hydrogenolysis
14
15
16 of alkanes¹⁰⁷ and dehydrogenation of cyclohexane.¹⁰⁸ Therefore, Laura investigated the properties
17
18
19 of a new Mo-supported on activated carbon (AC) as support for Pt NPs.¹⁰⁹
20
21
22

23
24 Mo-supported AC was prepared by incipient-wetness impregnation method using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$
25
26
27 as metal precursor to have a loading of 40 wt.% Mo. Pt nanoparticles were then supported on the
28
29
30
31 40%Mo@AC by impregnation.
32
33

34
35 Mo supported on activated carbon is active in furfural hydrogenation, which was addressed to the
36
37
38 presence of Mo_4O_{11} orthorhombic phase. The addition of Pt to Mo/AC enhances the activity, which
39
40
41 was higher than that of the reference Pt-AC. From structural/morphological analyses, it was found
42
43
44 that Pt nanoparticles supported on Mo-AC have particle size distribution between 1nm and 3nm
45
46
47 smaller than Pt/AC and more homogeneously dispersed, thus explaining the higher catalytic
48
49
50 activity of the Pt/Mo system with respect to Pt/AC. Moreover, this Mo_4O_{11} orthorhombic phase
51
52
53 could have a central role interacting with Pt and promoting hydrogen spill over. As conclusion,
54
55
56
57
58
59
60

1
2
3
4 Mo-supported on activated carbon is a promising material either as precious metal free-catalyst,
5
6
7 or as support, improving Pt nanoparticles distribution and the final catalytic activity in furfural
8
9
10 hydrogenation.

11
12
13
14 Continuing this research line, novel Mo-Pt bimetallic catalysts have been synthesized from two
15
16
17 different molybdenum precursors, i.e., Na_2MoO_4 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$. Indeed, Mo-based catalysts
18
19
20 synthesized by different approaches have been shown to present different activities, that is not a
21
22
23 novelty in heterogeneous catalysis, but the reason remains still unclear. The effect of the two Mo
24
25
26 salt precursors in this case was studied based on the catalytic activity showed by the two catalysts
27
28
29 in the selective hydrogenation of cinnamaldehyde.¹¹⁰ Hydrogenation of α,β -unsaturated aldehydes
30
31
32 to the corresponding unsaturated alcohols is often studied as a model reaction for discriminating
33
34
35 the catalytic selectivity for C=C or C=O hydrogenation. Overall, the hydrogenation and
36
37
38 hydrodeoxygenation of aldehydes are important industrial processes to produce a wide range of
39
40
41 chemicals,¹¹¹ as well as aldehydes can be found in several biomass-derived feedstocks. Thus, the
42
43
44 conversion of aldehydes is playing a crucial role, as the valuing of biomass-derived compounds is
45
46
47 a critical step toward the replacement of fossil fuel as source of chemicals. This is another
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 important chapter of Laura Prati's research, which will be reported as conclusion of this
4
5
6
7 manuscript.
8
9

10
11 Concerning Pt-Mo supported on carbon catalysts, characterization by means of TEM analysis
12
13
14 showed very homogeneously dispersed Pt NPs only when they were deposited on the heat-treated
15
16
17 Mo/C supports.
18
19

20
21
22 Moreover, Mo precursors direct the functionalization of C during the calcination step and form a
23
24
25 different ratio of MoO₂ and MoO₃. These different species have a different impact in the dispersion
26
27
28 of Pt and in its final oxidation state, which in turn modify the catalytic activity. On the other hand,
29
30
31 the explanation of the different selectivity was found in a different acidity, which played a decisive
32
33
34 role in the hydrogenation rates of C=C/C=O. The sample prepared from (NH₄)₆Mo₇O₂₄ has
35
36
37 stronger acid sites compared to that synthesized from Na₂MoO₄; such decrease in acidity resulted
38
39
40 in greater electron density on the metal particles,¹¹² which may cause a suppression in the C=C
41
42
43 hydrogenation by enhancing the delocalization of electrons in the adsorbed conjugated substrate.
44
45
46 On the contrary, a more acidic Pt catalyst has poorer electron density, which reduces the electron
47
48
49 repulsion related to the C=C adsorption, favouring the formation of hydrocinnamaldehyde.¹¹³
50
51
52
53
54
55
56
57
58
59
60

4.2.2. Support modification in carbon-based catalysts

After the study of Pt as active metal, she studied ruthenium-based catalysts. In this case, one of the initial target was the investigation of the possible role of different carbonaceous supports.¹¹⁴

Carbons from second generation biomass as sustainable supports for catalytic systems were in fact another crucial step of Laura's research.¹¹⁵ For example, she studied the properties of activated carbons produced from wood using different wood species, as supports for AuPt 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, ¹¹⁴ Ru was supported on activated carbon (AC) and carbon nanofibers (CNFs) for the selective production of liquid fuel dimethylfuran (DMF) and fuel additives alkoxymethyl furfurals (AMF): simply by using a different support, the selectivity of the reaction drastically changed, where DMF was produced with AC as support, while a high amount of AMF was produced using CNFs.

As next step carbon nanofibers (CNFs) have been functionalized by introducing O, N, and P containing groups to investigate the effect of support functionalization.¹¹⁶ Ru was once again used as active metal species, and the HMF and levulinic acid (LA) hydrogenation were studied as

1
2
3 model reactions. In the case of LA, despite all the catalysts produced selectively gamma-
4
5
6
7 valerolactone (GVL), the functionalization strongly affected the activity of the reaction, where O-
8
9
10 containing and N-containing supports showed higher activity than the bare support. On the
11
12
13 contrary, in HMF hydrogenation, functionalization had a detrimental effect on the activity and
14
15
16 changed the selectivity increasing the production of ethers. CNFs-N appeared as the best support
17
18
19
20 in the Ru-catalysed LA hydrogenation in water, not only due to the higher hydrophilicity of the
21
22
23 support but also to the strong interaction of N-groups with Ru particles.
24
25
26
27

28 Then, to overcome some limitations such as deactivation coming from Ru leaching and particles
29
30
31 aggregation, Laura worked with Ru supported on activated (Ru/AC) or mesoporous carbon
32
33
34 (Ru/MC), to see if the spatial restriction on metal nanoparticles could limit aggregation reducing
35
36
37 performance losses.¹¹⁷ In fact, electron tomography characterization showed preferential Ru
38
39
40
41 location depending on the material porosity (Figure 7).
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

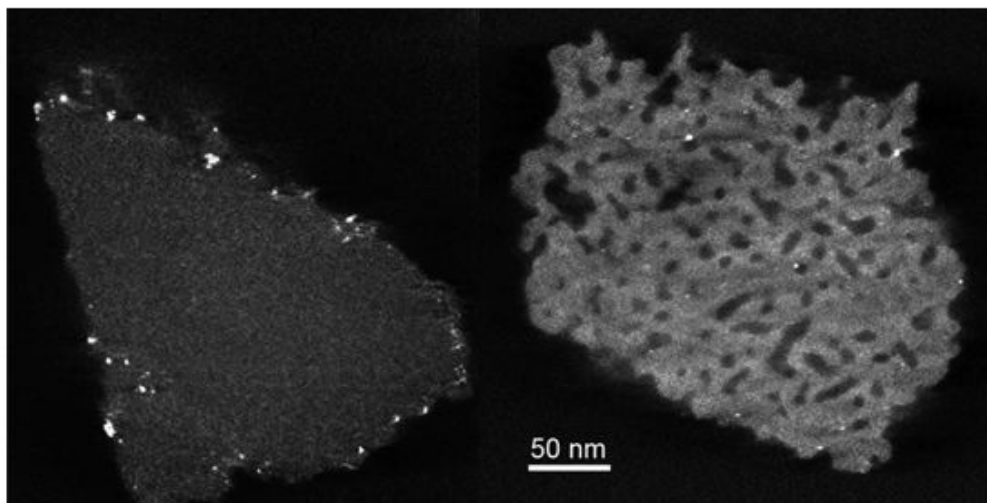


Figure 7. Representative cross section slices from STEM tomogram of Ru/AC (left) and Ru/MC (right). Reproduced with permissions from ref 117, Copyright 2020, Elsevier.

