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Strategies to improve hydrogen activation on gold catalysts

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# 1 Strategies to improve hydrogen activation on gold catalysts

2 Nikolaos Dimitratos<sup>1,2</sup>, Gianvito Vilé<sup>3</sup>, Stefania Albonetti<sup>1,2</sup>, Fabrizio Cavani<sup>1,2</sup>, Jhonatan  
3 Fiorio<sup>4</sup>, Nuria López<sup>5</sup>, Liane M. Rossi<sup>6</sup>, Robert Wojcieszak<sup>7,\*</sup>

4  
5 <sup>1</sup>*Dipartimento di Chimica Industriale “Toso Montanari”, Alma Mater Studiorum Università di Bologna, Viale*  
6 *Risorgimento 4, Bologna 40126, Italy*

7 <sup>2</sup>*Center for Chemical Catalysis-C3, Alma Mater Studiorum Università di Bologna, Viale Risorgimento 4, Bologna*  
8 *40136, Italy*

9 <sup>3</sup>*Department of Chemistry, Materials and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Piazza*  
10 *Leonardo da Vinci 32, 20133 Milano, Italy*

11 <sup>4</sup>*Technische Universität Dresden, School of Science, Faculty of Chemistry and Food Chemistry, Mommsenstr. 13,*  
12 *01069 Dresden, Germany.*

13 <sup>5</sup>*Institute of Chemical Research of Catalonia, The Barcelona Institute of Science and Technology, Tarragona,*  
14 *Spain*

15 <sup>6</sup>*Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu*  
16 *Prestes 748, São Paulo 05508-000, SP, Brazil*

17 <sup>7</sup>*Univ. 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  
23 the chemical industry. Classically, hydrogenations are carried out on Pd, Pt, Ru, or Ni catalysts.  
24 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  
26 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 H<sub>2</sub> 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 (H<sub>2</sub>) 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 H<sub>2</sub> 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  
42 discovered that gold (Au), typically considered inert, can catalyze the activation of H<sub>2</sub> and other  
43 H-donors, and exhibit remarkable catalytic properties in hydrogenation reactions.<sup>1-2</sup> 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 processes<sup>5-7</sup>, often involving finely  
47 dispersed metallic nanoparticles. One such catalytic system is Au nanoparticles (Au NPs)  
48 dispersed on solid carriers<sup>8</sup>, which were initially demonstrated for selective CO oxidation  
49 reactions<sup>9-11</sup>. Dispersing the Au nanoparticles in this way provides a large number of low-  
50 coordination surface sites which offer improved catalytic properties over conventional Au  
51 surfaces<sup>10,12</sup>. 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  
54 physical and chemical properties of Au are fundamentally altered.<sup>13</sup> For example, quantum-  
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  
58 of Au nanoparticles owing to the strong quantum confinement effect.<sup>13</sup> Together with Au-  
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  
63 heterogeneous chemistry<sup>14-16</sup>. Understanding the mechanisms by which hydrogen can be  
64 activated on Au is crucial to designing stable and efficient supported Au catalysts for  
65 hydrogenation reactions<sup>17-18</sup>.

66 Generally, hydrogenation reactions on metal surfaces, including Au, follow the Horiuti-  
67 Polanyi mechanism that involves the homolytic splitting of a hydrogen molecule adsorbed on  
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<sup>2,19-21</sup>. By  
71 combining theory and experiment, the nature and structure of the active sites responsible for  
72 the adsorption and dissociation of molecular hydrogen are now well understood. The presence  
73 of the low-coordinated atoms located at the corner and edge of the Au particle is necessary for  
74 H<sub>2</sub> splitting on Au NPs<sup>2,19-22</sup>. Hydrogen adsorption is only possible on low coordinated atoms  
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

78 mobility of H species on the Au NPs<sup>23</sup>. The main challenge in using Au for hydrogenation  
79 reactions is its low efficiency in dissociating H<sub>2</sub> under standard conditions. The important  
80 factors that make bulk Au the most noble metal and ineffective for hydrogen dissociation owe  
81 to the largest orbital overlap with the adsorbed hydrogen and highly filled antibonding  
82 adsorbate-metal *d* states<sup>24</sup>.

