

Alma Mater Studiorum Università di Bologna Archivio istituzionale della ricerca

Strategies to improve hydrogen activation on gold catalysts

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Dimitratos, N., Vilé, G., Albonetti, S., Cavani, F., Fiorio, J., López, N., et al. (2024). Strategies to improve hydrogen activation on gold catalysts. NATURE REVIEWS. CHEMISTRY, 8, 195-210 [10.1038/s41570-024-00578-2].

Availability:

This version is available at: https://hdl.handle.net/11585/982916 since: 2024-09-11

Published:

DOI: http://doi.org/10.1038/s41570-024-00578-2

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (https://cris.unibo.it/). When citing, please refer to the published version.

(Article begins on next page)

1 Strategies to improve hydrogen activation on gold catalysts

Nikolaos Dimitratos^{1,2}, Gianvito Vilé³, Stefania Albonetti^{1,2}, Fabrizio Cavani^{1,2}, Jhonatan
 Fiorio⁴, Nuria López⁵, Liane M. Rossi⁶, Robert Wojcieszak^{7,*}

- 4
- ¹Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum Università di Bologna, Viale
 Risorgimento 4, Bologna 40126, Italy
- ²Center for Chemical Catalysis-C3, Alma Mater Studiorum Università di Bologna, Viale Risorgimento 4, Bologna
 40136, Italy
- ³Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza
 Leonardo da Vinci 32, 20133 Milano, Italy
- ¹¹ ⁴Technische Universität Dresden, School of Science, Faculty of Chemistry and Food Chemistry, Mommsenstr. 13,
- 12 01069 Dresden, Germany.
- ⁵Institute of Chemical Research of Catalonia, The Barcelona Institute of Science and Technology, Tarragona,
 Spain
- ⁶Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu
 Prestes 748, São Paulo 05508-000, SP, Brazil
- 17 ⁷Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 UCCS Unité de catalyse et chimie du solide, F-
- 18 59000 Lille, France
- 19

20 *Corresponding author. E-mail: robert.wojcieszak@univ-lille.fr

21 ABSTRACT

- 22 Catalytic reactions involving molecular hydrogen are at the heart of many transformations in
- the chemical industry. Classically, hydrogenations are carried out on Pd, Pt, Ru, or Ni catalysts.
- However, the use of supported Au catalysts has garnered attention in recent years owing to their
- 25 exceptional selectivity in hydrogenation reactions. This is despite the limited understanding of
- the physicochemical aspects of hydrogen activation and reaction on Au surfaces. Similarly, a
- 27 rational design of new improved catalysts relies on better exploiting the hydrogenating
- 28 properties of Au. This review analyses the strategies employed to improve hydrogen-Au
- 29 interactions, from addressing the importance of the Au particle size to exploring alternative
- 30 mechanisms for H₂ dissociation on Au cations and Au-ligand interfaces. These insights hold
- 31 the potential to drive future applications of gold catalysis.
- 32

33

34 **[H1] Introduction**

35 Catalytic transformations involving molecular hydrogen (H₂) are named 36 hydrogenations, and are common in the chemical industry. For a long time, it was believed that 37 only certain metals, such as platinum (Pt), palladium (Pd), and nickel (Ni) possessed the 38 catalytic ability to dissociate H₂ efficiently. These metals have been extensively used in 39 industrial processes owing to their ability to facilitate hydrogenation reactions. However, issues 40 related to overhydrogenation with Ni catalysts and the high cost and limited availability of Pt 41 and Pd have prompted researchers to explore alternative catalysts. In this pursuit, scientists discovered that gold (Au), typically considered inert, can catalyze the activation of H₂ and other 42 43 H-donors, and exhibit remarkable catalytic properties in hydrogenation reactions.¹⁻² This 44 finding has shattered a long-standing limitation in the field and opened up new possibilities for 45 increasing the selectivity of various hydrogenation processes (BOX 1).

46 Heterogenous catalysts are used in many industrial processes⁵⁻⁷, often involving finely dispersed metallic nanoparticles. One such catalytic system is Au nanoparticles (Au NPs) 47 48 dispersed on solid carriers⁸, which were initially demonstrated for selective CO oxidation 49 reactions⁹⁻¹¹. Dispersing the Au nanoparticles in this way provides a large number of lowcoordination surface sites which offer improved catalytic properties over conventional Au 50 51 surfaces^{10,12}. This enhanced activity and selectivity are linked to the quantum effects unique to 52 the nanoscale. When Au nanoparticles are very small (below <2 nm in diameter), significant 53 quantization occurs to the conduction band. In these quantum-sized nanoparticles, many of the physical and chemical properties of Au are fundamentally altered.¹³ For example, quantum-54 55 sized Au nanoparticles show multiple optical absorption peaks in the optical spectrum whereas 56 a single surface plasmon resonance (SPR) peak at 520 nm is observed for larger spherical Au 57 nanoparticles. In addition, removing or adding one Au atom can alter the electronic properties of Au nanoparticles owing to the strong quantum confinement effect.¹³ Together with Au-58 59 support interactions, these quantum effects are responsible for the unusual catalytic properties 60 of Au which allow Au NPs to activate small molecules such as carbon monoxide at low 61 temperatures. The discovery that very small Au particles, specifically those with sizes smaller 62 than 10 nm, can be a viable catalysts for hydrogenation reactions was a breakthrough in heterogeneous chemistry¹⁴⁻¹⁶. Understanding the mechanisms by which hydrogen can be 63 64 activated on Au is crucial to designing stable and efficient supported Au catalysts for hydrogenation reactions¹⁷⁻¹⁸. 65

66 Generally, hydrogenation reactions on metal surfaces, including Au, follow the Horiuti-Polanyi mechanism that involves the homolytic splitting of a hydrogen molecule adsorbed on 67 68 the metal surface and the sequential transferring of each H atom to the reactive molecule. This 69 critical activation step has been explored using Infra-red (IR), X-ray absorption fine structure 70 (XAFS), and Hydrogen/Deuterium exchange experiments on supported Au NPs^{2,19-21}. By combining theory and experiment, the nature and structure of the active sites responsible for 71 72 the adsorption and dissociation of molecular hydrogen are now well understood. The presence of the low-coordinated atoms located at the corner and edge of the Au particle is necessary for 73 H₂ splitting on Au NPs^{2,19-22}. Hydrogen adsorption is only possible on low coordinated atoms 74 75 whereas AuNPs become repulsive at high coordination numbers (>8). Despite these efforts, 76 some key questions remain concerning the charge transfer between the Au surface and the 77 adsorbed H species, the presence of alternative hydrogen dissociation paths, and the degree of

mobility of H species on the Au NPs²³. The main challenge in using Au for hydrogenation reactions is its low efficiency in dissociating H₂ under standard conditions. The important factors that make bulk Au the most noble metal and ineffective for hydrogen dissociation owe to the largest orbital overlap with the adsorbed hydrogen and highly filled antibonding adsorbate-metal *d* states²⁴.

83 In this Review, we will discuss the main strategies to assess the hydrogenation activity 84 of Au nanoparticles and single atoms. We will focus our discussion on strategies that can 85 enhance Au-H interactions and thus improve the hydrogenation ability of Au. This review reports on hydrogenation and hydroconversion reactions using Au nanoparticles and single 86 87 atoms. Specifically, we highlight the most substantial advances concerning hydrogenation on 88 Au-based catalysts from the last 5 years. Following this, we identify challenges to the design 89 of more efficient Au formulations for the selective hydrogenation processes in heterogeneous 90 and single atom catalysis. Next, we discuss the chemical aspects of the catalytic reaction during 91 the selective hydrogenation process and, finally, the theoretical aspects of hydrogenation on Au 92 surfaces including hydrogen dissociation and transfer. We hope to contribute to advancing the 93 understanding of the relationships between reactions involving H₂ and Au catalysts in the 94 catalysis and materials chemistry communities. 95

96 [H1] Hydrogenations on Au

The fundamental development of Au based catalytic formulations^{18, 25-27} and the 97 enhancement of existing systems²⁸⁻³⁰ require a deep understanding of the impacts of active 98 99 metals, supports, solvents, metal additives, co-catalysts, catalyst preparation methods, and the 100 study of active site. The catalytic performance of Au is substantially improved through the design of multi-phase formulations (bimetallic and promoted Au catalysts) as well as synthesis 101 102 methodologies to enhance the active phase dispersion and modulate the size and localization of 103 Au nanoparticles within a support material. Theoretical investigations have provided insights into the mechanism of H_2 activation, hydride formation,³¹ and the adsorption of the substrates 104 105 on both Au and oxide (playing role of the support) surfaces. Furthermore, these studies have 106 contributed to the understanding of reaction mechanisms in these systems, from homolytic to 107 heterolytic H₂ dissociation (BOX 2).

108 The development of Au catalysts remains hampered by a number of obstacles. For 109 example, the ability to control and tune the chemical composition of Au and Au bimetallic 110 nanoparticles and/or nanoclusters is limited, especially when catalysts are prepared with 111 traditional methods such as co-precipitation or co-impregnation of metal salts. These 112 procedures frequently allow for limited control over the size and uniformity of the particles, 113 leading to the formation of mixed particles that consist of both mono- and bimetallic nanoparticles. Another problem is the deactivation of the catalyst from structure degradation, 114 leaching, and carbon deposition³⁴. The mechanisms underlying the degradation of the catalyst 115 116 performances are still not fully understood and need additional attention to mitigate the 117 deactivation. Finally, various fundamental aspects of the mechanism remain not completely 118 understood, such as kinetic modelling, adsorption geometry and active phase modelling.

119 One motivation behind research into catalysis on Au is the potential to enhance the 120 efficiency of hydrogenation reactions. The design of nanostructured supported Au catalysts 121 allows the development of catalyst systems with high activity and selectivity, and excellent

122 resistance to both chemical and structural degradation. One of the crucial parameters of the 123 catalyst design is the optimisation of the structure of the active sites to enhance catalyst selectivity in hydrogenation reactions¹⁵⁻¹⁶. In addition, while the mechanism of hydrogen 124 125 adsorption on a pure Au surface is well established, the fate of hydrogen species after 126 dissociation from the metal is not completely understood, including the degree of H atom 127 mobility on Au particles²³. Several uncertainities remain around the reactivity of specific Au 128 atoms and the origin of the dissociation (activated or/and spontaneous). Theoretical 129 investigations have helped to develop more efficient Au-based catalysts for hydrogenations, 130 such as open surfaces as Au(100) and low coordinated sites (edges or defects) that enhance the 131 Au activity 35 .

132 A fundamental understanding of the interactions of hydrogen with Au as well as those 133 between the Au-ligand and Au-support are necessary to rationalize the performance of the 134 catalysts, from the nano to the single-atom catalysts (SACs) level³⁶⁻³⁸. For example, in the semihydrogenation of alkynes, Au was predicted to exhibit a higher selectivity to alkenes than 135 Pd by Density Functional Theory (DFT) and it was also confirmed experimentally³⁵. In 136 137 hydrogenation on Pd catalysts, both triple and double C-C bonds are adsorbed at the same rate 138 and thus the competition between both types of bonds occurs resulting in a mix of products³⁵. 139 Conversely, the triple C–C bonds of alkynes are preferentially adsorbed and are subsequently activated on Au³⁵. That is to say that triple C–C bonds can be preferentially hydrogenated and 140 141 the alkene products can desorb from the Au surface avoiding further hydrogenation³⁵. This high chemoselectivity of supported small Au nanoparticles enabled the hydrogenation of α , β -142 unsaturated aldehydes to the corresponding unsaturated alcohols³⁹⁻⁴⁰, and the deprotection of 143 epoxides via deoxygenation to the corresponding alkenes⁴¹, in both cases preserving the C=C 144 145 bonds.