Looking at the catalytic behaviour, Ru/MC reached the complete conversion of levulinic acid while Ru/AC converted only 83 % (in both cases with a selectivity to γ -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 an important project in collaboration with TotalEnergies about tailoring catalyst active sites in hydrogenation/hydrogenolysis reactions for biofuel production.

1
2
3
4 The design of a catalytic material starts from the principle that the active site properties derive
5
6
7 from an ensemble of factors, as demonstrated in many of the Laura's works described in the
8
9
10 previous paragraphs. Hydrogenation reactions are among the pillars of the chemical industry and
11
12
13 particularly relevant in the field of biomass transformation. Indeed, the use of biomass appears a
14
15
16 good alternative for replacing fossil sources of energy, but the high oxygen content has to be
17
18
19 removed by hydrogenation and hydrogenolysis catalytic processes. Therefore, Laura concentrated
20
21
22 her efforts of these last years on the study of a better understanding of catalyst structure–activity
23
24
25 relationships in the hydrogenation/hydrogenolysis reactions of highly functionalized, oxygen
26
27
28 containing reactants, with the final goal to indicate requisites for the design of specific catalytic
29
30
31 materials which minimize waste and energy consumption thus reducing risks, hazards and costs.
32
33
34
35
36
37

38 The hydrogenation and hydrodeoxygenation of aldehydes, in particular, are important industrial
39
40
41 processes for the production of a wide range of chemicals that find use as solvents, fuels,
42
43
44 plasticizers, detergents, pharmaceutical precursors, and fine chemicals. Aldehydes, in fact, can be
45
46
47 found in several biomass-derived feedstock.¹¹⁸ Firstly, Laura investigated one of the critical
48
49
50 parameters that govern the reactivity of the carbonylic group toward hydrogenation and
51
52
53 hydrodeoxygenation, that is the effect of the side chains of aldehydes.¹¹⁹ In this work, she
54
55
56
57
58
59
60

1
2
3 demonstrated that the presence of a p-electron conjugation on the side chains strongly affects the
4
5
6
7 conversion of aldehydes to alcohols and hydrocarbons. Indeed, a Pd supported carbon catalyst was
8
9
10 tested and, while in the presence of a strong p-electron conjugation (aromatic ring) the catalyst
11
12
13 was active towards the hydrogenation and further hydrodeoxygenation of the carbonylic group, it
14
15
16 was inactive with molecules with no or weak p-electron conjugation (alkyl chains).
17
18
19

20
21 As next step, she disclosed some still existing uncertainty with respect to the properties governing
22
23
24 the catalyst activity of Pd/C, using the hydrogenation of benzaldehyde as a model reaction.¹²⁰ The
25
26
27
28 research work demonstrated that which are the dominant parameters determining catalyst activity
29
30
31 of Pd nanoparticles supported on a carbonaceous material, varying its physico-chemical properties
32
33
34 such as nanoparticle size, Pd oxidation state and Pd surface exposure. Indeed, a linear correlation
35
36
37
38 between catalyst activity and the amount of surface Pd(0) atoms was found, pointing out the nature
39
40
41 of the active site of the Pd/GNP catalyst represented by exposed Pd(0) species.
42
43
44

45
46 Lastly, she started to investigate the possibility to understand the phenomena responsible for
47
48
49 catalytic performance not only looking only at the structural properties of the catalytic material,
50
51
52 but considering the whole catalytic system, as complex interplay between catalyst, reactant and
53
54
55
56 reaction medium. The extent of interaction between a reactant and a catalyst can be in fact
57
58
59

1
2
3
4 evaluated through Nuclear Magnetic Resonance spectroscopy looking at the spin relaxation. This
5
6
7 is considered a sensitive probe for molecular dynamics. Laura, once again, focused on Pd
8
9
10 nanoparticles supported on a carbon for aldehydes hydrogenation: what was shown in the previous
11
12
13 work,¹²¹ i.e. benzaldehyde could be readily converted by Pd/C catalyst while negligible activity
14
15
16 was observed with octanal, was finally disclosed by using ¹³C T1 NMR.¹²² Two different T1
17
18
19 relaxation times were used: the T1_{ads} which is measured when the molecule adsorbed on the
20
21
22 catalyst (in the presence of the catalyst in the reaction medium) and the T1_{bulk} which is for the
23
24
25 free diffusing (bulk) molecule. The ratio (T1_{ads}/T1_{bulk}) can be used as an indicator of the relative
26
27
28 strength of interaction between the reactant and the catalytic surface.
29
30
31

32
33
34 Comparing and correlating the different T1_{ads}/T1_{bulk} values, Laura was able to prove that the
35
36
37 different catalytic results mainly depend on the contrasting adsorption behaviour of substrates on
38
39
40 the catalyst, and, in addition, by NMR she found that the adsorption of the reactants depended on
41
42
43 the choice of solvent, proving that T1_{ads}/T1_{bulk} measurements can provide a guide to the
44
45
46 selection of appropriate reaction conditions for improving catalytic activity.
47
48
49

50
51
52 She is continuing to work on this technique in parallel with the catalytic studies of new materials.
53
54

55
56 Her latest results in this field are reported in a very recent publication on Pt-WO_x supported on
57
58
59

1
2
3 carbon catalysts, used for the hydrogenation of α , β -unsaturated aldehydes. ^{123}Pt supported on
4
5
6
7 carbon catalysts have been modified by WO_x species, differentiating the sequential addition of W
8
9
10 precursors and Pt. Coupling Pt with WO_x had a positive effect on the catalytic activity, which can
11
12
13 be correlated to the W/Pt atomic ratio: the less active catalyst showed the lowest W/Pt ratio, while
14
15
16
17 the most active showed the highest W/Pt atomic ratio.

18
19
20 Moreover, the catalysts showed a different selectivity toward C=C or C=O hydrogenation,
21
22
23 explained by the different superficial amount of WO_2 or WO_3 .

24
25
26
27 By ^{13}C -NMR relaxation times ($T_{1\text{bulk}}/T_{1\text{ads}}$) Laura still found a direct correlation between the
28
29
30 strength of reactant interaction and the catalytic surface with the reaction selectivity.
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45

46 **Conclusions**

47
48
49
50
51 During the last 35 years, Laura Prati has had an extraordinary career in catalysis, using colloidal
52
53
54 Au based nanoparticles for a number of successful and important catalytic applications. Her work
55
56
57
58
59
60

1
2
3
4 has inspired many research groups around the world for the use of Au NPs not only for catalytic
5
6
7 but also biomedical and energy related applications that are essential for our society and economy.
8
9

10 Especially Laura Prati was pioneer and one of the first groups worldwide to show the high catalytic
11
12
13 efficiency of mono and bimetallic preformed colloidal nanoparticles with well-defined structural
14
15
16 design for sustainable catalytic processes, especially the selective liquid phase oxidation of
17
18
19 alcohols, sugars, for tuning the selectivity to desired products, as well as for improving catalyst's
20
21
22 stability. A prominent example is the selective oxidation of glycerol where the systematic control
23
24
25 of specific experimental parameters led to the synthesis of novel and size and shape controlled
26
27
28 supported nanoparticles and especially the deeper understanding of reaction pathways and
29
30
31 identification of active sites using *ex situ* and *in-situ* spectroscopy. She has also developed new
32
33
34 synthesis approaches for the development of novel catalysts for hydrogenation reactions from
35
36
37 biomass resources with TotalEnergies, especially the production of fine chemicals. Moreover, the
38
39
40 nature and influence of support was exploited in many cases, and the use of functionalised carbon
41
42
43 materials showed new directions for improving not only catalytic efficiency but also emphasising
44
45
46 on the role of controlling the surface functionality of carbon-based materials and how it affect
47
48
49 catalytic performance. Her approach was to investigate first the fundamental chemistry of
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 functionalised colloidal metal nanoparticles and supports that have applicability for different
5
6
7 catalytic model reactions and then to try to develop better understanding between the morphology
8
9
10 of the catalyst and the catalytic performance, using advanced characterisation techniques. Then,
11
12
13 the outcome of this knowledge especially can be used either for improving existing catalytic
14
15
16 processes or to generate new catalytic applications and synthesising highly efficient nanomaterials.
17
18