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  
86 reports on hydrogenation and hydroconversion reactions using Au nanoparticles and single  
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 H<sub>2</sub> and Au catalysts in the  
94 catalysis and materials chemistry communities.  
95

## 96 [H1] Hydrogenations on Au

97 The fundamental development of Au based catalytic formulations<sup>18, 25-27</sup> and the  
98 enhancement of existing systems<sup>28-30</sup> require a deep understanding of the impacts of active  
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  
101 design of multi-phase formulations (bimetallic and promoted Au catalysts) as well as synthesis  
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  
104 into the mechanism of H<sub>2</sub> activation, hydride formation,<sup>31</sup> and the adsorption of the substrates  
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 H<sub>2</sub> 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  
114 nanoparticles. Another problem is the deactivation of the catalyst from structure degradation,  
115 leaching, and carbon deposition<sup>34</sup>. The mechanisms underlying the degradation of the catalyst  
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  
124 selectivity in hydrogenation reactions<sup>15-16</sup>. In addition, while the mechanism of hydrogen  
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 particles<sup>23</sup>. Several uncertainties 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<sup>35</sup>.

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) level<sup>36-38</sup>. For example, in the  
135 semihydrogenation of alkynes, Au was predicted to exhibit a higher selectivity to alkenes than  
136 Pd by Density Functional Theory (DFT) and it was also confirmed experimentally<sup>35</sup>. In  
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 products<sup>35</sup>.  
139 Conversely, the triple C–C bonds of alkynes are preferentially adsorbed and are subsequently  
140 activated on Au<sup>35</sup>. That is to say that triple C–C bonds can be preferentially hydrogenated and  
141 the alkene products can desorb from the Au surface avoiding further hydrogenation<sup>35</sup>. This high  
142 chemoselectivity of supported small Au nanoparticles enabled the hydrogenation of  $\alpha,\beta$ -  
143 unsaturated aldehydes to the corresponding unsaturated alcohols<sup>39-40</sup>, and the deprotection of  
144 epoxides via deoxygenation to the corresponding alkenes<sup>41</sup>, in both cases preserving the C=C  
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 hydrogenations<sup>24</sup>. In this context, several strategies have been  
150 developed to enhance the rate of H<sub>2</sub> dissociation to improve the catalytic efficiency of supported  
151 Au catalysts (**Figure 1**). The main approaches are the heterolytic hydrogen dissociation  
152 occurring on Au interacting with nitrogen-containing ligands<sup>42</sup> (**Figure 1a**) or at the metal-  
153 support interface in case of strong metal support interactions (SMSI)<sup>43</sup> (**Figure 1b**). H<sub>2</sub>  
154 dissociation could be also induced by hot electrons generated by plasmon enhancement<sup>44</sup>  
155 (**Figure 1c**) or at single Au atoms (**Figure 1d**)<sup>45</sup>, as well as by alloying gold with a second metal  
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**

160 Auxiliary ligands can help to enhance selectivity in heterogeneous catalysis. In hydrogenation  
161 on Au NPs, the addition of certain ligands has demonstrated enhanced activity in the selective  
162 hydrogenation of alkynes to *cis*-alkenes (**Figure 2a**). An inactive silica-supported Au  
163 nanoparticle catalyst (Au/SiO<sub>2</sub>) exhibited a substantial increase of activity in the presence of  
164 various nitrogen-containing ligands<sup>42</sup>. In the presence of piperazine, for example, the Au  
165 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 H<sub>2</sub> 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 H<sub>2</sub>, 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 H<sub>2</sub> dissociation  
173 through a heterolytic mechanism. First, the H<sub>2</sub> molecule approaches the ligand–Au interface.  
174 The H<sub>2</sub> 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  
182 affected the stability of the Au surface<sup>42</sup>. Piperazine was selected as the best ligand, among  
183 nineteen amines tested, to promote the catalytic hydrogenation of alkynes on Au NP catalyst<sup>42</sup>.  
184 The Au-ligand catalytic system can be considered a frustrated Lewis pairs (FLP) analogue<sup>46</sup>.  
185 Other studies in the literature showed similar observations when combining Au NPs either with  
186 other nitrogen-containing<sup>47-48</sup> and phosphorous-containing<sup>49</sup> ligands for hydrogenations.  
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 important 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/TiO<sub>2</sub>) showed an enhanced catalytic activity (**Figure 2c**) when compared to uncoated  
194 Au/TiO<sub>2</sub> for alkyne semihydrogenation<sup>47</sup>. The main advantage compared to the previous study,  
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 study<sup>5</sup>. A combination of experimental and computational studies revealed a N-assisted  
199 heterolytic H<sub>2</sub> 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 an essentially barrierless heterolytic dissociation of  
202 H<sub>2</sub> (**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 H<sub>2</sub><sup>47</sup>. 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  
206 species A. The mechanism illustrates the major role of N-heteroatoms on the H<sub>2</sub> activation.  
207 In another example, verified by DFT calculations, Lewis bases, such as NH<sub>3</sub>, adsorbed on four  
208 different models for Au surfaces and clusters (Au(111)-close-packed, Au(211)-step-edged,  
209 Au(111)-single atom, and Au<sub>38</sub> cluster) were able to generate hydrides (H\*) and protons (NH<sub>4</sub>\*)