146

147 [H1] Improving Au-hydrogen interactions

148 The activation of hydrogen on Au (leading to its dissociation) is considered the rate-149 determining step in Au-catalyzed hydrogenations²⁴. In this context, several strategies have been 150 developed to enhance the rate of H₂ dissociation to improve the catalytic efficiency of supported Au catalysts (Figure 1). The main approaches are the heterolytic hydrogen dissociation 151 152 occurring on Au interacting with nitrogen-containing ligands⁴² (Figure 1a) or at the metalsupport interface in case of strong metal support interactions (SMSI)⁴³ (Figure 1b). H₂ 153 dissociation could be also induced by hot electrons generated by plasmon enhancement⁴⁴ 154 (Figure 1c) or at single Au atoms (Figure 1d)⁴⁵, as well as by alloying gold with a second metal 155 156 as schematically represented on Figure 1f. Here, we discuss the most important approaches to 157 enhance the reactivity of Au on hydrogenations.

158 159

[H2] Ligands

Auxiliary ligands can help to enhance selectivity in heterogeneous catalysis. In hydrogenation on Au NPs, the addition of certain ligands has demonstrated enhanced activity in the selective hydrogenation of alkynes to *cis*-alkenes (**Figure 2a**). An inactive silica-supported Au nanoparticle catalyst (Au/SiO₂) exhibited a substantial increase of activity in the presence of various nitrogen-containing ligands⁴². In the presence of piperazine, for example, the Au catalyst gained activity and selectivity to the alkene, even when allowed to continue to full

166 conversion (Figure 2b), where most catalysts lose selectivity. Ligands with two nitrogen donors 167 were more capable at decreasing the energy barrier (activation energy) for the heterolytic 168 dissociation of H₂ and improved the Au hydrogenation reaction rate (Figure 2d). Ligands with 169 only one nitrogen donor (red squares in Figure 2d), such as pyrazine, are capable of splitting 170 H₂, but do not show the same catalytic performance, because they easily leave the Au surface 171 after protonation and do not complete the H-transfer steps required to complete the catalyst 172 cycle. According to DFT studies, the ligand-Au interface is responsible for the H₂ dissociation 173 through a heterolytic mechanism. First, the H₂ molecule approaches the ligand–Au interface. 174 The H₂ molecule is cleaved heterolytically, the proton is transferred to the amine ligand, 175 forming a quaternary N center, and the hydride goes to the Au surface. Then, the H species 176 adsorbed on Au can be transferred to the adsorbed alkyne. The catalytic cycle is completed after 177 the proton transfer from the ligand to the organic moiety, which regenerates the amine ligand, 178 followed by desorption of the alkene. A number of experimental parameters needed to be 179 optimized to achieve an effective hydrogenation reaction. This included identifying a ligand 180 with optimal basicity for the lowest input energy for hydrogen activation, that did not bind too 181 strongly preventing blocking of the catalyst site, and also did not cause metal leaching that affected the stability of the Au surface⁴². Piperazine was selected as the best ligand, among 182 nineteen amines tested, to promote the catalytic hydrogenation of alkynes on Au NP catalyst⁴². 183 The Au-ligand catalytic system can be considered a frustrated Lewis pairs (FLP) analogue⁴⁶. 184 185 Other studies in the literature showed similar observations when combining Au NPs either with other nitrogen-containing⁴⁷⁻⁴⁸ and phosphorous-containing⁴⁹ ligands for hydrogenations. 186

187 It is noteworthy that the presence of nitrogen atoms in graphitic carbon materials (N-doped 188 carbon) prepared through 1,10-phenanthroline pyrolysis has shown a similar effect reported 189 above on the properties of Au nanoparticle catalysts, specifically in catalytic hydrogenation 190 reactions. The basic N atoms of the carbon support play an importan role for the hydrogen 191 activation (in heterolytic mode) at the Au-N-doped carbon interface. In this context, Au 192 nanoparticles coated with N-doped carbon materials supported on titania (Au@N-doped 193 C/TiO₂) showed an enhanced catalytic activity (Figure 2c) when compared to uncoated Au/TiO₂ for alkyne semihydrogenation⁴⁷. The main advantage compared to the previous study, 194 195 is that the catalyst is fully heterogeneous, meaning it can be reused and the products easily 196 separated by filtration. The nitrogen atoms present in the carbon material are part of the 197 catalyst's composition and do not need to be added, as external ligands, like in the previous 198 study⁵. A combination of experimental and computational studies revealed a N-assisted 199 heterolytic H₂ activation mechanism (Figures 2e). The creation of an interface that mimicked 200 the N-doped (pyridinic) graphene-like sheets experimentally observed after pyrolysis, revealed 201 a behaviour similar to an FLP that enables a essentially barrierless heterolytic dissociation of 202 H₂ (Figure 2e, TS-C). The FLP is formed due to the absence of a direct interaction between Au 203 and the lone pair of the nitrogen, allowing a unique interface that promotes the heterolytic 204 cleavage of H2⁴⁷. Then, the catalytic cycle is completed by two H-transfer steps (Figure 2e, TS-205 D and TS-E) and product desorption, closing the catalytic cycle and regenerating the initial species A. The mechanism illustrates the major role of N-heteroatoms on the H₂ activation. 206

In another example, verified by DFT calculations, Lewis bases, such as NH₃, adsorbed on four
different models for Au surfaces and clusters (Au(111)-close-packed, Au(211)-step-edged,
Au(111)-single atom, and Au₃₈ cluster) were able to generate hydrides (H*) and protons (NH₄*)

through heterolytic H₂ dissociation. The generated hydride and proton can then be concertedly transferred to CO₂ to produce formic acid in all four Au models⁵⁰. The cooperation between Au and adsorbed basic ligands has also been employed in the hydrogenation of other organic molecules, including quinolines⁵¹, imines or nitriles⁴⁸ and aldehydes⁵²⁻⁵³.

214 215

216

[H2] Au-support interactions

217 Another strategy to enhance the hydrogenation activity of Au is to exploit strong metal-218 support interactions (SMSIs). SMSIs refer to the interactions that occur between metal 219 nanoparticles or atoms and the support material in heterogeneous catalysts²⁹⁻³⁰. These 220 interactions play a critical role in the performance and stability of the catalysts and are 221 particularly important for catalysts supported on oxides, such as SiO₂, Al₂O₃, or TiO₂. In 222 catalysis, SMSIs can lead to several effects such as promotion of the dispersion of metal 223 nanoparticles on the support, preventing their aggregation and leading to a higher surface area 224 and more active sites. They enhance the stability of the metal nanoparticles on the support, 225 preventing their sintering or leaching during the catalytic process³⁰. In addition, SMSIs can influence the adsorption and activation of reactant molecules, affecting the selectivity of the 226 227 catalytic reaction. Thus, by exploting SMSIs, the support stabilizes heterolytically dissociated 228 hydrogen. This outcome arises from the intimate proximity between the support and the metal 229 catalyst (Figure 1b), fostering charge redistribution and electronic polarization. In 230 hydrogenations, these factors collectively contribute to the enhanced stability of the dissociated 231 hydrogen species. Compared to homolytic dissociation, heterolytic dissociation is much more 232 energy intense, as determined experimentally $(4.52 \text{ eV vs } 17.36 \text{ eV})^{54-55}$. Thus, the extra energy 233 needs must be compensated via the creation of new bonds, setting a minimum level of charge 234 separation for the process to occur efficiently⁵⁴. The interface of the oxide support can help to enhance this heterolytic process^{43, 56}. An illustration of this concept can be observed in the case 235 236 of $TiO_2(110)$, where the presence of low coordinated O_2 atoms adjacent to the Au clusters has 237 been observed. This arrangement has the potential to facilitate the dissociation of molecular H₂, 238 leading to the protonation of the oxygen atoms situated on the support 56 .

In contrast, the Au SACs supported in electron-rich cavities of N-doped carbon (such as graphitic carbon nitride obtained by the pyrolysis of organic amines– C₃N₄) dissociate H₂ homolytically⁴⁵. The catalyst was suggested by DFT to be composed of Au^{δ +} (1< δ <3) species stabilized in oxidized-4-pyridine cavities from the N-doped carbon. The developed catalyst led to thermodynamically more favored H₂ activation than the stepped surface Au(211) (-1.13 eV versus -0.17 eV, respectively).

245 The structure-sensitivity (the kinetics is dependent on the particle size due to changes in 246 the coordination of surface atoms with particle size) of Au can also promote catalysts. Small 247 Au NPs supported on TiO₂ of around 3 nm exhibited a higher selectivity to 3-vinylaniline (78%, 248 side product being 3-ethylnitrobenzene with 16%) than the those of 9 nm (39% of 3-vinylaniline 249 and 51% of 3-ethylnitrobenzene) in the hydrogenation of 3-nitrostyrene. In addition, a model catalyst containing both Au particle sizes (3 nm and 9 nm) showed a moderate selectivity to 3-250 251 vinylaniline (55%) at relatively high conversion $(25\%)^{57}$. Nevertheless, the application of a 252 reduction process to the Au catalysts resulted in an enhanced selectivity for both particle sizes. 253 In both cases, with particle sizes of 3 nm and 9 nm, the selectivity surpassed 95% after the 254 reduction process. The main difference was that the catalyst with the larger Au nanoparticles (~9 nm) exhibited a substantially lower conversion (14.9%) than the catalyst with 3 nm Au NPs 255 256 (or combination of 3 and 9 nm, 15.4 and 24.8% respectively) which maintained a high 257 conversion level⁵⁷. By characterizing the catalysts by high resolution transmission electron 258 microscopy (HRTEM), it was found that the catalyst with the larger Au nanoparticles (9 nm) 259 had a larger degree of encapsulation, which reduced the catalytic activity. For smaller Au 260 nanoparticles, only partial encapsulation was observed. This was explained by the surface tensions of the metal and support during the encapsulation process⁵⁷. Typically, the metal has 261 a higher surface tension than the TiO_2 support, which is often observed experimentally. In the 262 263 case of Au, its relatively low surface tension ($\gamma Au = 1.51 \text{ Jm}^{-2}$) has been considered as a hindrance for the formation of SMSIs⁵⁷. Recent discoveries of SMSIs in TiO₂ supported Au 264 265 catalysts have challenged the previously reported surface tension of TiO₂ ($1.3-1.9 \text{ Jm}^{-2}$) and 266 raised questions about its potential overestimation⁵⁸. This opens up the possibility that Au may possess a higher surface tension than TiO₂, allowing it to be wetted by TiO₂, and leading to the 267 268 encapsulation of Au nanoparticles as a result of the minimization of their surface free energy. 269 Furthermore, at the nanoscale, the size-dependence of surface tension plays a significant role. 270 While both positive and negative correlations between surface tension and particle size have 271 been observed, a positive correlation is more likely at high temperatures owing to the non-272 negligible contribution of surface entropy. A higher degree of encapsulation can be obtained 273 for larger Au nanoparticles because their higher surface energy facilitates their wetting by 274 TiO_2^{57} .

275 An alternative strategy to enhance the hydrogenation activity of Au uses uniform Au 276 NPs decorated with carbon atoms. Located in the interstitial positions in the lattice, carbon 277 atoms can strongly affect the electronic properties of Au. The Au NP catalytic performance was 278 investigated using synthesized Au interstitial nanocatalysts supported on ordered mesoporous 279 carbonaceous materials (C-Au/OMC) and commercial catalysts (Au supported on SiO2 and 280 activated carbon)⁵⁹. The material with interstitial carbon species showed an improved catalytic 281 performance and a high selectivity (well beyond 99%) compared to commercial catalysts. To 282 understand the observed catalytic trend, DFT and XPS studies were carried out. The presence 283 of interstitial C enables the activation of H₂ molecules. Specifically, the electron transfer 284 between C and Au leads to the heterolytic dissociation of H₂ on the C-Au interface. The unique adsorption configuration of C-Au further influences the chemisorption process due to its 285 286 distinct electronic properties. This selective adsorption and activation of H₂ on Au surfaces 287 containing interstitial C, as compared to pure surfaces, explains the remarkable 288 chemoselectivity observed for the C-Au/OMC catalysts when compared to commercial Au/C and Au/SiO₂ catalysts⁵⁹. Additionally, there may be a continuous exchange of C atoms between 289 290 the surface and subsurface, potentially facilitating the adsorption of H₂ molecules. Moreover, 291 in case of the 3-nitrostyrene hydrogenation on Au supported mesoporous carbon catalysts high chemoselectivity to 3-vinylaniline was observed⁵⁹. This was attributed to the perpendicular 292 293 adsorption of the substrate, stronger interaction of the 3-nitrostyrene with the C containg Au 294 surface and its enhanced activation on it. It was concluded that the high d-electron transfer from 295 C to Au due to the C-Au interactions promotes the activation of the 3-nitrostyrene on the C-Au 296 interface. This enhanced H₂ dissociation improved the catalytic performance of the Au NPs in 297 hydrogenation reactions⁵⁹.