19
20 We wish Laura Prati to continue her wonderful academic success in the next years.
21
22
23
24
25
26
27
28

29 AUTHOR INFORMATION

30
31
32

33 **Corresponding Author**

34
35

36 *Alberto Villa – Dipartimento di Chimica, Università degli Studi di Milano, Via Camillo Golgi
37
38
39
40 19, 20133, Milano, Italy. alberto.villa@unimi.it
41
42
43

44 Authors

45
46

47 Sebastiano Campisi - Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19,
48
49
50
51 20133, Milano (Italy)
52
53
54
55
56
57
58
59
60

1
2
3
4 Marta Stucchi - Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19,
5
6
7 20133, Milano (Italy)
8
9

10 Nikolaos Dimitratos - Department of Industrial Chemistry, Alma Mater Studiorum-University of
11
12
13 Bologna, 40136 Bologna, Italy
14
15

16 REFERENCES

- 17
18
19
20 (1) Prati, L.; Rossi, M.; Ravasio, N. *Interaction of Molecular Oxygen with Aminophenols*
21 *Mediated by Copper Metal and Copper Compounds*; 1992; Vol. 75.
22
23
24 (2) Lanfranchi, M.; Prati, L.; Rossi, M.; Tiripicchio, A. The Oxidation of Ethane-1,2-Diol
25 Resulting from Molecular Oxygen Activation by Copper: Formation of an Oxoethanoate
26 Complex Precedes Carbon–Carbon Bond Cleavage. *J. Chem. Soc., Chem. Commun.* **1993**,
27 *0*(22), 1698–1699. <https://doi.org/10.1039/C39930001698>.
28
29
30
31 (3) Prati, L.; Rossi, M. Stepwise Oxidation of 1,2-Diols Resulting from Molecular Oxygen
32 Activation by Copper. *J Mol Catal A Chem* **1996**, *110* (3), 221–226.
33 [https://doi.org/10.1016/1381-1169\(96\)00187-2](https://doi.org/10.1016/1381-1169(96)00187-2).
34
35
36
37 (4) Lanfranchi, M.; Prati, L.; Rossi, M.; Tiripicchio, A. *Facile Benzene Ring Contraction to*
38 *Cyclopentene Derivatives during the Copper Promoted Oxidation of Phenol with Dioxygen*;
39 1995; Vol. 101.
40
41
42
43 (5) Okumura, M.; Fujitani, T.; Huang, J.; Ishida, T. A Career in Catalysis: Masatake Haruta.
44 *ACS Catalysis*. American Chemical Society August 7, 2015, pp 4699–4707.
45 <https://doi.org/10.1021/acscatal.5b01122>.
46
47
48
49 (6) Bartley, J. K.; Dimitratos, N.; Edwards, J. K.; Kiely, C. J.; Taylor, S. H. A Career in
50 Catalysis: Graham J. Hutchings. *ACS Catal* **2021**, *11* (10), 5916–5933.
51 <https://doi.org/10.1021/acscatal.1c00569>.
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (7) Prati, L.; Rossi, M. Chemoselective Catalytic Oxidation of Polyols with Dioxygen on Gold
5 Supported Catalysts; 1997; pp 509–516. [https://doi.org/10.1016/S0167-2991\(97\)81012-9](https://doi.org/10.1016/S0167-2991(97)81012-9).
6
7
8 (8) Prati, L.; Rossi, M. Gold on Carbon as a New Catalyst for Selective Liquid Phase Oxidation
9 of Diols. *J Catal* **1998**, *176* (2), 552–560. <https://doi.org/10.1006/jcat.1998.2078>.
10
11
12 (9) Prati, L.; Villa, A. The Art of Manufacturing Gold Catalysts. *Catalysts*. MDPI AG
13 December 21, 2011, pp 24–37. <https://doi.org/10.3390/catal2010024>.
14
15
16 (10) Prati, L.; Martra, G. New Gold Catalysts for Liquid Phase Oxidation. *Gold Bull* **1999**, *32*
17 (3), 96–101. <https://doi.org/10.1007/BF03216617>.
18
19
20 (11) Grunwaldt, J.-D.; Kiener, C.; Baiker, A. *Preparation of Supported Gold Catalysts for Low-*
21 *Temperature CO Oxidation via “Size-Controlled” Gold Colloids*, 1999; Vol. 181.
22
23
24 (12) Prati, L.; Villa, A. Gold Colloids: From Quasi-Homogeneous to Heterogeneous Catalytic
25 Systems. *Acc Chem Res* **2014**, *47* (3), 855–863. <https://doi.org/10.1021/ar400170j>.
26
27
28 (13) Bianchi, C.; Porta, F.; Prati, L.; Rossi, M.; Al, oxide. *Selective Liquid Phase Oxidation*
29 *Using Gold Catalysts*, 2000; Vol. 13.
30
31
32
33 (14) Porta, F.; Prati, L.; Rossi, M.; Coluccia, S.; Martra, G. *Metal Sols as a Useful Tool for*
34 *Heterogeneous Gold Catalyst Preparation: Reinvestigation of a Liquid Phase Oxidation*;
35 2000; Vol. 61.
36
37
38 (15) Porta, F.; Prati, L.; Rossi, M.; Scari, G. New Au(0) Sols as Precursors for Heterogeneous
39 Liquid-Phase Oxidation Catalysts. *J Catal* **2002**, *211* (2), 464–469.
40 <https://doi.org/10.1006/jcat.2002.3745>.
41
42
43
44 (16) Biella, S.; Porta, F.; Prati, L.; Rossi, M. Surfactant-Protected Gold Particles: New Challenge
45 for Gold-on-Carbon Catalysts. *Catal Letters* **2003**, *90* (1), 23–29.
46 <https://doi.org/10.1023/A:1025808024943>.
47
48
49
50 (17) Villa, A.; Schiavoni, M.; Prati, L. Material Science for the Support Design: A Powerful
51 Challenge for Catalysis. *Catalysis Science and Technology*. April 2012, pp 673–682.
52 <https://doi.org/10.1039/c2cy00355d>.
53
54
55
56
57
58
59
60