210 through heterolytic H<sub>2</sub> dissociation. The generated hydride and proton can then be concertedly  
211 transferred to CO<sub>2</sub> to produce formic acid in all four Au models<sup>50</sup>. The cooperation between Au  
212 and adsorbed basic ligands has also been employed in the hydrogenation of other organic  
213 molecules, including quinolines<sup>51</sup>, imines or nitriles<sup>48</sup> and aldehydes<sup>52-53</sup>.

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 catalysts<sup>29-30</sup>. 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 SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, or TiO<sub>2</sub>. 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 process<sup>30</sup>. In addition, SMSIs can  
226 influence the adsorption and activation of reactant molecules, affecting the selectivity of the  
227 catalytic reaction. Thus, by exploiting 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 eV vs 17.36 eV)<sup>54-55</sup>. 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 efficiently<sup>54</sup>. The interface of the oxide support can help to  
235 enhance this heterolytic process<sup>43, 56</sup>. An illustration of this concept can be observed in the case  
236 of TiO<sub>2</sub>(110), where the presence of low coordinated O<sub>2</sub> atoms adjacent to the Au clusters has  
237 been observed. This arrangement has the potential to facilitate the dissociation of molecular H<sub>2</sub>,  
238 leading to the protonation of the oxygen atoms situated on the support<sup>56</sup>.

239 In contrast, the Au SACs supported in electron-rich cavities of N-doped carbon (such  
240 as graphitic carbon nitride obtained by the pyrolysis of organic amines– C<sub>3</sub>N<sub>4</sub>) dissociate H<sub>2</sub>  
241 homolytically<sup>45</sup>. The catalyst was suggested by DFT to be composed of Au<sup>δ+</sup> (1<δ<3) species  
242 stabilized in oxidized-4-pyridine cavities from the N-doped carbon. The developed catalyst led  
243 to thermodynamically more favored H<sub>2</sub> activation than the stepped surface Au(211) (–1.13 eV  
244 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 TiO<sub>2</sub> 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  
250 catalyst containing both Au particle sizes (3 nm and 9 nm) showed a moderate selectivity to 3-  
251 vinylaniline (55%) at relatively high conversion (25%)<sup>57</sup>. 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  
255 (~9 nm) exhibited a substantially lower conversion (14.9%) than the catalyst with 3 nm Au NPs  
256 (or combination of 3 and 9 nm, 15.4 and 24.8% respectively) which maintained a high  
257 conversion level<sup>57</sup>. 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  
261 tensions of the metal and support during the encapsulation process<sup>57</sup>. Typically, the metal has  
262 a higher surface tension than the TiO<sub>2</sub> support, which is often observed experimentally. In the  
263 case of Au, its relatively low surface tension ( $\gamma_{\text{Au}} = 1.51 \text{ J m}^{-2}$ ) has been considered as a  
264 hindrance for the formation of SMSIs<sup>57</sup>. Recent discoveries of SMSIs in TiO<sub>2</sub> supported Au  
265 catalysts have challenged the previously reported surface tension of TiO<sub>2</sub> (1.3–1.9 J m<sup>-2</sup>) and  
266 raised questions about its potential overestimation<sup>58</sup>. This opens up the possibility that Au may  
267 possess a higher surface tension than TiO<sub>2</sub>, allowing it to be wetted by TiO<sub>2</sub>, and leading to the  
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<sub>2</sub><sup>57</sup>.