298

299 [H2] Plasmon enhancement

300 Exploiting the plasmonic properties of Au NPs (localized surface plasmons, LSPR) is an alternative strategy to activate $H_2^{23,44,60}$. Here, hot electrons are formed from light 301 illumination which then relax or scatter, initiating the catalytic hydrogenation reaction. Hot 302 303 electrons are high-energy electrons produced through the interaction of light with metallic 304 nanoparticles or nanostructures, and are being explored in new and exciting applications within 305 nanotechnology and photonics. For catalysis, using hot electrons decreases the energy barrier 306 for H–H activation owing to the transfer of electrons to the antibonding orbital of hydrogen⁴⁴. 307 Hot electrons induced dissociation of hydrogen on small Au particles. When a Au NP is exposed 308 to light with sufficient energy (e.g., visible light), absorbed photons excite electrons in the Au 309 to higher energy levels. These hot electrons have excess energy compared to the equilibrium 310 Fermi level of Au. This excess energy can be transferred to hydrogen molecule and provide the 311 activation energy required to activate H₂ molecules. Small Au supported on SiO₂ nanoparticles 312 prepared by chemical deposition precipitation method were used in H₂ dissociation experiments 313 (Figures 3a-c). Figure 3a illustrates the rate of H–D formation on the Au/SiO₂ photocatalyst 314 both with and without supercontinuum laser excitation. Initially, the photocatalyst was 315 maintained in the dark at 22–24 °C, yielding a constant background H–D level (Figure 3a)⁶⁰. 316 Upon laser activation, the rate of H–D generation immediately surged by approximately 150 317 times. This heightened rate stabilized within 10 minutes of laser stimulation. Concurrently, the 318 sample's temperature rose by roughly 8 °C (up to 30°C) due to laser-induced heating (Figure 319 **3a**). After 10 minutes, the laser was deactivated, promptly restoring the system to its initial rate and temperature, showcasing the process' reversibility⁶⁰. For a direct comparison of H_2 320 321 dissociation efficiency between the Au/SiO₂ and Au/TiO₂ photocatalysts, Figures 3b and 3c 322 display the monitored photocatalytic H–D formation rates for both catalysts. In contrast to the 323 approximately 150-fold increase observed for Au/SiO₂ (Figure 3b), the enhancement in the 324 case of Au/TiO₂ (Figure 3c) was modest, measuring around 2.7 times. The subdued rate for 325 Au/TiO₂ may be attributed to the formation of a Schottky barrier (with a nominal height of 326 0.8-1 eV) at the Au-TiO₂ metal-semiconductor junction. During laser excitation, hot electrons 327 possessing energies surpassing the barrier's height can effectively transfer from the Au 328 nanoparticles to the TiO₂, contributing to the observed effects⁶⁰. As the rate of hydrogen 329 dissociation decreased substantially when SiO₂ was replaced by TiO₂, (Figures 3b-c) indicates 330 that H₂ dissociation occurring on the illuminated AuNP surface and the dielectric oxide is not participating in the process.⁶⁰ A key challenge remains in the diffusion of hydrogen through the 331 support and its recombination, which is essential to understanding the activity of hydrogen on 332 333 a Au surface. The redshift in the Localized Surface Plasmon Resonance (LSPR) of Au 334 nanoparticles is attributed to the charge transfer between Au and hydrogen atoms during 335 hydrogen adsorption and diffusion. The charge transfer induces alterations in the properties of 336 the Au nanoparticles, causing a redshift in the LSPR. The observed red-shifted intensities are 337 closely linked to variations in the sizes of the Au nanoparticles, suggesting that hydrogen atoms 338 predominantly adhere to specific facets or flat surfaces of the Au particles. H atoms may also 339 recombine at this site and desorb into the gas phase again²³. The measured LSPR shifts was of about 0.02 nm during H₂ adsorption (as messured by Transmittance Anisotropy 340

Spectroscopy)²³. Hydrogen chemisorption occurred directly on Au. Furthermore, the 341 342 relationship between the redshift intensity and the size of nanoparticles indicates that 343 dissociated hydrogen (H) atoms migrate across the NP surfaces, predominantly on the (100) 344 facets. These atoms subsequently recombine and desorb into the gas phase. Under atmospheric 345 pressure of H₂, an average negative charge transfer of approximately -0.06 electron charge units 346 from each surface Au atom to hydrogen (H) occurs, with a localized charge back-bonding 347 estimated to be around -0.2 electron charge units for each Au-H bond. Consequently, these 348 results confirmed, in line with theoretical studies, that after H adsorption the electron population in Au nanoparticles decreases²³. This enhanced comprehension of the chemisorption 349 mechanism of H₂ onto Au NPs is anticipated to facilitate advancements in the fabrication and 350 351 utilization of catalytic Au NPs for hydrogenation reactions²³.

352 In photocatalytic reactions, Au NPs have exhibited unique catalytic properties, even at 353 low temperatures or low light intensity. This suggests that the use of Au photocatalysts in chemical reactions governed by mechanisms involving plasmonic effects and hot electron 354 transfer may also be advantageous $^{61-63}$. This is espacilly true for hydrogenation reactions were 355 356 the hydrogen dissociation is often one of the limiting steps, as discussed above in the case of 357 the photocatalytic hydrogen dissociation and H-D formation. The hot electrons transferred to 358 H₂ were vital for high yields and the plasmon decay substantially lowered the energy barrier for hydrogen dissociation⁶⁰. Moreover, the dissociation of H₂ on the Au surface under visible light 359 360 excitation opens up the possibility of developing more effcient catalysts for the hydrogenation 361 processes. For example, increased chemoselectivity was reported for the semi-hydrogenation 362 of phenylacetylene under visible light irradiation using a nano-designed hybrid catalyst 363 composed of plasmonic core (Au or bimetallic Au@Ag) and Pt shells compared to classical Au 364 supported SiO₂ catalysts⁶⁴.

To increase the catalytic performance of non-plasmonic metals like Pt, a successful 365 366 integration of plasmonic and catalytic properties is required. The most widely used approach to 367 achieve this is by harnessing the hot carriers generated through LSPR excitation. These hot 368 carriers play a pivotal role in enhancing the catalytic activity of the material. Au NPs supported 369 on SiO₂ and TiO₂ showed both negative (reduced reaction rate) and positive (catalytic 370 enhancement) effects for 4-nitrophenol hydrogenation under visible-light illumination. The difference in plasmonic catalytic activities⁶⁵ were attributed to the charge transfer at the 371 372 interface of Au and the support as well as to the reducing agent (H₂ and NaBH₄) used during 373 the catalyst synthesis. Au/SiO₂ NPs were substantially more active under plasmon excitation, 374 while Au/TiO₂ catalysts were only enhanced by plasmons when H₂(g) was used as reductor. 375 Reduced reaction rate observed upon reduction with BH4 (aq) was attributed to the transfer of 376 hot electrons from Au to TiO₂.

377 378

[H2] Cationic Au

An alternative approach for improving the activation of hydrogen is by using dispersed cationic Au species, in which isolated Au ions are dispersed throughout a carrier. The synthesis of these type of material is not trivial and usually requires several steps as illustrated in **Figure 4a**. In case of gold supported on carbon nitride two most important steps are linked to the thermal treatment, firstly at low (686°C) and then at high temperature above 1246°C (**Figure 4a**). This structure resembles traditional organometallic catalysts⁶⁶⁻⁷¹, comprising isolated 385 metals that are bonded to organic ligands (Figure 4b and Figure 1e). These structures are also described as single-atom catalysts (SACs), which are attracting growing interest because they 386 387 can make better use of the metal phase compared to standard metal nanoparticles, and have 388 provided excellent levels of selectivity, activity, stability in hydrogenations⁷²⁻⁷⁶. Cationic Au 389 single-atom catalyst (Au SACs) decorated on multiwalled carbon nanotubes provided a highly 390 efficient hydrogenation of 1,3-butadiene and 1-butyne under parahydrogen (an isomeric form 391 of molecular hydrogen)⁷⁷. Atomically dispersed Au catalyst provided a better selectivity and 392 activity in the pairwise addition of hydrogen than the supported Au NPs catalysts. Similarly, 393 isolated Au species (Au⁺) supported on iron oxide (FeO_x) showed higher resistance to sintering 394 (increase of the particle size) compared to other Au nanostructures for alkene hydrogenations⁷⁸⁻ 395 ⁸². Theoretical studies revealed that surface-anchored Au^+ species provided very high stability 396 and improved catalytic activity compared to other Au nanoparticle catalysts, because of the 397 covalent Au-support interactions. For example, a supported Au(III) species anchored on the MgO surface induced high activity and selectivity in ethene hydrogenation⁷⁹. The conversion 398 399 of ethene strongly depended on Au-Au coordination number (Figure 4c). The Au NPs were 400 less efficient catalysts for ethene hydrogenation than Au SACs, and the atomic dispersion of 401 the active phase (in SACs) was beneficial to drive the hydrogenation catalysis⁷⁹.

402 The developments in SAC design were made possible by advances in atomic-resolution 403 microscopy that can image the dispersed metal atoms and their evolution under reaction conditions⁸³⁻⁸⁴. However, the practical use of Au SACs is often compromised by challenging 404 405 synthesis protocols, including the use of aqua regia as a dispersing agent, as well as low 406 resistance to sintering for non-functionalized carbon materials under reaction conditions⁴³. To 407 address the difficulty of making such materials, a co-precipitation strategy can be applied⁸⁵. 408 Here, the metal is added during synthesis of the metallic organic framework (MOF) precursors, 409 intercalated through the layers via electrostatic surface interactions replacing anions present in 410 the MOF structures (for exemple sulfate ion). The positively charged Au atoms were detected 411 using high-angle annular dark-field STEM imaging (HAADF-STEM) and extended x-ray 412 absorption fine structure (EXAFS) measurements. This approach draws analogy with the 413 copolymerization route used for the immobilization of isolated atoms on graphitic C₃N₄⁸⁶⁻⁸⁷. 414 Au-SACs prepared by co-precipitation methods were tested in the hydrogenation of p-415 nitrophenol to *p*-aminophenol and showed improved activity compared to classically prepared MOFs⁸⁵. In addition, after 10 catalytic cycles, the catalyst retained its original morphology and 416 417 activity, indicating an excellent stability.⁸⁵

418 A kg-scale synthesis of Au₁/CeO₂ SAC was reported using a dry ball milling synthetic 419 protocol⁸⁸. This catalyst was then tested in the hydrogen oxidation (1 vol% H₂ + 1 vol% O₂ 420 balanced with He). In the latter, the catalyst showed only ~10% of hydrogen conversion at 160 421 $^{\circ}C^{88}$. Despite a modest yield, this approach demonstrates that a proof of concept that noble 422 metal supported SACs can be prepared at large scale using a facile and reproducible 423 methodology.

424 [H2] Alloying and bimetallic synergy

Hydrogen dissociation can also be improved by exploiting Au alloying to generate
weakly bound H atoms ⁸⁹⁻⁹¹. Ideally, an alloy structure (**BOX 3**) should effectively combine
one metal (Pt-group metals and metals in the Pd and Pt triads especially) that promotes

428 hydrogen dissociation and another (Au, Cu or Ag) that can react with the dissociated H atoms and therefore promote hydrogenation¹⁰⁴⁻¹⁰⁵. The most promising bimetallic catalysts for 429 430 processes involving hydrogen are Au-Pd nanoparticles in either an alloy where the two 431 different metals are homogeneously arranged or in a core-shell structure when one metal is at the core and the second metal forms the shell¹⁰⁶. The optimal ensemble configuration for 432 433 heterolytic H₂ activation remains up for debate. In Au-Pd alloys with a controlled density of 434 Pd atom ensembles in the surface (monomers, dimers, trimers) the presence of neighboring Pd 435 atoms is crucial for hydrogen activation. That is, the ensemble must be at least a dimer as Pd 436 monomers are not able to adsorb hydrogen¹⁰⁷.