- 1
2
3
4 (18) Prati, L.; Villa, A.; Lupini, A. R.; Veith, G. M. Gold on Carbon: One Billion Catalysts under
5 a Single Label. *Physical Chemistry Chemical Physics*. February 28, 2012, pp 2969–2978.
6 <https://doi.org/10.1039/c2cp23405j>.
7
8
9 (19) Bianchi, C. L.; Biella, S.; Gervasini, A.; Prati, L.; Rossi, M. Gold on Carbon: Influence of
10 Support Properties on Catalyst Activity in Liquid-Phase Oxidation. *Catal Letters* **2003**, *85*
11 (1), 91–96. <https://doi.org/10.1023/A:1022176909660>.
12
13
14 (20) Biella, S.; Prati, L.; Rossi, M. Selectivity Control in the Oxidation of Phenylethane-1,2-Diol
15 with Gold Catalyst. *Inorganica Chim Acta* **2003**, *349*, 253–257.
16 [https://doi.org/10.1016/S0020-1693\(03\)00040-9](https://doi.org/10.1016/S0020-1693(03)00040-9).
17
18
19 (21) Biella, S.; Prati, L.; Rossi, M. Selective Oxidation of D-Glucose on Gold Catalyst. *J Catal*
20 **2002**, *206* (2), 242–247. <https://doi.org/10.1006/jcat.2001.3497>.
21
22
23 (22) Biella, S.; Prati, L.; Rossi, M. Gold Catalyzed Oxidation of Aldehydes in Liquid Phase. *J*
24 *Mol Catal A Chem* **2003**, *197* (1–2), 207–212. [https://doi.org/10.1016/S1381-1169\(02\)00618-0](https://doi.org/10.1016/S1381-1169(02)00618-0).
25
26
27 (23) Pina, C. della; Falletta, E.; Prati, L.; Rossi, M. Selective Oxidation Using Gold. *Chem Soc*
28 *Rev* **2008**, *37* (9), 2077–2095. <https://doi.org/10.1039/b707319b>.
29
30
31 (24) Villa, A.; Wang, D.; Su, D. S.; Prati, L. New Challenges in Gold Catalysis: Bimetallic
32 Systems. *Catalysis Science and Technology*. Royal Society of Chemistry 2015, pp 55–68.
33 <https://doi.org/10.1039/c4cy00976b>.
34
35
36 (25) Wang, D.; Villa, A.; Porta, F.; Su, D.; Prati, L. Single-Phase Bimetallic System for the
37 Selective Oxidation of Glycerol to Glycerate. *Chemical Communications* **2006**, No. 18,
38 1956–1958. <https://doi.org/10.1039/b518069d>.
39
40
41 (26) Villa, A.; Campione, C.; Prati, L. Bimetallic Gold/Palladium Catalysts for the Selective
42 Liquid Phase Oxidation of Glycerol. *Catal Letters* **2007**, *115* (3–4), 133–136.
43 <https://doi.org/10.1007/s10562-007-9077-x>.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (27) Wang, D.; Villa, A.; Porta, F.; Prati, L.; Su, D. Bimetallic Gold/Palladium Catalysts:
5 Correlation between Nanostructure and Synergistic Effects. *Journal of Physical Chemistry*
6 *C* **2008**, *112* (23), 8617–8622. <https://doi.org/10.1021/jp800805e>.
7
8
9 (28) Villa, A.; Wang, D.; Su, D.; Veith, G. M.; Prati, L. Using Supported Au Nanoparticles as
10 Starting Material for Preparing Uniform Au/Pd Bimetallic Catalysts. *Physical Chemistry*
11 *Chemical Physics* **2010**, *12* (9), 2183–2189. <https://doi.org/10.1039/b919322g>.
12
13 (29) Cattaneo, S.; Stucchi, M.; Villa, A.; Prati, L. Gold Catalysts for the Selective Oxidation of
14 Biomass-Derived Products. *ChemCatChem*. Wiley Blackwell January 9, 2019, pp 309–323.
15 <https://doi.org/10.1002/cctc.201801243>.
16
17 (30) Campisi, S.; Bellomi, S.; Chinchilla, L. E.; Prati, L.; Villa, A. Base-Free Oxidative
18 Esterification of HMF over AuPd/NNiO-TiO₂. When Alloying Effects and Metal-Support
19 Interactions Converge in Producing Effective and Stable Catalysts. *ChemCatChem* **2022**,
20 *14* (15). <https://doi.org/10.1002/cctc.202200494>.
21
22 (31) Villa, A.; Schiavoni, M.; Campisi, S.; Veith, G. M.; Prati, L. Pd-Modified Au on Carbon as
23 an Effective and Durable Catalyst for the Direct Oxidation of HMF to 2,5-
24 Furandicarboxylic Acid. *ChemSusChem* **2013**, *6* (4), 609–612.
25 <https://doi.org/10.1002/cssc.201200778>.
26
27 (32) Villa, A.; Dimitratos, N.; Chan-Thaw, C. E.; Hammond, C.; Veith, G. M.; Wang, D.;
28 Manzoli, M.; Prati, L.; Hutchings, G. J. Characterisation of Gold Catalysts. *Chemical*
29 *Society Reviews*. Royal Society of Chemistry September 21, 2016, pp 4953–4994.
30 <https://doi.org/10.1039/c5cs00350d>.
31
32 (33) Dodekatos, G.; Schünemann, S.; Tüysüz, H. Recent Advances in Thermo-, Photo-, and
33 Electrocatalytic Glycerol Oxidation. *ACS Catalysis*. American Chemical Society July 6,
34 2018, pp 6301–6333. <https://doi.org/10.1021/acscatal.8b01317>.
35
36 (34) Villa, A.; Dimitratos, N.; Chan-Thaw, C. E.; Hammond, C.; Prati, L.; Hutchings, G. J.
37 Glycerol Oxidation Using Gold-Containing Catalysts. *Acc Chem Res* **2015**, *48* (5), 1403–
38 1412. <https://doi.org/10.1021/ar500426g>.
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (35) Dimitratos, N.; Messi, C.; Porta, F.; Prati, L.; Villa, A. Investigation on the Behaviour of
5 Pt(0)/Carbon and Pt(0),Au(0)/Carbon Catalysts Employed in the Oxidation of Glycerol with
6 Molecular Oxygen in Water. *J Mol Catal A Chem* **2006**, *256* (1–2), 21–28.
7 <https://doi.org/10.1016/j.molcata.2006.04.019>.
8
9
10
11 (36) Porta, F.; Prati, L. Selective Oxidation of Glycerol to Sodium Glycerate with Gold-on-
12 Carbon Catalyst: An Insight into Reaction Selectivity. *J Catal* **2004**, *224* (2), 397–403.
13 <https://doi.org/10.1016/j.jcat.2004.03.009>.
14
15
16
17 (37) Dimitratos, N.; Villa, A.; Bianchi, C. L.; Prati, L.; Makkee, M. Gold on Titania: Effect of
18 Preparation Method in the Liquid Phase Oxidation. *Appl Catal A Gen* **2006**, *311* (1–2),
19 185–192. <https://doi.org/10.1016/j.apcata.2006.06.026>.
20
21
22
23 (38) Bianchi, C. L.; Canton, P.; Dimitratos, N.; Porta, F.; Prati, L. Selective Oxidation of
24 Glycerol with Oxygen Using Mono and Bimetallic Catalysts Based on Au, Pd and Pt
25 Metals. In *Catalysis Today*; 2005; Vol. 102–103, pp 203–212.
26 <https://doi.org/10.1016/j.cattod.2005.02.003>.
27
28
29
30 (39) Prati, L.; Villa, A.; Campione, C.; Spontoni, P. Effect of Gold Addition on Pt and Pd
31 Catalysts in Liquid Phase Oxidations. *Top Catal* **2007**, *44* (1–2), 319–324.
32 <https://doi.org/10.1007/s11244-007-0305-9>.
33
34
35