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 SiO<sub>2</sub> and  
280 activated carbon)<sup>59</sup>. 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 H<sub>2</sub> molecules. Specifically, the electron transfer  
284 between C and Au leads to the heterolytic dissociation of H<sub>2</sub> on the C–Au interface. The unique  
285 adsorption configuration of C–Au further influences the chemisorption process due to its  
286 distinct electronic properties. This selective adsorption and activation of H<sub>2</sub> 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  
289 and Au/SiO<sub>2</sub> catalysts<sup>59</sup>. Additionally, there may be a continuous exchange of C atoms between  
290 the surface and subsurface, potentially facilitating the adsorption of H<sub>2</sub> molecules. Moreover,  
291 in case of the 3-nitrostyrene hydrogenation on Au supported mesoporous carbon catalysts high  
292 chemoselectivity to 3-vinylaniline was observed<sup>59</sup>. This was attributed to the perpendicular  
293 adsorption of the substrate, stronger interaction of the 3-nitrostyrene with the C containing 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 H<sub>2</sub> dissociation improved the catalytic performance of the Au NPs in  
297 hydrogenation reactions<sup>59</sup>.

298  
299

### **[H<sub>2</sub>] Plasmon enhancement**

300 Exploiting the plasmonic properties of Au NPs (localized surface plasmons, LSPR) is  
301 an alternative strategy to activate H<sub>2</sub><sup>23,44,60</sup>. Here, hot electrons are formed from light  
302 illumination which then relax or scatter, initiating the catalytic hydrogenation reaction. Hot  
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 hydrogen<sup>44</sup>.  
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 H<sub>2</sub> molecules. Small Au supported on SiO<sub>2</sub> nanoparticles  
312 prepared by chemical deposition precipitation method were used in H<sub>2</sub> dissociation experiments  
313 (**Figures 3a-c**). **Figure 3a** illustrates the rate of H–D formation on the Au/SiO<sub>2</sub> 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**)<sup>60</sup>.  
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  
320 and temperature, showcasing the process' reversibility<sup>60</sup>. For a direct comparison of H<sub>2</sub>  
321 dissociation efficiency between the Au/SiO<sub>2</sub> and Au/TiO<sub>2</sub> 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/SiO<sub>2</sub> (**Figure 3b**), the enhancement in the  
324 case of Au/TiO<sub>2</sub> (**Figure 3c**) was modest, measuring around 2.7 times. The subdued rate for  
325 Au/TiO<sub>2</sub> may be attributed to the formation of a Schottky barrier (with a nominal height of  
326 0.8–1 eV) at the Au–TiO<sub>2</sub> 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 TiO<sub>2</sub>, contributing to the observed effects<sup>60</sup>. As the rate of hydrogen  
329 dissociation decreased substantially when SiO<sub>2</sub> was replaced by TiO<sub>2</sub>, (**Figures 3b-c**) indicates  
330 that H<sub>2</sub> dissociation occurring on the illuminated AuNP surface and the dielectric oxide is not  
331 participating in the process.<sup>60</sup> A key challenge remains in the diffusion of hydrogen through the  
332 support and its recombination, which is essential to understanding the activity of hydrogen on  
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 again<sup>23</sup>. The measured LSPR shifts was of  
340 about 0.02 nm during H<sub>2</sub> adsorption (as measured by Transmittance Anisotropy

341 Spectroscopy)<sup>23</sup>. Hydrogen chemisorption occurred directly on Au. Furthermore, the  
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 H<sub>2</sub>, 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  
349 in Au nanoparticles decreases<sup>23</sup>. This enhanced comprehension of the chemisorption  
350 mechanism of H<sub>2</sub> onto Au NPs is anticipated to facilitate advancements in the fabrication and  
351 utilization of catalytic Au NPs for hydrogenation reactions<sup>23</sup>.

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  
354 chemical reactions governed by mechanisms involving plasmonic effects and hot electron  
355 transfer may also be advantageous<sup>61-63</sup>. This is especially true for hydrogenation reactions where  
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 H<sub>2</sub> were vital for high yields and the plasmon decay substantially lowered the energy barrier for  
359 hydrogen dissociation<sup>60</sup>. Moreover, the dissociation of H<sub>2</sub> on the Au surface under visible light  
360 excitation opens up the possibility of developing more efficient 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 SiO<sub>2</sub> catalysts<sup>64</sup>.

365 To increase the catalytic performance of non-plasmonic metals like Pt, a successful  
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 SiO<sub>2</sub> and TiO<sub>2</sub> showed both negative (reduced reaction rate) and positive (catalytic  
370 enhancement) effects for 4-nitrophenol hydrogenation under visible-light illumination. The  
371 difference in plasmonic catalytic activities<sup>65</sup> were attributed to the charge transfer at the  
372 interface of Au and the support as well as to the reducing agent (H<sub>2</sub> and NaBH<sub>4</sub>) used during  
373 the catalyst synthesis. Au/SiO<sub>2</sub> NPs were substantially more active under plasmon excitation,  
374 while Au/TiO<sub>2</sub> catalysts were only enhanced by plasmons when H<sub>2</sub>(g) was used as reductor.  
375 Reduced reaction rate observed upon reduction with BH<sub>4</sub><sup>-</sup>(aq) was attributed to the transfer of  
376 hot electrons from Au to TiO<sub>2</sub>.