437 It is important to identify the sites responsible for the activation of H₂ in Au–Pd alloyed 438 systems. This facilitates not only the identification of the minimal Pd ensemble (quantity of Pd 439 needed to catalyse a reaction with optimal efficiency) for the activation of H₂ but also to reveal 440 the energy profile for the spillover and release of hydrogen. The hydrogen spillover effect 441 (HSPE) is an interfacial phenomenon in which active H atoms generated by the dissociation of 442 H₂ on one phase (metal surface) migrate to another phase (support surface) and participate in 443 the catalytic reaction of the substance adsorbed on that site. By modelling Au-Pd systems, it 444 was anticipated that Pd atoms in a (111) surface of Au could activate H2⁹⁴. By combining TPD 445 and high-resolution STEM it was shown that the a low number of isolated atoms of Pd are 446 responsible for hydrogen dissociation. The quantity of surface atoms of Pd in Au reflects the 447 number of H atoms adsorbed on the surface. Further TPD-H-D exchange and DFT studies 448 provided the energetic landscape for the adsorption of H₂ including an understanding of the 449 activation and desorption of hydrogen from isolated Pd atoms, the typical reaction pathway for 450 activating H₂ and the mechanism of the release of hydrogen along the Pd atoms with minimum 451 spillover of hydrogen species to the Au⁹⁵.

452 Using spatially resolved tip-enhanced Raman spectroscopy (TERS)¹⁰⁸⁻¹¹⁰, a study of the catalytic hydrogenation of chloronitrobenzenethiol to chloroaminobenzenethiol (Figure 5a) 453 over Au–Pd catalyst was carried out¹¹⁰ (Figures 5 a-f). TERS studies the topography and 454 455 chemical composition of a surface with high accuracy and an excellent resolution of ~10 nm. 456 To gain a more comprehensive understanding of the chloronitrobenzenethiol hydrogenation 457 process, a quantitative characterization of the relationship between the active regions (blue regions on Figures 5 c and e) and surface structures was conducted¹¹⁰. In Figures 5 d and f, 458 459 two distinct regions, each measuring 100 nm in width, featuring Pd islands (Figure 5d) and Au 460 craters (Figure 5f) in the TERS maps are represented. Co-localized scanning tunneling 461 microscopy (STM) images with accompanying height profiles are also given (as inserts in 462 Figure 5d and f). In these representations, the active region is highlighted in light blue, while 463 the non-reactive region is depicted in light red. In the case of Pd_{LC}/Au (Au surface with low Pd 464 coverage, Figure 5c and d), the size of the active regions, is approximately 50 nm¹¹⁰. However, 465 the size of the Pd islands within both regions measures only 20 nm. Conversely, for Pd_{HC}/Au 466 (Au surface with high Pd coverage, Figure 5e and f), the active regions are approximately 15 467 nm larger than the Pd layer itself. The results reveal that the active regions extend approximately 15-30 nm beyond the boundaries of the Pd areas, where hydrogenation reactions occur. These 468 469 spillover regions, however, exhibit an asymmetrical relationship with the shape of the Pd 470 islands (Figure 5c)¹¹⁰. The obtained results revealed that hydrogenation takes place beyond the 471 Pd active sites and was initiated by the spilt-over hydrogen dissociated on Pd. After dissociation on Pd, hydrogen atoms migrated to adjacent Au surfaces over relatively long distance of 15-30
nm¹¹⁰. The mechanism of this hydrogenation involving hydrogen spillover was also determined
by DFT and confirmed the feasibility of the long-distance diffusion and explained the enhanced
chemoselectivity to the reactant in the Au–Pd bimetallic.

- 476 Single-atom alloys (SAAs) are a class of single-site catalysts in which small amounts of isolated metal atoms are present in the surface layer of a metal play the role of the host¹⁰⁴⁻¹⁰⁵, 477 ¹¹¹⁻¹¹². Typically, SAAs are comprised of single atoms of a catalytically active metal alloyed 478 479 into the surface of a less reactive host metal. For example, for the hydrogenation of butadiene 480 to butene, hydrogen is dissociated at isolated metal sites, for example Pt, and the hydrogen 481 atoms spill over onto the host metal, such as Cu, where the reactant (butadiene) reacts to 482 form the product (butene). This then desorbs prior to complete hydrogenation, demonstrating 483 the chemoselectivity of this catalyst¹⁰⁵. Such materials have also drawn interest owing to their 484 potential to break linear scaling relationships in alloy catalysis. Under standard conditions (low 485 temperature) Au is not able to activate hydrogen, however using SAAs of Au, highly selective 486 hydrogenation reactions are enabled, such as selective hydrogenation of 1-hexyne to 1-hexene 487 using Au-Pd SAA catalyst (Figure 5 g and h). The facile activation of hydrogen on Pd is 488 possible using Au–Pd SAAs, where Au is incapable of dissociating molecular hydrogen¹¹². To 489 overcome this limitation, addition of small amounts of Pd to form a Au-Pd SAA has been 490 reported to activate molecular hydrogen, although the dissociated hydrogen does not spill over 491 onto the Au host¹¹¹. In operando spectroscopy studies confirmed that the transformation occurs 492 by first dissociating H₂ and splitting of the hydrogen species on the Pd sites followed by the reaction of the adsorbed H species on Au¹¹¹. Moreover, by DFT studies performed on Pd-493 494 Au(111) surface, it was shown that C atom is bound to the Pd atom. Because the H atom is also 495 bound more strongly to the Pd atom, it is more kinetically favorable to hydrogenate this mid-496 compound C atom than a terminal C atom. This considerably limits over-hydrogenation and 497 oligomerization side reactions.
- 498 In bimetallic nanoparticles the chemical composition and order affect the catalytic properties of bimetallic systems¹¹³. The incorporation of a second metal can help to overcome 499 500 the limitations observed for monometallic nanoparticles such as redox properties, stability and 501 substrate adsorption. DFT predicted that by overcoming the size dependent relationship on 502 monometallic Pt catalysts, a monolayer of Pt and Au catalyst would lead to higher activity as well as higher chemoselectivity in the hydrogenation of halonitrobenzenes²⁶. As such, an 503 504 Au@Pt/SiO₂ core-shell structure with a monolayer (ML) Pt shell was prepared using atomic 505 layer deposition (ALD) methodology. In addition, the catalytic activity of a range of bimetallic 506 Au-Pt catalysts using 0.5, 1 and 2 ML Pt shells, with 1 ML of Pt shell (Figure 6a) were compared in terms of the selectivity to *para*-chloroaniline²⁶ (Figures 6b). The core-shell 507 508 structure was confirmed using high resolution microscopy (Figure 6c) and reveled the Pt shell 509 thicknes of about 0.3 nm (blue line in Figure 6c) in case of Au@1ML-Pt catalyst. The 510 Au@Pt/SiO₂ catalyst exhibited a high catalytic activity (Figure 6b) owing to the enhanced 511 charge transfer between Au and Pt atoms facilitated by the substantial ligand effect. The ligand effect can have a profound impact on the catalytic activity and specificity of the catalyst as the 512 513 ligands can bind to the metal surface, and significantly modify its electronic and steric 514 properties. The DFT studies also confirmed the terrace sites responsible for high selectivity 515 were preserved²⁶, which improves the stability of the catalyst. These flat nanoparticle surface

516 regions with regularly arranged atoms play a vital role in catalysis by providing stable and well-517 defined surfaces for chemical reactions. Finally, the catalyst presented high stability compared 518 to the monometallic Pt catalyst, that generally suffers from the agglomeration and leaching of 519 Pt particles and chlorine poisoning²⁵.

520 Au-based bimetallic catalysts were also shown to possess excellent CO₂ hydrogenation 521 activity, forming CO. For example, Ni-Au bimetallic catalytic systems based on core-shell structure are very active in this reaction¹⁰² (**Figure 6d**). SiO₂ was chosen as a support of the 522 523 core-shell nanoparticles, consisted of a fcc (face centered cubic structure in which atoms are 524 arranged at the corners and center of each cube face of the cell) Ni core and Au shell formed by 525 2-3 atomic layers (Figure 6d).-Catalytic studies showed the Ni-Au bimetallic catalyst provided 526 a high selectivity to CO (95%) with a conversion of 4.5-18% in the temperature range of 340-600 °C¹⁰² (Figure 6e). Ex situ STEM characterization showed the presence of core-shell 527 528 structure, with an ultrathin Au shell. However, during *in situ* STEM imaging, a phase transition 529 was observed with the creation of a new Au-Ni alloy phase at similar reaction temperatures. In 530 addition, in situ TEM analysis revealed that during the heat treatment from 450- 600 °C the Au 531 species at the outmost surface were dissolved in the Ni matrix forming an alloy¹⁰² (Figure 6d, top part). However, during the cooling process to 450°C, the dealloying process occurred and 532 533 Ni@Au core shell structure was recovered (Figure 6d, bottom part). Control experiments 534 carried out in a gas-cell reactor minimized the 'pressure gap' observed between the in situ 535 environmental TEM measurements (~9 mbar) and the actual reaction conditions (1 bar) and 536 reproduced the reaction-driven alloying of Au-Ni NPs, which confirmed the credibility of their 537 original TEM results. Finally, DFT calculations confirmed the most energetically favoured 538 reaction pathway, which consisted of two stages. The first was CO₂ hydrogenation to form 539 adsorbed CO and the second was the diffusion of CO adsorbed on Ni to the Au sites and finally 540 the desorption of CO (Figure 6f). These results confirmed that the Ni active sites were 541 responsible for the CO₂ hydrogenation and the Au active site for the high selectivity CO 542 formation¹⁰². These results confirmed the alloying-dealloying mechanism occurred in the 543 bimetallic Au-Ni systems. This is also the case of Au-Pd alloys. Pretreatment in oxygen leads 544 enhances the activity in dilute Au–Pd alloys by bringing Pd to the surface of the Au particle. In 545 the contrary, during the hydrogen treatment the Pd returns to the bulk and the catalyst suffers from deactivation⁹⁶⁻⁹⁷. 546

547

548 [H1] Conclusion and Outlook

549 Au-based nanomaterials remain promising catalysts for selective hydrogenation 550 reactions. The hydrogen activation pathway can be promoted in catalytic hydrogenations in four 551 ways: assistance from light, the size of the metal nanoparticles, the Au-support interaction, and 552 the presence of ligands or modifiers on the metal surface. Additionally, exploring the two 553 activation modes (homolytic scission to H atoms or heterolytic scission into H^+/H^- pairs) in turn 554 can make these catalytic processes more efficient. For example, to perform selective 555 hydrogenations, organic linkers must be present on the Au surface to promote heterolytic 556 scission.

557 Two key challenges in the development of Au-based nanomaterials for hydrogenation 558 catalysts are the need to control the sintering of the Au species during reaction as well as the 559 low solvent tolerance of these catalysts. Research continues in the search for appropriate 560 promoters and components able to enhance the catalytic activity of supported Au catalysts. The choice of promoter depends on the specific catalytic reaction and the desired enhancement in 561 562 catalytic properties. Promoters play a crucial role in tailoring the activity, selectivity, and 563 stability of Au nanoparticles for various applications in catalysis. Some of most important being 564 organic ligands, sulfur containing species, metals and oxides (especially for core-shell 565 structures). Moreover, shifting from neutral Au nanoparticles to cationic Au single atoms 566 appears to improve the catalysts durability and open new pathways for the regeneration of the catalysts¹¹⁴. 567

Another important challenge will be the use of hybrid catalysts mixing single atoms and nanoscale particles¹¹⁵⁻¹¹⁷. In this case, cascade reactions may be performed or the reaction rate can be substantially improved. This could be a useful parameter to explore in reactions involving hydrogen as the hydrogen dissociation and reactivity strongly depends on the size of the Au particle.