36 (40) Dimitratos, N.; Lopez-Sanchez, J. A.; Lennon, D.; Porta, F.; Prati, L.; Villa, A. Effect of
37 Particle Size on Monometallic and Bimetallic (Au,Pd)/C on the Liquid Phase Oxidation of
38 Glycerol. *Catal Letters* **2006**, *108* (3–4), 147–153. [https://doi.org/10.1007/s10562-006-](https://doi.org/10.1007/s10562-006-0036-8)
39 [0036-8](https://doi.org/10.1007/s10562-006-0036-8).
40
41
42
43 (41) Prati, L.; Villa, A.; Porta, F.; Wang, D.; Su, D. Single-Phase Gold/Palladium Catalyst: The
44 Nature of Synergistic Effect. *Catal Today* **2007**, *122* (3–4), 386–390.
45 <https://doi.org/10.1016/j.cattod.2006.11.003>.
46
47
48
49 (42) Stucchi, M.; Jouve, A.; Villa, A.; Nagy, G.; Németh, M.; Evangelisti, C.; Zanella, R.; Prati,
50 L. Gold-Silver Catalysts: Ruling Factors for Establishing Synergism. *ChemCatChem* **2019**,
51 *11* (16), 4043–4053. <https://doi.org/10.1002/cctc.201900591>.
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (43) Jouve, A.; Nagy, G.; Somodi, F.; Tiozzo, C.; Villa, A.; Balerna, A.; Beck, A.; Evangelisti,
5 C.; Prati, L. Gold-Silver Catalysts: Effect of Catalyst Structure on the Selectivity of
6 Glycerol Oxidation. *J Catal* **2018**, *368*, 324–335. <https://doi.org/10.1016/j.jcat.2018.10.019>.
7
8
9 (44) Dimitratos, N.; Villa, A.; Prati, L. Liquid Phase Oxidation of Glycerol Using a Single Phase
10 (Au-Pd) Alloy Supported on Activated Carbon: Effect of Reaction Conditions. *Catal Letters*
11 **2009**, *133* (3–4), 334–340. <https://doi.org/10.1007/s10562-009-0192-8>.
12
13
14 (45) Prati, L.; Bergna, D.; Villa, A.; Spontoni, P.; Bianchi, C. L.; Hu, T.; Romar, H.; Lassi, U.
15 Carbons from Second Generation Biomass as Sustainable Supports for Catalytic Systems.
16 *Catal Today* **2018**, *301*, 239–243. <https://doi.org/10.1016/j.cattod.2017.03.007>.
17
18
19 (46) Prati, L.; Villa, A.; Chan-Thaw, C. E.; Arrigo, R.; Wang, D.; Su, D. S. Gold Catalyzed
20 Liquid Phase Oxidation of Alcohol: The Issue of Selectivity. *Faraday Discuss* **2011**, *152*,
21 353–365. <https://doi.org/10.1039/c1fd00016k>.
22
23
24 (47) Prati, L.; Spontoni, P.; Gaiassi, A. From Renewable to Fine Chemicals through Selective
25 Oxidation: The Case of Glycerol. *Top Catal* **2009**, *52* (3), 288–296.
26 <https://doi.org/10.1007/s11244-008-9165-1>.
27
28
29 (48) Villa, A.; Wang, D.; Chan-Thaw, C. E.; Campisi, S.; Veith, G. M.; Prati, L. The
30 Confinement Effect on the Activity of Au NPs in Polyol Oxidation. *Catal Sci Technol* **2016**,
31 *6* (3), 598–601. <https://doi.org/10.1039/c5cy01593f>.
32
33
34 (49) Chan-Thaw, C. E.; Villa, A.; Wang, D.; Santo, V. D.; Orbelli Biroli, A.; Veith, G. M.;
35 Thomas, A.; Prati, L. PdH_x Entrapped in a Covalent Triazine Framework Modulates
36 Selectivity in Glycerol Oxidation. *ChemCatChem* **2015**, *7* (14), 2149–2154.
37 <https://doi.org/10.1002/cctc.201500055>.
38
39
40 (50) Jouve, A.; Stucchi, M.; Barlocco, I.; Evangelisti, C.; Somodic, F.; Villa, A.; Prati, L.
41 Carbon-Supported Au Nanoparticles: Catalytic Activity Ruled Out by Carbon Support. *Top*
42 *Catal* **2018**, *61* (18–19), 1928–1938. <https://doi.org/10.1007/s11244-018-1001-7>.
43
44
45 (51) Wang, D.; Villa, A.; Su, D.; Prati, L.; Schlögl, R. Carbon-Supported Gold Nanocatalysts:
46 Shape Effect in the Selective Glycerol Oxidation. *ChemCatChem* **2013**, *5* (9), 2717–2723.
47 <https://doi.org/10.1002/cctc.201200535>.
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (52) Villa, A.; Chan-Thaw, C. E.; Prati, L. Au NPs on Anionic-Exchange Resin as Catalyst for
5 Polyols Oxidation in Batch and Fixed Bed Reactor. *Appl Catal B* **2010**, *96* (3–4), 541–547.
6 <https://doi.org/10.1016/j.apcatb.2010.03.017>.
7
8
9 (53) Villa, A.; Veith, G. M.; Ferri, D.; Weidenkaff, A.; Perry, K. A.; Campisi, S.; Prati, L. NiO
10 as a Peculiar Support for Metal Nanoparticles in Polyols Oxidation. *Catal Sci Technol* **2013**,
11 *3* (2), 394–399. <https://doi.org/10.1039/c2cy20370g>.
12
13
14 (54) Villa, A.; Gaiassi, A.; Rossetti, I.; Bianchi, C. L.; van Benthem, K.; Veith, G. M.; Prati, L.
15 Au on MgAl₂O₄ Spinels: The Effect of Support Surface Properties in Glycerol Oxidation.
16 *J Catal* **2010**, *275* (1), 108–116. <https://doi.org/10.1016/j.jcat.2010.07.022>.
17
18
19 (55) Villa, A.; Veith, G. M.; Prati, L. Selective Oxidation of Glycerol under Acidic Conditions
20 Using Gold Catalysts. *Angewandte Chemie - International Edition* **2010**, *49* (26), 4499–
21 4502. <https://doi.org/10.1002/anie.201000762>.
22
23
24 (56) Villa, A.; Campisi, S.; Mohammed, K. M. H.; Dimitratos, N.; Vindigni, F.; Manzoli, M.;
25 Jones, W.; Bowker, M.; Hutchings, G. J.; Prati, L. Tailoring the Selectivity of Glycerol
26 Oxidation by Tuning the Acid-Base Properties of Au Catalysts. *Catal Sci Technol* **2015**, *5*
27 (2), 1126–1132. <https://doi.org/10.1039/c4cy01246a>.
28
29
30 (57) Wenkin, M.; Ruiz, P.; Delmon, B.; Devillers, M. The Role of Bismuth as Promoter in Pd-
31 Bi Catalysts for the Selective Oxidation of Glucose to Gluconate. *J Mol Catal A Chem* **2002**,
32 *180* (1–2), 141–159. [https://doi.org/10.1016/S1381-1169\(01\)00421-6](https://doi.org/10.1016/S1381-1169(01)00421-6).
33
34
35 (58) Keresszegi, C.; Mallat, T.; Grunwaldt, J. D.; Baiker, A. A Simple Discrimination of the
36 Promoter Effect in Alcohol Oxidation and Dehydrogenation over Platinum and Palladium.
37 *J Catal* **2004**, *225*, 138–146. <https://doi.org/10.1016/j.jcat.2004.04.002>.
38
39
40 (59) Campisi, S.; Capelli, S.; Ferri, M.; Villa, A.; Dann, E.; Wade, A.; Wells, P. P.; Dimitratos,
41 N. On the Role of Bismuth as Modifier in AuPdBi Catalysts: Effects on Liquid-Phase
42 Oxidation and Hydrogenation Reactions. *Catal Commun* **2021**, *158*.
43 <https://doi.org/10.1016/j.catcom.2021.106340>.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (60) Capelli, S.; Cattaneo, S.; Stucchi, M.; Villa, A.; Prati, L. Iron as Modifier of Pd and Pt-