377

### 378 *[H<sub>2</sub>] Cationic Au*

379 An alternative approach for improving the activation of hydrogen is by using dispersed  
380 cationic Au species, in which isolated Au ions are dispersed throughout a carrier. The synthesis  
381 of these type of material is not trivial and usually requires several steps as illustrated in **Figure**  
382 **4a**. In case of gold supported on carbon nitride two most important steps are linked to the  
383 thermal treatment, firstly at low (686°C) and then at high temperature above 1246°C (**Figure**  
384 **4a**). This structure resembles traditional organometallic catalysts<sup>66-71</sup>, comprising isolated

385 metals that are bonded to organic ligands (**Figure 4b** and **Figure 1e**). These structures are also  
386 described as single-atom catalysts (SACs), which are attracting growing interest because they  
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 hydrogenations<sup>72-76</sup>. 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)<sup>77</sup>. 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<sup>+</sup>) supported on iron oxide (FeO<sub>x</sub>) showed higher resistance to sintering  
394 (increase of the particle size) compared to other Au nanostructures for alkene hydrogenations<sup>78-</sup>  
395 <sup>82</sup>. Theoretical studies revealed that surface-anchored Au<sup>+</sup> 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  
398 MgO surface induced high activity and selectivity in ethene hydrogenation<sup>79</sup>. The conversion  
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 catalysis<sup>79</sup>.

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  
404 conditions<sup>83-84</sup>. However, the practical use of Au SACs is often compromised by challenging  
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 conditions<sup>43</sup>. To  
407 address the difficulty of making such materials, a co-precipitation strategy can be applied<sup>85</sup>.  
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 example 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 C<sub>3</sub>N<sub>4</sub><sup>86-87</sup>.  
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  
416 MOFs<sup>85</sup>. In addition, after 10 catalytic cycles, the catalyst retained its original morphology and  
417 activity, indicating an excellent stability.<sup>85</sup>

418 A kg-scale synthesis of Au<sub>1</sub>/CeO<sub>2</sub> SAC was reported using a dry ball milling synthetic  
419 protocol<sup>88</sup>. This catalyst was then tested in the hydrogen oxidation (1 vol% H<sub>2</sub> + 1 vol% O<sub>2</sub>  
420 balanced with He). In the latter, the catalyst showed only ~10% of hydrogen conversion at 160  
421 °C<sup>88</sup>. 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**

425 Hydrogen dissociation can also be improved by exploiting Au alloying to generate  
426 weakly bound H atoms<sup>89-91</sup>. Ideally, an alloy structure (**BOX 3**) should effectively combine  
427 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  
429 and therefore promote hydrogenation<sup>104-105</sup>. The most promising bimetallic catalysts for  
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  
432 the core and the second metal forms the shell<sup>106</sup>. The optimal ensemble configuration for  
433 heterolytic H<sub>2</sub> 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 hydrogen<sup>107</sup>.

437 It is important to identify the sites responsible for the activation of H<sub>2</sub> 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 H<sub>2</sub> 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 H<sub>2</sub> 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 H<sub>2</sub><sup>94</sup>. 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 H<sub>2</sub> including an understanding of the  
449 activation and desorption of hydrogen from isolated Pd atoms, the typical reaction pathway for  
450 activating H<sub>2</sub> and the mechanism of the release of hydrogen along the Pd atoms with minimum  
451 spillover of hydrogen species to the Au<sup>95</sup>.

452 Using spatially resolved tip-enhanced Raman spectroscopy (TERS)<sup>108-110</sup>, a study of the  
453 catalytic hydrogenation of chloronitrobenzenethiol to chloroaminobenzenethiol (**Figure 5a**)  
454 over Au–Pd catalyst was carried out<sup>110</sup> (**Figures 5 a-f**). TERS studies the topography and  
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  
458 regions on **Figures 5 c and e**) and surface structures was conducted<sup>110</sup>. In **Figures 5 d and f**,  
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<sub>LC</sub>/Au (Au surface with low Pd  
464 coverage, **Figure 5c and d**), the size of the active regions, is approximately 50 nm<sup>110</sup>. However,  
465 the size of the Pd islands within both regions measures only 20 nm. Conversely, for Pd<sub>HC</sub>/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  
468 15-30 nm beyond the boundaries of the Pd areas, where hydrogenation reactions occur. These  
469 spillover regions, however, exhibit an asymmetrical relationship with the shape of the Pd  
470 islands (**Figure 5c**)<sup>110</sup>. 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