573 Finally, we need an improved fundamental understanding of the hydrogenation mechanisms as this should provide information for the rational design of new Au catalysts. To 574 575 better understand the catalyst reduction process, and the nature and formation of intermediates, 576 advanced in-situ characterization techniques will be required. The main issues are still linked 577 to the very small size of acive Au species. The use of synchrotron facilities is required to fully 578 characterize these materials. However, these facilities are in high demand among researchers 579 from various scientific disciplines, including physics, chemistry or materials science. In situ 580 techniques are also challenging as very often these experiments require extended setup and data 581 collection times owing to their complexity. A crucial factor often neglected is also the very first 582 atomic layer in case of bimetallic nanoparticles. Probing the core and surface composition of 583 nanoalloys to rationalize their selectivity is of high importance for understanding their catalytic 584 selectivity. Characterization methodology must be developed to distinguish between the surface 585 and core composition. Identification of the optimal balance between the two metals will help to 586 tune the relative rates of various reaction pathways and, consequently, control the selectivity of 587 the catalytic process. A combination of experimental analysis and DFT simulations will also be 588 required to understand the adsorption-desorption process and the selectivity path to a specific 589 product.

590 In summary, by adopting a multidisciplinary approach (material sciences, physics, 591 chemistry, biology, and engineering) as well as leveraging advanced characterization and 592 computational methods, researchers can explore future applications of Au-based materials. The 593 integration of advanced characterization techniques and computational methods enhances our 594 understanding and paves the way for new advances. Gold-based materials, when viewed through this multidisciplinary lens, hold immense promise, not only in hydrogenation processes 595 596 but also in other domains. Beyond their traditional roles, these materials have emerged as 597 catalysts in the realm of sensing technologies, enabling novel possibilities for detecting and 598 responding to various stimuli. Moreover, in the field of nanomedicine, Au-based materials may 599 contribute to advances in diagnostics and therapies. As nanocarriers, they have the potential to 600 stand at the forefront of innovative drug delivery systems, offering tailored solutions for 601 precision medicine and revolutionizing the landscape of therapeutic interventions. Au-based 602 materials are poised to be versatile tools across a spectrum of applications that transcend 603 disciplinary boundaries.

605 Acknowledgements

- 606 R.W. discloses support for publication of this work from Programme Investissement d'Avenir
- 607 [I-SITE ULNE / ANR-16-IDEX-0004 ULNE], Métropole Européenne de Lille (MEL) and
- 608 Region Hauts-de-France for the [CatBioInnov project].

609 Author contributions

610 The authors contributed equally to all aspects of the article.

611 **Competing interests**

612 The authors declare no competing interests.

613 **Peer review information**

- 614 *Nature Reviews Chemistry* thanks Mathilde Luneau, Hio Tong Ngan, Philippe Sautet, and the
- anonymous reviewers for their contribution to the peer review of this work.
- 616
- 617

618 **References**

- 619 1. Wood, B. & Wise, H. The role of adsorbed hydrogen in the catalytic hydrogenation of 620 cyclohexene. *J. Catal.* **5**, 135-145 (1966).
- 621 2. Fujitani, T.; Nakamura, I.; Akita, T.; Okamura, M. & Haruta, M. Hydrogen Dissociation by
- 622 Gold Clusters. Angew. Chem. Int. Ed. 48, 9515-9518 (2009).
- 623 3. Nobel prize Sabatier : Paul Sabatier Nobel Lecture. NobelPrize.org. Nobel Prize Outreach
- 624 AB 2023. 2023. <u>https://www.nobelprize.org/prizes/chemistry/1912/sabatier/lecture/</u>
- 625 4. Hastert, R.C. Hydrogenation of fatty acids. *J Am Oil Chem Soc* 56, 732A–739A (1979).
- 626 5. Vogt, C. & Weckhuysen, B.M. The concept of active site in heterogeneous catalysis. *Nat.*
- 627 *Rev. Chem.* **6**, 89–111 (2022).
- 628 6. Navarro-Jaén, S., Virginie, M., Bonin, J. et al. Highlights and challenges in the selective 629 reduction of carbon dioxide to methanol. *Nat. Rev. Chem.* **5**, 564–579 (2021).
- 630 7. Shuo, Ch., Wojcieszak, R., Dumeignil, F., Marceau, E. & Royer, S. How Catalysts and
- Experimental Conditions Determine the Selective Hydroconversion of Furfural and 5Hydroxymethylfurfural. *Chem. Rev.* 118, 11023-11117 (2018).
- 633 8. Zugic, B., Wang, L., Heine, C. et al. Dynamic restructuring drives catalytic activity on
- 634 nanoporous gold–silver alloy catalysts. *Nature Mater.* **16**, 558–564 (2017).
- 635 9. Hvolbæk, B. et al. Catalytic activity of Au nanoparticles. *Nano Today* **2**, 14–18 (2007).
- 636 10. Fujita, T., Guan, P. & McKenna, K. et al. Atomic origins of the high catalytic activity of
 637 nanoporous gold. *Nature Mater.* 11, 775–780 (2012).
- 638 11. Wang, H., Wang, L., Lin, D. et al. Strong metal–support interactions on gold nanoparticle
 639 catalysts achieved through Le Chatelier's principle. *Nat. Catal.* 4, 418–424 (2021).
- 640 12. Lopez, N. et al. On the origin of the catalytic activity of gold nanoparticles for low-641 temperature CO oxidation. *J. Catal.* **223**, 232–235 (2004).
- 642 13. Qian, H.; Zhu, M.; Wu, Z.; & Jin, R. Quantum Sized Gold Nanoclusters with Atomic
- 643 Precision. Acc. Chem. Res. 45, 1470-1479 (2012).
- 644 14. Haruta, M. When Gold Is Not Noble: Catalysis by Nanoparticles. Chem. Rec. 3, 75-87
- 645 (2003).

- 646 15. Corma A. & Garcia, H. Supported gold nanoparticles as catalysts for organic reactions.
- 647 *Chem. Soc. Rev.* **37**, 2096-2126 (2008).
- 648 16. Bond, G.C. Hydrogenation by gold catalysts: an unexpected discovery and a current 649 assessment. *Gold Bull.* **49**, 53–61 (2016).
- 650 17. Delgado, J.A. & Godard, C. (2020). Progress in the Selective Semi-hydrogenation of
- 651 Alkynes by Nanocatalysis. In: van Leeuwen, P., Claver, C. (eds) Recent Advances in
- 652 Nanoparticle Catalysis. Molecular Catalysis, vol 1. Springer, Cham.
- 653 <u>https://doi.org/10.1007/978-3-030-45823-2_10</u>
- 18. Hutchings, G. Heterogeneous Gold Catalysis. ACS Cent. Sci. 4, 1095–1101, (2018).
- 19. Bus, E., Miller, J.T. & van Bokhoven, J.A. Hydrogen Chemisorption on Al₂O₃-Supported
- 656 Gold Catalysts. J. Phys. Chem. B 109, 14581–14587 (2005).
- 657 20. Green, I.X., Tang, W., Neurock, M.& Yates, J.T. Low-Temperature Catalytic H₂ Oxidation
- over Au Nanoparticle/TiO₂ Dual Perimeter Sites. *Angew. Chem. Int. Ed.* 50, 10186–10189
 (2011).
- 660 21. Manzoli, M., Chiorino, A., Vindigni, F. & Boccuzzi, F. Hydrogen interaction with gold
- nanoparticles and clusters supported on different oxides: A FTIR study. *Catal. Today* 181, 62–
 67 (2012).
- 663 22. Boronat, M., Concepcion, P. & Corma, A. Unravelling the Nature of Gold Surface Sites by
- 664 Combining IR Spectroscopy and DFT Calculations. Implications in Catalysis. J. Phys. Chem.
 665 C 113, 16772–16784 (2009).
- Watkins, W.L. & Borensztein, Y. Mechanism of hydrogen adsorption on gold nanoparticles
 and charge transfer probed by anisotropic surface plasmon resonance. *Phys. Chem. Chem. Phys.*
- 668 19, 27397-27405 (2017).
- 669 24. Hammer, B. & Norskov, J. Why gold is the noblest of all the metals. *Nature* 376, 238–240
 670 (1995).
- 5. Sun, X., Dawson, S.R. & Parmentier, T.E. et al. Facile synthesis of precious-metal singlesite catalysts using organic solvents. *Nat. Chem.* 12, 560–567 (2020).
- 673 26. Guan, Q., Zhu, C., Lin, Y. et al. Bimetallic monolayer catalyst breaks the activity-selectivity
- trade-off on metal particle size for efficient chemoselective hydrogenations. *Nat. Catal.* 4, 840–
 849 (2021).
- 676 27. Chmielewski, A. et al. Reshaping Dynamics of Gold Nanoparticles under H_2 and O_2 at
- 677 Atmospheric Pressure. *ACS Nano* **13** (**2**), 2024-2033, (2019).
- 678 28. Bai, S.T., De Smet, G., Liao, Y. et al. Homogeneous and heterogeneous catalysts for
- hydrogenation of CO₂ to methanol under mild conditions. *Chemical Society Reviews* 50, 42594298 (2021).
- 681 29. Gesesse D., Wang, C., Chang Bor, K., Tai S-H. et al. A soft-chemistry assisted strong metal–
 682 support interaction on a designed plasmonic core–shell photocatalyst for enhanced
 683 photocatalytic hydrogen production. *Nanoscale* 12, 7011-7023 (2020).
- 684 30. Ferraz P, C., Navarro-Jaén, S., Rossi, L. et al. Enhancing the activity of gold supported
- catalysts by oxide coating: towards efficient oxidations. *Green Chemistry* 23, 8453-8457,
 (2021).
- 687 31. Nguyen, K.T., Hiep Vuong, V., Nguyen, T.N. et al. Unusual hydrogen implanted gold with
- 688 lattice contraction at increased hydrogen content. *Nat. Commun.* **12**, 1560 (2021).

- 689 32. Luza, L., Rambor, C., Gual, A., Alves Fernandes, J., Eberhardt, D., Dupont, J., Revealing
- Hydrogenation Reaction Pathways on Naked Gold Nanoparticles. ACS Catal. 7, 2791–2799(2017).
- 692 33. Luza, L., Gual, A., Alves Fernandes, J., Eberhardt, D., Dupont, J., Tunneling effects in
- 693 confined gold nanoparticle hydrogenation catalysts. Phys. Chem. Chem. Phys., 21, 16615-
- 694 16622 (2019).
- 695 34. Martín, A.J., Mitchell, S., Mondelli, C. et al. Unifying views on catalyst deactivation. *Nat.*696 *Catal.* 5, 854–866 (2022).
- 697 35. Segura, Y., Lopez, N. & Perez-Ramirez, J. Origin of the superior hydrogenation selectivity
- of gold nanoparticles in alkyne + alkene mixtures: Triple- versus double-bond activation. J.
 Catal. 247, 383-386 (2007).
- 36. van Deelen, T. W., Hernández Mejía, C. & de Jong, K. P. Control of metal-support
 interactions in heterogeneous catalysts to enhance activity and selectivity. *Nat. Catal.* 2, 955–
- 702 970 (2019).
- 37. Vijay, S., Ju, W., Brückner, S. et al. Unified mechanistic understanding of CO₂ reduction
 to CO on transition metal and single atom catalysts. *Nat. Catal.* 4, 1024–1031 (2021).
- 38. Nørskov, J., Bligaard, T., Rossmeisl, J. et al. Towards the computational design of solid
 catalysts. *Nature. Chem.* 1, 37–46 (2009). 39
- 707 39. Milone, C., Ingoglia, R., Pistone, A., Neri, G., Frusteri, F. & Galvagno, S. Selective
- 708 hydrogenation of *α*,*β*-unsaturated ketones to *α*,*β*-unsaturated alcohols on gold-supported 709 catalysts. J. Catal. **222**, 348-356 (2004).
- 710 40. Silva, R., Fiorio, J., Vidinha, P., Rossi, L.M., Gold Catalysis for Selective Hydrogenation
- 711 of Aldehydes and Valorization of Bio-Based Chemical Building Blocks. J. Braz. Chem. Soc.,
- 712 **30**, 2162-2169 (2019).
- 41. Fiorio, J. & Rossi, L. Clean protocol for deoxygenation of epoxides to alkenes *via* catalytic
 hydrogenation using Au. *Catal. Sci. Technol.* 11, 312-318 (2021).
- 715 42. Fiorio, J., Lopez, N. & Rossi, L. Au–Ligand-Catalyzed Selective Hydrogenation of Alkynes
- into *cis*-Alkenes via H₂ Heterolytic Activation by Frustrated Lewis Pairs. ACS Catal. 7(4),
 2973–2980 (2017).
- 43. Whittaker, T., Kumar, S., Peterson, Ch. et al. H₂ Oxidation over Supported Au Nanoparticle
- 719 Catalysts: Evidence for Heterolytic H₂ Activation at the Metal–Support Interface. J. Am. Chem.
- 720 Soc. **140(48)**, 16469–16487 (2018).
- 44. Mukherjee, S., Libisch, F. Large, N., et al. Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H₂ on Au. *Nano Lett.* **13(1)**, 240–247 (2013).
- 45. Lin, R., Albani, D., Fako, E., Kaiser, S. et al. Design of Single Au Atoms on Nitrogen-
- Doped Carbon for Molecular Recognition in Alkyne Semi-Hydrogenation. *Angew. Chim. Int. Ed.* 58, 504-509 (2019).
- 46. Stephan, D. The broadening reach of frustrated Lewis pair chemistry. *Science* 354, aaf7229(2016).
- 728 47. Fiorio, J., Gonçalves, R.V., Teixeira-Neto, E. et al. Accessing Frustrated Lewis Pair
- 729 Chemistry through Robust Au@N-Doped Carbon for Selective Hydrogenation of Alkynes.
- 730 ACS Catal. 8(4), 3516–3524 (2018).