5 Based Catalysts for Sustainable and Green Processes. *Inorganica Chimica Acta*. Elsevier
6 B.V. May 24, 2022. <https://doi.org/10.1016/j.ica.2022.120856>.
7
8
9 (61) Kimura, H. Selective Oxidation of Glycerol on a Platinum-Bismuth Catalyst by Using a
10 Fixed Bed Reactor. *Appl Catal A Gen* **1993**, *105* (c), 147–158.
11 [https://doi.org/10.1016/0926-860X\(93\)80245-L](https://doi.org/10.1016/0926-860X(93)80245-L).
12
13
14 (62) Villa, A.; Wang, D.; Veith, G. M.; Prati, L. Bismuth as a Modifier of Au-Pd Catalyst:
15 Enhancing Selectivity in Alcohol Oxidation by Suppressing Parallel Reaction. *J Catal* **2012**,
16 *292*, 73–80. <https://doi.org/10.1016/j.jcat.2012.04.021>.
17
18
19 (63) Villa, A.; Campisi, S.; Chan-Thaw, C. E.; Motta, D.; Wang, D.; Prati, L. Bismuth Modified
20 Au-Pt Bimetallic Catalysts for Dihydroxyacetone Production. *Catal Today* **2015**, *249*, 103–
21 108. <https://doi.org/10.1016/j.cattod.2014.12.012>.
22
23
24 (64) Motta, D.; Trujillo, F. J. S.; Dimitratos, N.; Villa, A.; Prati, L. An Investigation on AuPt
25 and AuPt-Bi on Granular Carbon as Catalysts for the Oxidation of Glycerol under
26 Continuous Flow Conditions. *Catal Today* **2018**, *308*, 50–57.
27 <https://doi.org/10.1016/j.cattod.2017.10.012>.
28
29
30 (65) Campisi, S.; Chan-Thaw, C. E.; Wang, D.; Villa, A.; Prati, L. Metal Nanoparticles on
31 Carbon Based Supports: The Effect of the Protective Agent Removal. *Catal Today* **2016**,
32 *278*, 91–96. <https://doi.org/10.1016/j.cattod.2016.04.026>.
33
34
35 (66) Villa, A.; Wang, D.; Su, D. S.; Prati, L. Gold Sols as Catalysts for Glycerol Oxidation: The
36 Role of Stabilizer. *ChemCatChem* **2009**, *1* (4), 510–514.
37 <https://doi.org/10.1002/cctc.200900118>.
38
39
40 (67) Villa, A.; Wang, D.; Veith, G. M.; Vindigni, F.; Prati, L. Sol Immobilization Technique: A
41 Delicate Balance between Activity, Selectivity and Stability of Gold Catalysts. *Catal Sci*
42 *Technol* **2013**, *3* (11), 3036–3041. <https://doi.org/10.1039/c3cy00260h>.
43
44
45 (68) Gaiassi, A.; Prati, L. Gold Catalysts for the Direct Oxidation of Aminoalcohols to
46 Aminoacids. *Catal Today* **2009**, *141* (3–4), 378–384.
47 <https://doi.org/10.1016/j.cattod.2008.07.017>.
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (69) Villa, A.; Campisi, S.; Schiavoni, M.; Prati, L. Amino Alcohol Oxidation with Gold
5 Catalysts: The Effect of Amino Groups. *Materials* **2013**, *6* (7), 2777–2788.
6 <https://doi.org/10.3390/ma6072777>.
7
8
9 (70) Dimitratos, N.; Villa, A.; Wang, D.; Porta, F.; Su, D.; Prati, L. Pd and Pt Catalysts Modified
10 by Alloying with Au in the Selective Oxidation of Alcohols. *J Catal* **2006**, *244* (1), 113–
11 121. <https://doi.org/10.1016/j.jcat.2006.08.019>.
12
13
14 (71) Wang, D.; Villa, A.; Spontoni, P.; Su, D. S.; Prati, L. In Situ Formation of Au-Pd Bimetallic
15 Active Sites Promoting the Physically Mixed Monometallic Catalysts in the Liquid-Phase
16 Oxidation of Alcohols. *Chemistry - A European Journal* **2010**, *16* (33), 10007–10013.
17 <https://doi.org/10.1002/chem.201001330>.
18
19 (72) Villa, A.; Janjic, N.; Spontoni, P.; Wang, D.; Su, D. S.; Prati, L. Au-Pd/AC as Catalysts for
20 Alcohol Oxidation: Effect of Reaction Parameters on Catalytic Activity and Selectivity.
21 *Appl Catal A Gen* **2009**, *364* (1–2), 221–228. <https://doi.org/10.1016/j.apcata.2009.05.059>.
22
23 (73) Villa, A.; Wang, D.; Dimitratos, N.; Su, D.; Trevisan, V.; Prati, L. Pd on Carbon Nanotubes
24 for Liquid Phase Alcohol Oxidation. *Catal Today* **2010**, *150* (1–2), 8–15.
25 <https://doi.org/10.1016/j.cattod.2009.06.009>.
26
27 (74) Villa, A.; Plebani, M.; Schiavoni, M.; Milone, C.; Piperopoulos, E.; Galvagno, S.; Prati, L.
28 Tuning Hydrophilic Properties of Carbon Nanotubes: A Challenge for Enhancing
29 Selectivity in Pd Catalyzed Alcohol Oxidation. *Catal Today* **2012**, *186* (1), 76–82.
30 <https://doi.org/10.1016/j.cattod.2011.09.041>.
31
32 (75) Prati, L.; Chan-Thaw, C. E.; Campisi, S.; Villa, A. N-Modified Carbon-Based Materials:
33 Nanoscience for Catalysis. *The Chemical Record* **2016**, *16* (5), 2187–2197.
34 <https://doi.org/10.1002/tcr.201500257>.
35
36 (76) Chan-Thaw, C. E.; Villa, A.; Prati, L.; Thomas, A. Triazine-Based Polymers as
37 Nanostructured Supports for the Liquid-Phase Oxidation of Alcohols. *Chemistry - A*
38 *European Journal* **2011**, *17* (3), 1052–1057. <https://doi.org/10.1002/chem.201000675>.
39
40 (77) Chan-Thaw, C. E.; Villa, A.; Veith, G. M.; Kailasam, K.; Adamczyk, L. A.; Unocic, R. R.;
41 Prati, L.; Thomas, A. Influence of Periodic Nitrogen Functionality on the Selective
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 Oxidation of Alcohols. *Chem Asian J* **2012**, *7* (2), 387–393.
5 <https://doi.org/10.1002/asia.201100565>.
6
7
8 (78) Chan-Thaw, C. E.; Villa, A.; Veith, G. M.; Prati, L. Identifying the Role of N-Heteroatom
9 Location in the Activity of Metal Catalysts for Alcohol Oxidation. *ChemCatChem* **2015**, *7*
10 (8), 1338–1346. <https://doi.org/10.1002/cctc.201402951>.
11
12
13 (79) Campisi, S.; Ferri, D.; Villa, A.; Wang, W.; Wang, D.; Kröcher, O.; Prati, L. Selectivity
14 Control in Palladium-Catalyzed Alcohol Oxidation through Selective Blocking of Active
15 Sites. *Journal of Physical Chemistry C* **2016**, *120* (26), 14027–14033.
16 <https://doi.org/10.1021/acs.jpcc.6b01549>.
17
18
19 (80) Villa, A.; Chan-Thaw, C. E.; Veith, G. M.; More, K. L.; Ferri, D.; Prati, L. Au on Nanosized
20 NiO: A Cooperative Effect between Au and Nanosized NiO in the Base-Free Alcohol
21 Oxidation. *ChemCatChem* **2011**, *3* (10), 1612–1618.
22 <https://doi.org/10.1002/cctc.201100161>.
23
24
25 (81) Marelli, M.; Jouve, A.; Villa, A.; Psaro, R.; Balerna, A.; Prati, L.; Evangelisti, C. Hybrid
26 Au/CuO Nanoparticles: Effect of Structural Features for Selective Benzyl Alcohol