472 on Pd, hydrogen atoms migrated to adjacent Au surfaces over relatively long distance of 15-30  
473 nm<sup>110</sup>. The mechanism of this hydrogenation involving hydrogen spillover was also determined  
474 by DFT and confirmed the feasibility of the long-distance diffusion and explained the enhanced  
475 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  
477 isolated metal atoms are present in the surface layer of a metal play the role of the host<sup>104-105,</sup>  
478 <sup>111-112</sup>. Typically, SAAs are comprised of single atoms of a catalytically active metal alloyed  
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 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 catalyst<sup>105</sup>. 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 hydrogen<sup>112</sup>. 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 host<sup>111</sup>. In operando spectroscopy studies confirmed that the transformation occurs  
492 by first dissociating H<sub>2</sub> and splitting of the hydrogen species on the Pd sites followed by the  
493 reaction of the adsorbed H species on Au<sup>111</sup>. Moreover, by DFT studies performed on Pd–  
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  
499 properties of bimetallic systems<sup>113</sup>. The incorporation of a second metal can help to overcome  
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  
503 well as higher chemoselectivity in the hydrogenation of halonitrobenzenes<sup>26</sup>. As such, an  
504 Au@Pt/SiO<sub>2</sub> 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  
507 compared in terms of the selectivity to *para*-chloroaniline<sup>26</sup> (**Figures 6b**). The core-shell  
508 structure was confirmed using high resolution microscopy (**Figure 6c**) and revealed the Pt shell  
509 thickness of about 0.3 nm (blue line in **Figure 6c**) in case of Au@1ML-Pt catalyst. The  
510 Au@Pt/SiO<sub>2</sub> 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  
512 effect can have a profound impact on the catalytic activity and specificity of the catalyst as the  
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 preserved<sup>26</sup>, 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 poisoning<sup>25</sup>.

520 Au-based bimetallic catalysts were also shown to possess excellent CO<sub>2</sub> hydrogenation  
521 activity, forming CO. For example, Ni–Au bimetallic catalytic systems based on core-shell  
522 structure are very active in this reaction<sup>102</sup> (**Figure 6d**). SiO<sub>2</sub> was chosen as a support of the  
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-  
527 600 °C<sup>102</sup> (**Figure 6e**). *Ex situ* STEM characterization showed the presence of core-shell  
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 alloy<sup>102</sup> (**Figure 6d**,  
532 top part). However, during the cooling process to 450°C, the dealloying process occurred and  
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 CO<sub>2</sub> 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 CO<sub>2</sub> hydrogenation and the Au active site for the high selectivity CO  
542 formation<sup>102</sup>. 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  
546 from deactivation<sup>96-97</sup>.

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<sup>+</sup>/H<sup>-</sup> 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  
561 choice of promoter depends on the specific catalytic reaction and the desired enhancement in  
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  
567 catalysts<sup>114</sup>.

568 Another important challenge will be the use of hybrid catalysts mixing single atoms and  
569 nanoscale particles<sup>115-117</sup>. In this case, cascade reactions may be performed or the reaction rate  
570 can be substantially improved. This could be a useful parameter to explore in reactions  
571 involving hydrogen as the hydrogen dissociation and reactivity strongly depends on the size of  
572 the Au particle.

573 Finally, we need an improved fundamental understanding of the hydrogenation  
574 mechanisms as this should provide information for the rational design of new Au catalysts. To  
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 active 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  
595 through this multidisciplinary lens, hold immense promise, not only in hydrogenation processes  
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.