- 731 48. Lu, G., Zhang, P., Sun, D. et al. Gold catalyzed hydrogenations of small imines and nitriles:
- 732 enhanced reactivity of Au surface toward H₂ via collaboration with a Lewis base. Chem. Sci. 5, 733 1082-1090 (2014).
- 734 49. Almora-Barrios, N., Cano, I., van Leeuwen, P. & Lopez, N. Concerted Chemoselective
- 735 Hydrogenation of Acrolein on Secondary Phosphine Oxide Decorated Gold Nanoparticles. ACS
- 736 Catal. 7(6), 3949–3954 (2017).
- 737 50. Lv, X., Lu, G., Wang, Z.Q. et al. Computational Evidence for Lewis Base-Promoted CO₂
- 738 Hydrogenation to Formic Acid on Gold Surfaces. ACS Catal. 7(7), 4519–4526 (2017).
- 739 51. Ren, D., He, L., Yu, L., Ding, R.-S. et al. An Unusual Chemoselective Hydrogenation of
- 740 Quinoline Compounds Using Supported Au Catalysts. J. Am. Chem. Soc. 134, 17592-17598 741 (2012).
- 742 52. Cano, I., Chapman, A. M., Urakawa, A., & van Leeuwen, P. W. N. M. Air-Stable Au
- 743 Nanoparticles Ligated by Secondary Phosphine Oxides for the Chemoselective Hydrogenation
- 744 of Aldehydes: Crucial Role of the Ligand. J. Am. Chem. Soc. 136, 2520-2528 (2014).
- 53. Cano, I., Huertos, M. A., Chapman, A. M., Buntkowsky, G., Gutmann, T., Groszewicz, P. 745
- 746 B., & van Leeuwen, P. W. N. M. Air-Stable Gold Nanoparticles Ligated by Secondary
- 747 Phosphine Oxides as Catalyst for the Chemoselective Hydrogenation of Substituted Aldehydes: 748
- a Remarkable Ligand Effect. J. Am. Chem. Soc. 137(5), 7718-7727 (2015).
- 749 54. Garcia-Melchor, M. & Lopez, N. Homolytic Products from Heterolytic Paths in H₂ 750 Dissociation on Metal Oxides: The Example of CeO₂. J. Phys. Chem. C 118(20), 10921–10926 751 (2014).
- 752 55. Aireddy, D., and Ding, K. Heterolytic Dissociation of H₂ in Heterogeneous Catalysis. ACS Catal. 12, 4707-4723 (2022). 753
- 754 56Lyalin, A. & Taketsugu, T. A computational investigation of H₂adsorption and dissociation 755 on Au nanoparticles supported on TiO₂ surface. Faraday Discuss. 152, 185-201 (2011).
- 756 57. Du, X. Huang, Y. Pan, X. et al. Size-dependent strong metal-support interaction in TiO₂ 757 supported Au nanocatalysts. Nat. Commun. 11, 5811 (2020).
- 758 58. Fu, Q., Wagner, T., Olliges, S. & Carstanjen, H.-D. Metal-oxide interfacial reactions: 759 encapsulation of Pd on TiO₂ (110). J. Phys. Chem. B 109, 944–951 (2005).
- 760 59. Sun, Y., Cao, Y., Wang, L. et al. Gold catalysts containing interstitial carbon atoms boost 761 hydrogenation activity. Nat. Commun. 11, 4600 (2020).
- 762 60. Mukherjee, S., Zhou, L., Goodman, A. et al. Hot-Electron-Induced Dissociation of H₂ on
- 763 Gold Nanoparticles Supported on SiO₂. J. Am. Chem. Soc. 136, 64-67 (2014).
- 764 61. Christopher, P., Xin, H., Marimuthu, A. et al. Singular characteristics and unique chemical
- 765 bond activation mechanisms of photocatalytic reactions on plasmonic nanostructures. Nature Mater. 11, 1044–1050 (2012). 766
- 767 62. Linic, S., Christopher, P., Xin, H., & Marimuthu, A. Catalytic and Photocatalytic 768 Transformations on Metal Nanoparticles with Targeted Geometric and Plasmonic Properties. 769 Acc. Chem. Res. 46, 1890-1899 (2013).
- 770 63. Brus, L. Noble Metal Nanocrystals: Plasmon Electron Transfer Photochemistry and Single-
- 771 Molecule Raman Spectroscopy. Acc. Chem. Res. 41, 1742-1749 (2008).
- 772 64. Quiroz, J., Barbosa, E., Araujo, T., Fiorio, J. et al. Controlling Reaction Selectivity over
- 773 Hybrid Plasmonic Nanocatalysts. Nano Lett. 18, 7289-7297 (2018).

- 774 65. Barbosa, E., Fiorio, J., Mou, T., Wang, B., Rossi, L. & Camargo, P. Reaction Pathway
- 775 Dependence in Plasmonic Catalysis: Hydrogenation as a Model Molecular Transformation.
 776 *Chem. Europ. J.* 24, 12330-12339 (2018).
- 777 66. Pyykkö, P. Theoretical Chemistry of Gold. Angew. Chem. 43, 4412-4456 (2004).
- 778 67. Pyykkö, P. Relativity, Gold, Closed-Shell Interactions, and CsAu·NH₃. Angew. Chem. Int.
- 779 *Ed.* **41**, 3573-3578 (2002).
- 780 68. De Vos, D. & Sels, B. Gold Redox Catalysis for Selective Oxidation of Methane to
- 781 Methanol. Angew. Chem. Int. Ed. 117, 30-32 (2005).
- 782 69. Guzman, J. Correttin, S. Fierro-Gonzalez, J. et al. CO Oxidation Catalyzed by Supported
- 783 Au: Cooperation between Gold and Nanocrystalline Rare-Earth Supports Forms Reactive
- Surface Superoxide and Peroxide Species. Angew. Chem. Int. Ed. 44, 4778-4781 (2005).
- 785 70. Jones, C., Taube, D., Ziatdinov, V., Periana, R., Nielsen, R., Oxgaard, J. & Goddard III, W.
- Selective Oxidation of Methane to Methanol Catalyzed, with C-H Activation, by
 Homogeneous, Cationic Gold. *Angew. Chem. Int. Ed.* 116, 4726-4729 (2004).
- 788 71. Corma, A. Gonzalez-Arellano, C. Iglesias, M. & Sanchez, F. Gold Nanoparticles and
- 789 Gold(III) Complexes as General and Selective Hydrosilylation Catalysts. Angew. Chem. Int.
- 790 *Ed.* **119**, 7966-7968 (2007).
- 791 72. Wang, L., Guan, E., Zhang, J. et al. Single-site catalyst promoters accelerate metal792 catalyzed nitroarene hydrogenation. *Nat. Commun.* 9, 1362 (2018).
- 793 73. Zhang, L., Ren, Y. at al. Single-atom catalyst: a rising star for green synthesis of fine 794 chemicals. *Nat. Sci. Rev.* **5**, 653–672 (2018).
- 795 74. Hannagan, R.T., Giannakakis, G., Flytzani-Stephanopoulos, M. & Sykes, E.Ch. Single-796 atom alloy catalysis. *Chem. Rev.* **120**, 12044–12088 (2020).
- 797 75. Cui, X., Li, W., Ryabchuk, P. et al. Bridging homogeneous and heterogeneous catalysis by
 798 heterogeneous single-metal-site catalysts. *Nat. Catal.* 1, 385–397 (2018).
- 799 76. Cao, S., Yang, M., Elnabawy, A.O. et al. Single-atom gold oxo-clusters prepared in alkaline
- solutions catalyse the heterogeneous methanol self-coupling reactions. *Nat. Chem.* 11, 1098–
 1105 (2019).
- 802 77. Corma, A., Salnikov, O.G., Barskiy, D.A., Kovtunov, K.V. &Koptyug, I.V. Single-Atom
- Au Catalysis in the Context of Developments in Parahydrogen-Induced Polarization. *Chem. Eur. J.* 21, 7012-7015 (2015).
- 78. Qiao, B., Liang, JX., Wang, A. et al. Ultrastable single-atom gold catalysts with strong
 covalent metal-support interaction (CMSI). *Nano Res.* 8, 2913–2924 (2015).
- 807 79. Guzman, J. & Gates, B.C. Structure and Reactivity of a Mononuclear Gold-Complex
 808 Catalyst Supported on Magnesium Oxide. *Angew. Chem. Int. Ed.* 115, 115-714 (2003).
- 809 80. Comas-Vives, A.; Gonzalez- Arellano, C., Corma, A., Iglesias, M. et al. Single-Site
- Homogeneous and Heterogenized Gold(III) Hydrogenation Catalysts: Mechanistic
 Implications. J. Am. Chem. Soc. 128, 4756-4765 (2006).
- 812 81. Sárkány, A., Schay, Z., Frey, K., Széles, É., Sajó I. Some features of acetylene
- 813 hydrogenation on Au-iron oxide catalyst. *Appl. Catal. A. Gen.* **380**, 133-141 (2010).
- 814 82. Zhang, X., Shi, H., & Xu, B. Catalysis by Gold: Isolated Surface Au³⁺ Ions are Active Sites
- 815 for Selective Hydrogenation of 1,3-Butadiene over Au/ZrO₂ Catalysts. *Angew. Chem. Int. Ed.*
- **816 44**, 7132-7135 (2005).