27 Oxidation. *Journal of Physical Chemistry C* **2019**, *123* (5), 2864–2871.
28 <https://doi.org/10.1021/acs.jpcc.8b09449>.
29
30
31 (82) Stucchi, M.; Capelli, S.; Cardaci, S.; Cattaneo, S.; Jouve, A.; Beck, A.; Sáfrán, G.;
32 Evangelisti, C.; Villa, A.; Prati, L. Synergistic Effect in Au-Cu Bimetallic Catalysts for the
33 Valorization of Lignin-Derived Compounds. *Catalysts* **2020**, *10* (3).
34 <https://doi.org/10.3390/catal10030332>.
35
36
37 (83) Stucchi, M.; Cattaneo, S.; Cappella, A.; Wang, W.; Wang, D.; Villa, A.; Prati, L. Catalytic
38 Oxidation of Methoxy Substituted Benzyl Alcohols as Model for Lignin Valorisation. *Catal*
39 *Today* **2020**, *357*, 15–21. <https://doi.org/10.1016/j.cattod.2019.03.022>.
40
41
42 (84) Villa, A.; Campisi, S.; Giordano, C.; Otte, K.; Prati, L. Mo and W Carbide: Tunable
43 Catalysts for Liquid Phase Conversion of Alcohols. *ACS Catal* **2012**, *2* (7), 1377–1380.
44 <https://doi.org/10.1021/cs300221w>.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (85) Campisi, S.; Marzorati, S.; Spontoni, P.; Chan-Thaw, C. E.; Longhi, M.; Villa, A.; Prati, L.
5 Tailored N-Containing Carbons as Catalyst Supports in Alcohol Oxidation. *Materials* **2016**,
6 *9*(2). <https://doi.org/10.3390/ma9020114>.
7
8
9 (86) Prati, L.; Porta, F. Oxidation of Alcohols and Sugars Using Au/C Catalysts: Part 1.
10 Alcohols. In *Applied Catalysis A: General*; 2005; Vol. 291, pp 199–203.
11 <https://doi.org/10.1016/j.apcata.2004.11.050>.
12
13
14 (87) Prati, L.; Porta, F.; Wang, D.; Villa, A. Ru Modified Au Catalysts for the Selective
15 Oxidation of Aliphatic Alcohols. *Catal Sci Technol* **2011**, *1* (9), 1624.
16 <https://doi.org/10.1039/c1cy00218j>.
17
18
19 (88) Villa, A.; E-chan-thaw, C.; Schiavoni, M.; Campisi, S.; Wang, D.; Prati, L. Fragrances by
20 Selective Oxidation of Long-Chain Alcohols. *Cuihua Xuebao/Chinese Journal of Catalysis*
21 **2014**, *35*(6), 945–951. [https://doi.org/10.1016/s1872-2067\(14\)60101-7](https://doi.org/10.1016/s1872-2067(14)60101-7).
22
23
24 (89) Cattaneo, S.; Freakley, S. J.; Morgan, D. J.; Sankar, M.; Dimitratos, N.; Hutchings, G. J.
25 Cinnamaldehyde Hydrogenation Using Au-Pd Catalysts Prepared by Sol Immobilisation.
26 *Catal Sci Technol* **2018**, *8*(6), 1677–1685. <https://doi.org/10.1039/c7cy02556d>.
27
28
29 (90) Maris, E. P.; Ketchie, W. C.; Murayama, M.; Davis, R. J. Glycerol Hydrogenolysis on
30 Carbon-Supported PtRu and AuRu Bimetallic Catalysts. *J Catal* **2007**, *251* (2), 281–294.
31 <https://doi.org/https://doi.org/10.1016/j.jcat.2007.08.007>.
32
33
34 (91) Hutchings, G. J.; Chan-Thaw, C. E.; Hammond, C.; Dimitratos, N.; Villa, A.; Prati, L.
35 Glycerol Oxidation Using Gold-Containing Catalysts. *Acc Chem Res* **2015**, *48* (5), 1403–
36 1412. <https://doi.org/10.1021/ar500426g>.
37
38
39 (92) Zanella, R.; Louis, C.; Giorgio, S.; Touroude, R. Crotonaldehyde Hydrogenation by Gold
40 Supported on TiO₂: Structure Sensitivity and Mechanism. *J Catal* **2004**, *223* (2), 328–339.
41 <https://doi.org/https://doi.org/10.1016/j.jcat.2004.01.033>.
42
43
44 (93) Mitsudome, T.; Kaneda, K. Gold Nanoparticle Catalysts for Selective Hydrogenations.
45 *Green Chemistry* **2013**, *15*(10), 2636–2654. <https://doi.org/10.1039/C3GC41360H>.
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (94) Liu, R.; Yu, Y.; Yoshida, K.; Li, G.; Jiang, H.; Zhang, M.; Zhao, F.; Fujita, S.; Arai, M.
5 Physically and Chemically Mixed TiO₂-Supported Pd and Au Catalysts: Unexpected
6 Synergistic Effects on Selective Hydrogenation of Citral in Supercritical CO₂. *J Catal* **2010**,
7 *269* (1), 191–200. [https://doi.org/https://doi.org/10.1016/j.jcat.2009.11.007](https://doi.org/10.1016/j.jcat.2009.11.007).
8
9
10
11 (95) Villa, A.; Chan-Thaw, C. E.; Campisi, S.; Bianchi, C. L.; Wang, D.; Kotula, P. G.; Kübel,
12 C.; Prati, L. AuRu/AC as an Effective Catalyst for Hydrogenation Reactions. *Physical*
13 *Chemistry Chemical Physics* **2015**, *17* (42), 28171–28176.
14 <https://doi.org/10.1039/c5cp00632e>.
15
16
17
18 (96) Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into
19 Chemicals. *Chem Rev* **2007**, *107* (6), 2411–2502. <https://doi.org/10.1021/cr050989d>.
20
21
22
23 (97) Prati, L.; Porta, F.; Wang, D.; Villa, A. Ru Modified Au Catalysts for the Selective
24 Oxidation of Aliphatic Alcohols. *Catal Sci Technol* **2011**, *1* (9), 1624–1629.
25 <https://doi.org/10.1039/C1CY00218J>.
26
27
28
29 (98) German, D.; Kolobova, E.; Pakrieva, E.; Carabineiro, S. A. C.; Sviridova, E.;
30 Perevezentsev, S.; Alijani, S.; Villa, A.; Prati, L.; Postnikov, P.; Bogdanchikova, N.;
31 Pestryakov, A. The Effect of Sibunit Carbon Surface Modification with Diazonium Tosylate
32 Salts of Pd and Pd-Au Catalysts on Furfural Hydrogenation. *Materials* **2022**, *15* (13).
33 <https://doi.org/10.3390/ma15134695>.
34
35
36
37
38 (99) Villa, A.; Schiavoni, M.; Chan-Thaw, C. E.; Fulvio, P. F.; Mayes, R. T.; Dai, S.; More, K.
39 L.; Veith, G. M.; Prati, L. Acid-Functionalized Mesoporous Carbon: An Efficient Support
40 for Ruthenium-Catalyzed γ -Valerolactone Production. *ChemSusChem* **2015**, *8* (15), 2520–
41 2528. <https://doi.org/10.1002/cssc.201500331>.
42
43
44
45 (100) Landenna, L.; Villa, A.; Zanella, R.; Evangelisti, C.; Prati, L. Gold-Iridium Catalysts for
46 the Hydrogenation of Biomass Derived Products. *Cuihua Xuebao/Chinese Journal of*
47 *Catalysis* **2016**, *37* (10), 1771–1775. [https://doi.org/10.1016/S1872-2067\(16\)62512-3](https://doi.org/10.1016/S1872-2067(16)62512-3).
48
49
50
51 (101) Brewster, T. P.; Miller, A. J. M.; Heinekey, D. M.; Goldberg, K. I. Hydrogenation of
52 Carboxylic Acids Catalyzed by Half-Sandwich Complexes of Iridium and Rhodium. *J Am*
53 *Chem Soc* **2013**, *135* (43), 16022–16025. <https://doi.org/10.1021/ja408149n>.
54
55
56
57
58
59
60