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902

903  
904 **Figure 1.** Types of H<sub>2</sub> activation on heterogeneous Au catalysts and strategies to enhance H<sub>2</sub> dissociation on Au. (a) two different  
905 types of H<sub>2</sub> activation that may occur on gold (b) Ligands containing 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 for hydrogen dissociation. On the Figure 1c one of the  
908 example of strong SMSI registered in the case of Au supported on TiO<sub>2</sub>. 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<sub>3</sub>N<sub>4</sub> structure (blue circles 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<sub>2</sub> can easily  
912 dissociated on Pd or Pt and then can migrate to Au thanks to spillover 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/SiO<sub>2</sub> in the presence of piperazine. (c) Time course of hydrogenation  
917 of phenylacetylene catalysed by Au@N-doped carbon/TiO<sub>2</sub>. (d) Experimental reaction rates vs computed activation energies  
918 for H<sub>2</sub> 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). 1a refers to  
922 phenylacetylene and 2a to styrene. (Au = yellow, N = blue, C = gray, H = white). Reprinted with permission from<sup>42,47</sup>. Part B-  
923 C adapted with permission from ref 42, ACS. Part D adapted with permission from ref 47, ACS. Part E reprinted  
924 with permission from ref 47, ACS.

925  
926 **Figure 3.** Hot electron induced H–D formation at 23 °C on 1% Au/SiO<sub>2</sub> catalyst. (a) The rate of H–D formation was  
927 continuously monitored in real-time under two conditions: with laser excitation (2.4 W/cm<sup>2</sup>, active) and without laser excitation  
928 (0.0 W/cm<sup>2</sup>, inactive). During the 10-minute period of laser excitation, the sample experienced a reversible temperature  
929 increase of 8 °C, as depicted in the figure, transitioning from 22 to 30 °C. (b) H–D formation rate for 1% Au/SiO<sub>2</sub>. (c) H–D  
930 formation rate for 1% Au/TiO<sub>2</sub> catalyst. In both cases the same reaction condition were applied with laser excitation of 2.4  
931 W/cm<sup>2</sup>.<sup>60</sup> Any activity was observed in the case of SiO<sub>2</sub> (blue curve) and TiO<sub>2</sub> (purple curve). The size of AuNPs were 5–30  
932 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 HAuCl<sub>4</sub> used as Au precursor. Impregnation step performed via incipient wetness  
935 impregnation of nitrogen doped carbon (NC) with HAuCl<sub>4</sub> in aqua regia solution. Two thermal treatment were applied:  
936 activation step in static air (at 473 K) and flowing N<sub>2</sub> (>973 K) for 16 h. Color code as follows Au-yellow, C-gray, N-blue, and  
937 Cl-green.<sup>45</sup> (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)<sup>45</sup>; (c) TOF (Turnover frequency) in  
939 ethene hydrogenation in function of the single Au–Au coordination number on different MgO supported catalysts containing  
940 Au<sup>3+</sup> and Au clusters<sup>79</sup>. 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 (Scanning 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<sup>-1</sup> (NO<sub>2</sub> stretching bond in Raman spectra) in TERS line scan spectra on Pd<sub>L</sub>C/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 direction<sup>110</sup> (d) The topographic height profile for Pd<sub>L</sub>C/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<sup>-1</sup> in TERS line scan spectra on Pd<sub>H</sub>C/Au (high Pd  
954 coverage on Au surface). (f) The topographic height profile for Pd<sub>H</sub>C/Au. (g) and (h) Reaction rate and selectivity profiles for  
955 time-resolved hydrogenation of 1-hexyne over PdAu-SAA/SiO<sub>2</sub> catalysts compared to monometallic Pd/SiO<sub>2</sub> 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 diffraction 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@IML-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 CO<sub>2</sub> hydrogenation as 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 CO<sub>2</sub> 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)<sup>3</sup>. The first  
980 large scale hydrogenation process was the hydrogenation of fatty acids and their glycerides using Ni  
981 catalyst in 1909 in Crosfield, USA<sup>4</sup>. The addition of hydrogen gas (H<sub>2</sub>) 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 nanoparticles<sup>32-33</sup>, as represented  
996 on the figure. The homolytic dissociation of H<sub>2</sub> 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<sub>2</sub> 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 where L = ligand)<sup>32</sup>.

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<sub>2</sub>, 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 acid<sup>32-33</sup>.

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 synthesis<sup>92</sup>. 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  
1029 most common of which are: Au–Pt<sup>26,93</sup>, Au–Pd<sup>94-98</sup>, Au–Ir<sup>99</sup>, Au–Ag<sup>100</sup>, Au–Cu<sup>101</sup>, Au–Ni<sup>102</sup> and Au–  
1030 SiO<sub>2</sub><sup>103</sup>.

1031 Part A (left) is adapted from ref 92, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). B (right)  
1032 adapted from ref.93, Springer Nature Limited. B (right) adapted from ref.98, Springer Nature Limited. B (right)  
1033 adapted from ref.103, Springer Nature Limited.