- 817 83. He, X., He, Q., Deng, Y. et al. A versatile route to fabricate single atom catalysts with high 818 chemoselectivity and regioselectivity in hydrogenation. *Nat. Commun.* **10**, 3663 (2019).
- 819 84. Single atom catalysts push the boundaries of heterogeneous catalysis. *Nat. Commun.* 12,
 820 5884 (2021).
- 821 85. Wang, Z., Gu, L., Song, L., Wang, H. & Yu, R. Facile one-pot synthesis of MOF supported
- gold pseudo-single-atom catalysts for hydrogenation reactions. *Mater. Chem. Front.* 2, 10241030 (2018).
- 824 86. Liu, J., Zou, Y., Cruz, D. et al. Ligand–Metal Charge Transfer Induced via Adjustment of
- 825 Textural Properties Controls the Performance of Single-Atom Catalysts during Photocatalytic
- 826 Degradation. ACS Appl. Mater. Interf. 13(22), 25858–25867 (2021).
- 827 87. Vilé, G., Di Liberto, G., Tosoni, S. et al. Azide-Alkyne Click Chemistry over a
 828 Heterogeneous Copper-Based Single-Atom Catalyst. ACS Catal. 12(5), 2947–2958 (2022).
- 829 88. Gan, T., He, Q., Zhang, H. et al. Unveiling the kilogram-scale gold single-atom catalysts
- via ball milling for preferential oxidation of CO in excess hydrogen. *Chem. Eng. J.* **389**, 124490,
- 831 (2020)
- 832 89. Greeley, J.& Mavrikakis, M. Alloy catalysts designed from first principles. *Nature Mater*.
 833 3, 810–815 (2004).
- 834 90. Fu, Q. & Luo, Y. Catalytic Activity of Single Transition-Metal Atom Doped in Cu(111)
 835 Surface for Heterogeneous Hydrogenation. *J. Phys. Chem. C* 117, 14618–14624 (2013).
- 836 91. Alayoglu, S., Nilekar, A., Mavrikakis, M. et al. Ru–Pt core–shell nanoparticles for
- 837 preferential oxidation of carbon monoxide in hydrogen. *Nature Mater.* **7**, 333–338 (2008).
- 838 92. Eom, N., Messing, M., Johansson, J., Deppert, K., General Trends in Core–Shell
 839 Preferences for Bimetallic Nanoparticles. *ACS Nano* 15, 8883–8895 (2021).
- 840 93. Ledendecker, M., Paciok, P., Osowiecki, W.T. et al. Engineering gold-platinum core-shell 841 nanoparticles by self-limitation in solution. *Commun Chem* **5**, 71 (2022).
- 94. Venkatachalam, S., Jacob, T. Hydrogen Adsorption on Pd- Containing Au(111) Bimetallic
 Surfaces. *Phys. Chem. Chem. Phys.* 11(17), 3263-3270 (2009).
- 844 95. van der Hoeven, J.E.S., Tong Ngan, H., Taylor, A., Eagan, N., Aizenberg, J., Sautet, Ph.,
- Madix, R., Friend, C., Entropic Control of H–D Exchange Rates over Dilute Pd-in-Au Alloy
 Nanoparticle Catalysts. *ACS Catal.* 11, 12, 6971–6981 (2021).
- 847 96. van der Hoeven, J.E.S., Jelic, J., Olthof, L.A. et al. Unlocking synergy in bimetallic catalysts
- 848 by core–shell design. *Nat. Mater.* **20**, 1216–1220 (2021).
- 97. Luneau, M., Guan, E., Chen, W. et al. Enhancing catalytic performance of dilute metal alloy
 nanomaterials. *Commun Chem* 3, 46 (2020).
- 851 98. Bruno, L., Scuderi, M., Priolo, F. et al. Enlightening the bimetallic effect of Au@Pd
- nanoparticles on Ni oxide nanostructures with enhanced catalytic activity. Sci Rep 13, 3203(2023).
- 854 99. Zhao, J., Ni, J., Xu, J., Cen, J., Li, X. Ir promotion of TiO₂ supported Au catalysts for 855 selective hydrogenation of cinnamaldehyde. *Catal. Comm.* **54**, 72-76 (2014).
- 856 100. Li, H., Zheng, J., Zheng, X., Gu, Z., Yuan, Y., Yang, Y. Improved chemoselective
- 857 hydrogenation of crotonaldehyde over bimetallic AuAg/SBA-15 catalyst. J. Catal. 330, 135-
- 858 144 (2015).

- 859 101. Chen, J., Sun, W., Wang, Y., Fang, W. Performant Au hydrogenation catalyst cooperated
- 860 with Cu-doped Al2O3 for selective conversion of furfural to furfuryl alcohol at ambient 861 pressure. *Green Energy & Envi*.**6**, 546-556 (2021).
- 862 102. Zhang, X., Han, S., Zhu, B. et al. Reversible loss of core–shell structure for Ni–Au
 863 bimetallic nanoparticles during CO₂ hydrogenation. *Nat. Catal.* 3, 411–417 (2020).
- 103. Tkachenko, G., Truong, V.G., Esporlas, C.L. et al. Evanescent field trapping and
 propulsion of Janus particles along optical nanofibers. *Nat Commun* 14, 1691 (2023)
- 866 104. Kyriakou, G., Boucher, M. B., Jewell, A. D., Lewis, E. et al. Isolated Metal Atom
- 867 Geometries as a Strategy for Selective Heterogeneous Hydrogenations. *Science* 335, 1209-1212
 868 (2012).
- 869 105. Boucher, M. B., Zugic, B., Cladaras, G. et al. Single Atom Alloy Surface Analogs in
- Pd_{0.18}Cu₁₅ Nanoparticles for Selective Hydrogenation Reactions. *Phys. Chem. Chem. Phys.* 15, 12187–12196 (2013).
- 872 106. Sankar, M., Dimitratos, N., Miedziak, P. et al. Designing bimetallic catalysts for a green
- and sustainable future. *Chem. Soc. Rev.* **41**, 8099-8139 (2012).
- 874 107. Maroun, F., Ozanam, F., Magnussen, O. M. & Behm, R. J. The Role of Atomic Ensembles
- 875 in the Reactivity of Bimetallic Electrocatalysts. *Science* **293**, 1811–1814 (2001).
- 876 108. Buurmans, I. & Weckhuysen, B. Heterogeneities of individual catalyst particles in space
 877 and time as monitored by spectroscopy. *Nature Chem.* 4, 873–886 (2012).
- 878 109. Sambur, J., Chen, TY., Choudhary, E. et al. Sub-particle reaction and photocurrent
 879 mapping to optimize catalyst-modified photoanodes. *Nature* 530, 77–80 (2016).
- 110. Yin, H., Zheng, LQ., Fang, W. et al. Nanometre-scale spectroscopic visualization of
 catalytic sites during a hydrogenation reaction on a Pd/Au bimetallic catalyst. *Nat. Catal.* 3,
 834–842 (2020).
- 883 111. Lucci, F.; Darby, M.; Mattera, M.; Ivimey, Ch. et al. Controlling Hydrogen Activation,
- Spillover, and Desorption with Pd– Au Single-Atom Alloys, J. Phys. Chem. Lett. 7, 480–485
 (2016).
- 886 112. Liu, J., Uhlman, M., Montemore, M. et al. Integrated Catalysis-Surface Science-Theory
- Approach to Understand Selectivity in the Hydrogenation of 1-Hexyne to 1-Hexene on PdAu
 Single-Atom Alloy Catalysts. *ACS Catal.* 9(9), 8757–8765 (2019).
- 889 113. Shi, D., Sadier, A., Girardon, J.S., Mamede, A.S. et al. Probing the core and surface 890 composition of nanoalloy to rationalize its selectivity: Study of Ni-Fe/SiO₂ catalysts for liquid-
- phase hydrogenation. *Chem. Catal.* 2(7), 1686–1708 (2022).
- 892 114. Datye A.K., & Guo, H. Single atom catalysis poised to transition from an academic
 893 curiosity to an industrially relevant technology. *Nat. Commun.* 12, 895 (2021).
- 894 115. Zhao, X., Fang, R., Wang, F. *et al.* Atomic design of dual-metal hetero-single-atoms for
 895 high-efficiency synthesis of natural flavones. *Nat Commun* 13, 7873 (2022).
- 896 116. Tian, S., Wang, B., Gong, W. *et al.* Dual-atom Pt heterogeneous catalyst with excellent
 897 catalytic performances for the selective hydrogenation and epoxidation. *Nat Commun* 12, 3181
 898 (2021).
- 899 117. Zhang, T.; Zheng, P.; Gu, F.; Xu, W. et al. The dual-active-site tandem catalyst containing
- 900 Ru single atoms and Ni nanoparticles boosts CO₂ methanation. Appl. Catal. B. Env. 323,
- 901 122190, (2023).
- 902

903

- **Figure 1**. Types of H_2 activation on heterogeneous Au catalysts and startegies to enhance H_2 disociation on Au. (a) two different types of H_2 activation that may occur on gold (b) Ligands containg N or P adsorbed on Au surface can heterotically dissociate
- 906 hydrogen due to the interactions between ligand and hydrogen. (c) Strong Support-Metal Interaction (SMSIs) can modify the
- 907 electronic properties of Au and provide sufficient energy required of hydrogen dissociation. On the Figure 1c one of the
- 908 example of strong SMSI registred in the case of Au supported on TiO₂. The partial encapsulation of Au can be observed. (d)
- 909 Schematic representation of hydrogen adsorption and charge distribution on Au induced by hot electrons. (e) schematic
- 910 representation of Au single atom inside of the C_{3N4} structure (blue cirlces represent N atoms, grey circles are carbon atoms).
- 911 (f) Alloying Au with other metal such as Pt or Pd permits to obtain highly efficient hydrogenation catalysts. H_2 can easily
- 912 dissociated on Pd or Pt and then can migrate to Au thanks to spillober phenomenon.
- 913
- 914 Figure 2. Selective hydrogenation on Au catalysts in the presence of ligands and in the case of Au-N-doped catalyst (a) Reaction 915 scheme of the catalytic hydrogenation of phenylacetylene (1a) into styrene (2a) and ethylbenzene (3a). (b) Time course of 916 hydrogenation of phenylacetylene (1a) catalysed by Au/SiO₂ in the presence of piperazine. (c) Time course of hydrogenation 917 of phenylacetylene catalysed by Au@N-doped carbon/TiO₂. (d) Experimental reaction rates vs computed activation energies 918 for H_2 dissociation in a heterolytic mode at the N ligand-Au(111) interface. Black squares refer to amines with two N-919 heteroatoms and red squares refer to amines with one N-heteroatoms in their structures. (e) Computed reaction energy profile 920 for the hydrogenation of an alkyne on phenanthroline-functionalized Au(111) surface. The inset corresponds to Au(111) surface 921 functionalized with phenanthroline in a configuration parallel (flat) to the surface (surface model A). Ia refers to 922 phenylacetylene and 2a to styrene. (Au = yellow, N = blue, C = gray, H = white). Reprinted with permission from^{42,47}. Part B-923 C adapted with permission from ref 42, ACS. Part D adapted with permission from ref 47, ACS. Part E reprinted
- 923 C adapted with permission from ref 42, ACS. Part D adapted with permission from ref 47, ACS. Part E reprin 924 with permission from ref 47, ACS.
- 925

Figure 3. Hot electron induced H–D formation at 23 °C on 1% Au/SiO₂ catalyst. (a) The rate of H–D formation was continuously monitored in real-time under two conditions: with laser excitation (2.4 W/cm², active) and without laser excitation (0.0 W/cm², inactive). During the 10-minute period of laser excitation, the sample experienced a reversible temperature increase of 8 °C, as depicted in the figure, transitioning from 22 to 30 °C. (b) H–D formation rate for 1% Au/SiO₂. (c) H–D formation rate for 1% Au/TiO₂ catalyst. In both cases the same reaction condition were applied with laser excitation of 2.4 W/cm² ⁶⁰. Any activity was observed in the case of SiO₂ (blue curve) and TiO₂ (purple curve). The size of AuNPs were 5–30 nm and the excitation wavelength ranged from 450 to 1000 nm. Part A-C adapted with permission from ref 60, ACS.

933 Figure 4. Au single atom catalysts (Au SACs). (a) Schematic representation of the nitrogen-doped carbon (Au(III)/NC) 934 synthesis and impregnation with HAuCl4 used as Au precursor. Impregnation step performed via incipient wetness 935 impregnation of nitrogen doped carbon (NC) with HAuCl₄ in aqua regia solution. Two thermal treatment were applied: 936 activation step in static air (at 473 K) and flowing N₂ (>973 K) for 16 h.Color code as follows Au-yellow, C-gray, N-blue, and 937 Cl-green.⁴⁵ (b) Aberration corrected HAADF-STEM (High-angle annular dark-field scanning transmission electron 938 microscopy) micrographs of Au/NC1073 catalyst with Au SACs circled (scale bar of 2 nm)⁴⁵; (c) TOF (Turnover frequency) in 939 ethene hydrogenation in function of the single Au-Au coordination number on different MgO supported catalysts containing 940 Au³⁺ and Au clusters⁷⁹. Part A reprinted with permission from ref 45, Wiley. Part B adapted with permission from 941 ref 45, Wiley. Part C reprinted with permission from ref 79, Wiley.