- 1
2
3
4 (102) Li, W.; Xie, J.-H.; Lin, H.; Zhou, Q.-L. Highly Efficient Hydrogenation of Biomass-Derived
5 Levulinic Acid to γ -Valerolactone Catalyzed by Iridium Pincer Complexes. *Green*
6 *Chemistry* **2012**, *14* (9), 2388–2390. <https://doi.org/10.1039/C2GC35650C>.
7
8
9 (103) Ly, N.; Al-Shamery, K.; Chan-Thaw, C. E.; Prati, L.; Carniti, P.; Gervasini, A. Impact of
10 Support Oxide Acidity in Pt-Catalyzed HMF Hydrogenation in Alcoholic Medium. *Catal*
11 *Letters* **2017**, *147* (2), 345–359. <https://doi.org/10.1007/s10562-016-1945-9>.
12
13
14 (104) Villa, A.; Manzoli, M.; Vindigni, F.; Chinchilla, L. E.; Botton, G. A.; Prati, L. Diols
15 Production From Glycerol Over Pt-Based Catalysts: On the Role Played by the Acid Sites
16 of the Support. *Catal Letters* **2017**, *147* (10), 2523–2533. [https://doi.org/10.1007/s10562-](https://doi.org/10.1007/s10562-017-2183-5)
17 [017-2183-5](https://doi.org/10.1007/s10562-017-2183-5).
18
19 (105) Jouve, A.; Cattaneo, S.; Delgado, D.; Scotti, N.; Evangelisti, C.; Nieto, J. M. L.; Prati, L.
20 Furfural Hydrogenation on Modified Niobia. *Applied Sciences (Switzerland)* **2019**, *9* (11).
21 <https://doi.org/10.3390/app9112287>.
22
23 (106) Chen, X.; Li, H.; Luo, H.; Qiao, M. Liquid Phase Hydrogenation of Furfural to Furfuryl
24 Alcohol over Mo-Doped Co-B Amorphous Alloy Catalysts. *Appl Catal A Gen* **2002**, *233*
25 (1), 13–20. [https://doi.org/https://doi.org/10.1016/S0926-860X\(02\)00127-8](https://doi.org/https://doi.org/10.1016/S0926-860X(02)00127-8).
26
27 (107) Choi, S. H.; Lee, J. S. XAFS Characterization of Pt–Mo Bimetallic Catalysts for CO
28 Hydrogenation. *J Catal* **1997**, *167* (2), 364–371.
29 <https://doi.org/https://doi.org/10.1006/jcat.1997.1578>.
30
31 (108) Leclercq, G.; Romero, T.; Pietrzyk, S.; Grimblot, J.; Leclercq, L. Properties of Platinum-
32 Molybdenum Bimetallic Catalysts Deposited on Silica. *Journal of Molecular Catalysis*
33 **1984**, *25* (1), 67–86. [https://doi.org/https://doi.org/10.1016/0304-5102\(84\)80032-2](https://doi.org/https://doi.org/10.1016/0304-5102(84)80032-2).
34
35 (109) Stucchi, M.; Alijani, S.; Manzoli, M.; Villa, A.; Lahti, R.; Galloni, M. G.; Lassi, U.; Prati,
36 L. A Pt-Mo Hybrid Catalyst for Furfural Transformation. *Catal Today* **2020**, *357* (March
37 2019), 122–131. <https://doi.org/10.1016/j.cattod.2019.04.045>.
38
39 (110) Stucchi, M.; Manzoli, M.; Bossola, F.; Villa, A.; Prati, L. Ruling Factors in Cinnamaldehyde
40 Hydrogenation: Activity and Selectivity of Pt-Mo Catalysts. *Nanomaterials* **2021**, *11* (2),
41 1–12. <https://doi.org/10.3390/nano11020362>.
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 (111) GALLEZOT, P.; RICHARD, D. Selective Hydrogenation of α,β -Unsaturated Aldehydes.
5 *Catalysis Reviews* **1998**, *40*(1–2), 81–126. <https://doi.org/10.1080/01614949808007106>.
6
7
8 (112) Gallezot, P. The State and Catalytic Properties of Platinum and Palladium in Faujasite-Type
9 Zeolites. *Catalysis Reviews* **1979**, *20* (1), 121–154.
10 <https://doi.org/10.1080/03602457908065108>.
11
12
13 (113) Lashdaf, M.; Nieminen, V.-V.; Tiitta, M.; Venäläinen, T.; Österholm, H.; Krause, O. Role
14 of Acidity in Hydrogenation of Cinnamaldehyde on Platinum Beta Zeolite. *Microporous*
15 *and Mesoporous Materials* **2004**, *75* (1), 149–158.
16 <https://doi.org/https://doi.org/10.1016/j.micromeso.2004.05.008>.
17
18
19 (114) Cattaneo, S.; Naslhajian, H.; Somodi, F.; Evangelisti, C.; Villa, A.; Prati, L. Ruthenium on
20 Carbonaceous Materials for the Selective Hydrogenation of HMF. *Molecules* **2018**, *23*(8),
21 1–13. <https://doi.org/10.3390/molecules23082007>.
22
23
24 (115) Prati, L.; Bergna, D.; Villa, A.; Spontoni, P.; Bianchi, C. L.; Hu, T.; Romar, H.; Lassi, U.
25 Carbons from Second Generation Biomass as Sustainable Supports for Catalytic Systems.
26 *Catal Today* **2018**, *301*, 239–243. <https://doi.org/10.1016/j.cattod.2017.03.007>.
27
28
29 (116) Jouve, A.; Cattaneo, S.; Capelli, S.; Stucchi, M.; Evangelisti, C.; Villa, A.; Prati, L. CNF-
30 Functionalization as Versatile Tool for Tuning Activity in Cellulose-Derived Product
31 Hydrogenation. *Molecules* **2019**, *24*(2). <https://doi.org/10.3390/molecules24020316>.
32
33
34 (117) Cattaneo, S.; Stucchi, M.; Veith, G. M.; Prati, L.; Wang, D.; Wang, W.; Villa, A. Ru
35 Supported on Micro and Mesoporous Carbons as Catalysts for Biomass-Derived Molecules
36 Hydrogenation. *Catal Today* **2020**, *357* (February 2019), 143–151.
37 <https://doi.org/10.1016/j.cattod.2019.05.009>.
38
39
40 (118) Lan, X.; Wang, T. Highly Selective Catalysts for the Hydrogenation of Unsaturated
41 Aldehydes: A Review. *ACS Catal* **2020**, *10* (4), 2764–2790.
42 <https://doi.org/10.1021/acscatal.9b04331>.
43
44
45 (119) Cattaneo, S.; Capelli, S.; Stucchi, M.; Bossola, F.; Dal Santo, V.; Araujo-Lopez, E.;
46 Sharapa, D. I.; Studt, F.; Villa, A.; Chierogato, A.; Vandegehuchte, B. D.; Prati, L.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 Discovering the Role of Substrate in Aldehyde Hydrogenation. *J Catal* **2021**, *399*, 162–169.
5 <https://doi.org/10.1016/j.jcat.2021.05.012>.
6
7
8 (120) Capelli, S.; Cattaneo, S.; Stucchi, M.; Vandegheuchte, B. D.; Chieregato, A.; Villa, A.;
9 Prati, L. The Nature of Active Sites in the Pd/C-Catalyzed
10 Hydrogenation/Hydrodeoxygenation of Benzaldehyde. *Catalysts* **2022**, *12* (3), 1–12.
11 <https://doi.org/10.3390/catal12030251>.
12
13
14
15 (121) Cattaneo, S.; Capelli, S.; Stucchi, M.; Bossola, F.; Dal Santo, V.; Araujo-Lopez, E.;
16 Sharapa, D. I.; Studt, F.; Villa, A.; Chieregato, A.; Vandegheuchte, B. D.; Prati, L.
17 Discovering the Role of Substrate in Aldehyde Hydrogenation. *J Catal* **2021**, *399*, 162–169.
18 <https://doi.org/10.1016/j.jcat.2021.05.012>.
19
20
21
22
23 (122) Stucchi, M.; Vasile, F.; Cattaneo, S.; Villa, A.; Chieregato, A.; Vandegheuchte, B. D.; Prati,
24 L. An Insight into the Role of Reactant Structure Effect in Pd/C Catalysed Aldehyde
25 Hydrogenation. *Nanomaterials* **2022**, *12* (6). <https://doi.org/10.3390/nano12060908>.
26
27
28
29 (123) Stucchi, M.; vasile, francesca; cattaneo, stefano; vomeri, alessandro; Hungria, A. B.; Prati,
30 L. Pt-WO_x/C Catalysts for α , β - Unsaturated Aldehydes Hydrogenation: A NMR Study of
31 the Effect of the Reactant Adsorption on Activity and Selectivity. *European J Org Chem*
32 **2022**, *n/a* (n/a). <https://doi.org/https://doi.org/10.1002/ejoc.202200735>.
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60