942

943 Figure 5. Spillover region identification. (a) Reaction scheme of the catalytic hydrogenation of chloronitrobenzenethiol to 944 chloroaminobenzenethiol on Au–Pd bimetallic catalysts at 25°C. (b) Illustration of STM-TERS (Sacanning Tunneling Microscopy 945 coupled with Tip-Enhanced Raman Spectroscopy) employing an Ag tip to investigate hydrogenation products on a Pd/Au 946 bimetallic substrate. The black lines culminating in black circles symbolize the electrical connections used to apply a bias 947 voltage between the tip and the sample. The grey hexatomic rings are benzene rings; the small blue balls represent hydrogen. 948 (c) Intensity of the peak at 1,336 cm⁻¹ (NO₂ stretching bond in Raman spectra) in TERS line scan spectra on Pd_{LC}/Au (low Pd 949 coverage on Au surface) The size of the active region is represented by the blue regions. Blue arrows indicate the hydrogen 950 spillover direction¹¹⁰ (d) The topographic height profile for Pd_{LC}/Au (indicated by the red line) of the surface along the dashed 951 line in the inset of the respective STM images is overlaid with a schematic of the surface structure. In this schematic 952 representation, Au is depicted in yellow shading, while Pd is in grey shading. The blue arrows, accompanied by dots, denote 953 the directions of hydrogen spillover. (e) Intensity of the peak at 1,336 cm⁻¹ in TERS line scan spectra on Pd_{HC}/Au (high Pd 954 coverage on Au surface). (f) The topographic height profile for Pd_{HC}/Au . (g) and (h) Reaction rate and selectivity profiles for 955 time-resolved hydrogenation of 1-hexyne over PdAu-SAA/SiO2 catalysts compared to monometallic Pd/SiO2 catalyst, 956 respectively. B-F reprinted from ref.110, Springer Nature Limited. Part G adapted with permission from ref 112, 957 ACS. Part H reprinted with permission from ref 112, ACS.

958

959 Figure 6. Morphology in the structure of the bimetallic Au@Pt core-shell nanocatalyst. (a), X-ray diffractometry patterns of 960 monometallic Au and bimetallic Au@Pt systems. The structure of Au core is preserved after Pt shell formation as identified 961 using the diffreaction peaks of Au from JCPDS-4-0784 database (b), Recycling tests for Au@ML-Pt catalyst in chemoselective 962 hydrogenation of chloronitrobenzene at 65°C. The activity of the catalyst is stable during 5 cycles. (c) HAADF-STEM image 963 of Au@1ML-Pt catalyst accompanied by the corresponding line intensity profiles along the numbered colored rectangles. 964 These profiles serve to reveal both the interplanar distance and the lattice distance. As depicted in the figure, yellow and blue 965 spheres correspond to the Au core and blues ones to the Pt shell. (d) Surface atom arrangement in Au-Ni bimetallic 966 nanoparticle at 600 °C (top image) at 400 °C (bottom image). After thermal treatment at 600 °C the alloy structure is formed 967 between Ni and Au. After thermperature decrease to 400°C the dealloying occurs and core-structure is formed. The formation 968 of an alloy at 600°C is responsible for the high selectivity of this catalyst in CO₂ hydrogenationas showed in (e) Selectivity and 969 conversion temperature resolved profiles for the Ni-Au bimetallic catalyst. The highest conversion is obtained at 600° C when 970 the alloy structure is formed. (scale bars, 2 nm). (f) The energy routes for the CO₂ hydrogenation reaction on the (111) surface 971 of the alloyed Ni–Au phase are depicted. The alloying process and reaction pathways are elucidated through DFT (Density 972 functional theory) calculations and FTIR (Fourier Transform Infrared Spectroscopy), shedding light on the mechanism. In this 973 context, TS represents the transition state. Part A adapted from ref.26, Springer Nature Limited. Part C reprinted from 974 ref.26, Springer Nature Limited. Parts E&F reprinted from ref.102, Springer Nature Limited. Part D adapted from 975 ref.102, Springer Nature Limited.

976 **BOX 1: The importance of the hydrogenation in chemical industry**

977 Hydrogenation reactions are fundamental processes in the chemical industry with widespread 978 applications. Catalytic hydrogenation process was firstly performed in 1897 by Sabatier who described 979 the reduction of ethylene using metals such as Ni, Co and Fe (1912 Nobel Prize in Chemistry)³. The first 980 large scale hydrogenation process was the hydrogenation of fatty acids and their glycerides using Ni 981 catalyst in 1909 in Crosfield, USA⁴. The addition of hydrogen gas (H₂) to a compound in the presence 982 of a catalyst can lead to significant change in the molecular structure of the substrate. One of the most 983 prevalent hydrogenation reactions involves reducing unsaturated compounds. When hydrogen gas reacts 984 with a molecule containing double bonds, these bonds become saturated, leading to the formation of 985 single bonds. This procedure is extensively employed in the production of saturated hydrocarbons, 986 including the conversion of unsaturated vegetable oils into solid fats, such as margarine. In addition to 987 reducing double and triple bonds, hydrogenation reactions are employed in a number of other functional 988 group conversions. For instance, the hydrogenation of carbonyl compounds, such as aldehydes and 989 ketones, leads to the formation of alcohols. This transformation is essential in the production of 990 pharmaceuticals, flavorings, and fragrances. Heterogenous catalytic hydrogenation can be performed 991 using metals such as Ni, Ru, Rh and Pd. In addition, numerous catalytic hydrogenation processes can 992 also be performed on Au-based catalysts, some of which are presented below.

993

994 BOX 2: The complexity of the H-Me interactions

995 Different hydrogen activation pathways can occur on clean-surface Au nanoparticles³²⁻³³, as represented 996 on the figure. The homolytic dissociation of H_2 to atoms on low-coordinated Au atoms is well 997 documented from the theoretical point of view (part a). Depending on the electronegativity of metals, 998 these bonds can more or less polarized. More electronegative metals (such as Au) form mostly covalent 999 bonds with hydrogen (M–H). It is worth noting that chemisorption of hydrogen is almost always 1000 exothermic (except on Au and silver surfaces).

1001 Heterolytic dissociation of hydrogen is more commonly observed whereby a metal hydride is formed 1002 after proton transfer to the support or substrate (part b). Typically, metal hydrogenation catalysts 1003 dissociate H_2 with a proton transfer to a strong conjugate base. This involves the formation of 1004 proton-hydride pairs.

- 1005 A third possibility is the activation of hydrogen molecule with a ligand adsorbed on the Au surface (part
- 1006 c) and the subsequent formation of a new active species $(H-L \text{ where } L = \text{ligand})^{32}$.

1007 Unlike the classical mechanisms of hydrogenation that involve the binding of substrates on the metal 1008 surface, a final mechanism, hydrogen transfer, enables the hydrogenation of sterically hindered 1009 substrates (part d). This "outer sphere" hydrogenation mechanism involves several steps (adsorption of 1010 reactant, adsorption of H_2 , complex formation, hydrogen transfer, and desorption) with the overall 1011 transformation of a proton transfer to an unsaturated substrate. This mechanism can be used to convert 1012 complex molecules, which is useful for the generation of pharmaceutically relevant structures. It also 1013 does not require gaseous hydrogen but can employ another liquid hydrogen donor such as ethanol, 1014 isopropanol or formic acid³²⁻³³.

1015 Part A-D adapted with permission from ref 32, ACS.

1016

1017 BOX 3: Bimetallic synergy

1018

1019 Bimetallic synergy can substantially improve the catalytic properties of a monometallic catalyst and can 1020 even promote new catalytic abilities that are not possible in a monometallic catalyst. The addition of a 1021 second metal can alter the activity, selectivity and resistance to deactivation inherent to the monometallic 1022 particles. The structure of bimetallic particles differs from bulk alloys, and are categorized into core-1023 shell, mixed and Janus structures (examples of different structures are given on figure below), which is 1024 mainly determined by the nature of the metal, molar ratio between both metals and the method used for 1025 their synthesis⁹². Bimetallic nanoparticles can experience surface segregation phenomena (distribution 1026 of the two different metal on the surface of the nanoparticle is not homogeneous and one of the metals 1027 tends to concentrate or segregate on the surface), which are crucial in both the synthesis and applications 1028 of these nanoparticles. Au based bimetallic catalysts have been studied in hydrogenation reactions, the most common of which are: Au-Pt^{26,93}, Au-Pd⁹⁴⁻⁹⁸, Au-Ir⁹⁹, Au-Ag¹⁰⁰, Au-Cu¹⁰¹, Au-Ni¹⁰² and Au-1029 SiO_2^{103} . 1030

1031 Part A (left) is adapted from ref 92, CC BY 4.0 (<u>https://creativecommons.org/licenses/by/4.0/</u>). B (right)

adapted from ref.93, Springer Nature Limited. B (right) adapted from ref.98, Springer Nature Limited. B (right)adapted from ref.103, Springer Nature Limited.

- 1034
- 1035
- 1036
- 1037

1038 Summary:

1039 Gold catalysts have gained attention for their ability to activate hydrogen towards the 1040 hydrogenation of organic molecules. This review explores strategies to enhance hydrogen-gold 1041 interactions to help design new efficient hydrogenation catalysts.

- 1042
- 1043

Author notes

Please check these figures carefully and return any comments/amendments that you might have to me as soon as possible. In particular, we would like you to check the following:

- Do the figures convey the intended message?
- Are all the labels accurate and in the correct place?
- Are all the arrows in the right place?
- Are any chemical structures correct?
- Have shapes and colours been used consistently and accurately throughout the figures?
- Please note, the Art Editors use colour to show hierarchy within the figure set. Please check and confirm that the most important parts of the figures have been emphasised correctly
- Have any of the figures been previously published, or have they been supplied by a colleague(s) who is not a named author on the article?
- For any maps, some style modifications may have been made, are they still correct?

To mark up any corrections, please use the commenting tools in the PDF, or print and draw by hand, rather than directly editing the PDFs.

Fig 1





C Strong support-metal interaction (SMSIs)



d Effect of hot electrons on Au properties



 \mathbf{e} Au single atoms inside $\mathbf{C}_{3}\mathbf{N}_{4}$



Fig 2

a Catalytic hydrogenation of phenylacetylene into styrene and ethylbenzene



 ${\bf b}\,$ Reaction course with ${\rm Au/SiO}_2$ catalyst and piperazine



d Reaction course with Au@N-doped carbon/TiO₂ catalyst





Au NP (2 mol%)/EtOH (2 mL) 100°C, H₂ (6 bar)

C Experimental reaction rates vs computed activation energies for H₂ dissociation at the N ligand-Au(111) interface



€ Computed reaction energy profile for hydrogenation on phenanthrolinefunctionalized Au(111) surface



Fig 3



20|12|23

Fig 4



Au-Au coordination number

Ed: This image is different from that which appears in the markup

Fig 5





b STM-TERS illustration of an Ag tip investigating hydrogenation on Pd/Au



e NO₂ stretching bond (Raman) intensity in TERS line scan spectra on PdHC/Au (high Pd coverage on Au).



f Topographic height profile for Pd_{HC} /Au



g Reaction rate for time-resolved hydrogenation of 1-hexyne over PdAu-SAA/SiO₂ v. monometallic Pd/SiO₂ catalyst







20|12|23

Fig 6

a X-ray diffractometry patterns of monometallic Au and bimetallic Au@Pt systems.



b Recycling of Au@ML-Pt catalyst in hydrogenation of chloronitrobenzene at 65°C.





 $d\,$ Surface atom arrangement in Au–Ni bimetallic nanoparticle at 600 $^\circ C$ and 400 $^\circ C$

e Selectivity and conversion profiles for the Ni-Au bimetallic catalyst

+ H₂O

560 600 20

18

16 00

14

12

10

-8 6

Л

. ?

, conversion (%)

 CH_4







Box 1







b Heterolytic dissociation of H_2



Box 3

 H_2



20|12|23

GA