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**Summary:**

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

**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?
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Fig 1

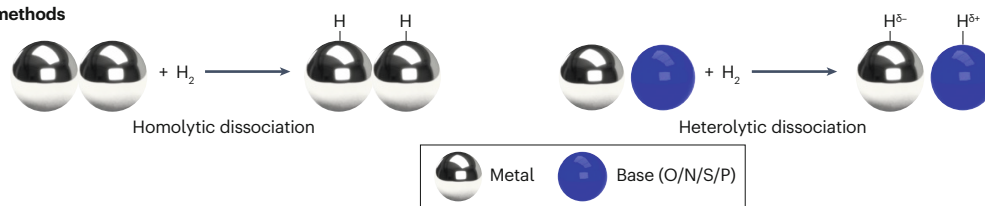
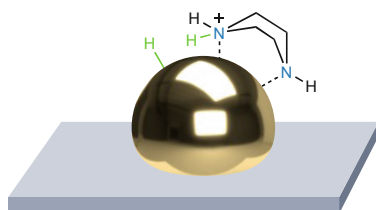
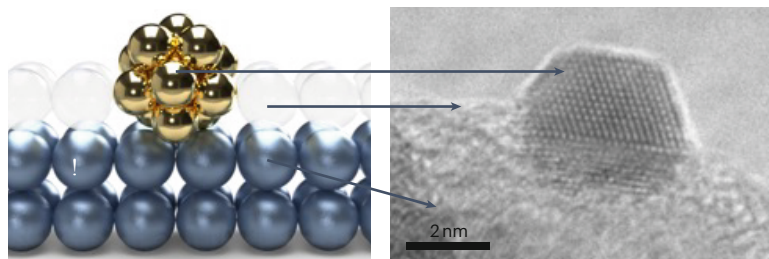
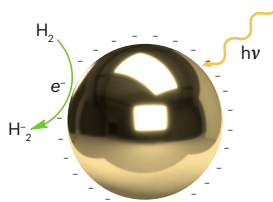
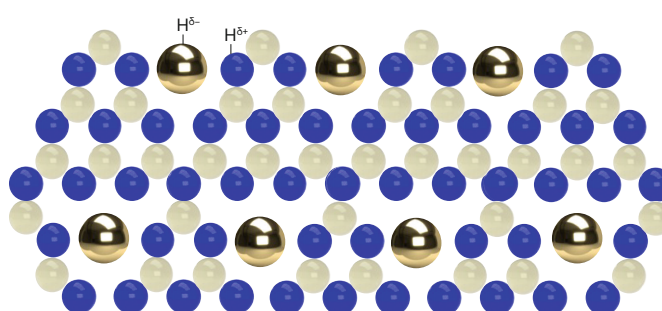
**a** H<sub>2</sub> activation methods**b** Ligand activation of H<sub>2</sub>**c** Strong support-metal interaction (SMSIs)**d** Effect of hot electrons on Au properties**e** Au single atoms inside C<sub>3</sub>N<sub>4</sub>**f** Au alloys

Fig 2

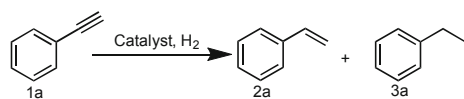
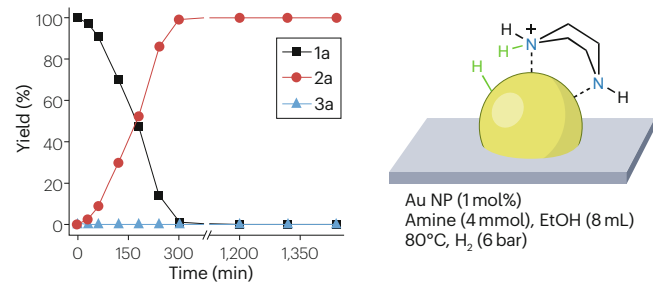
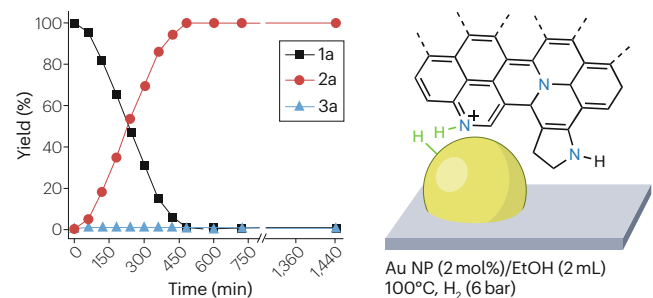
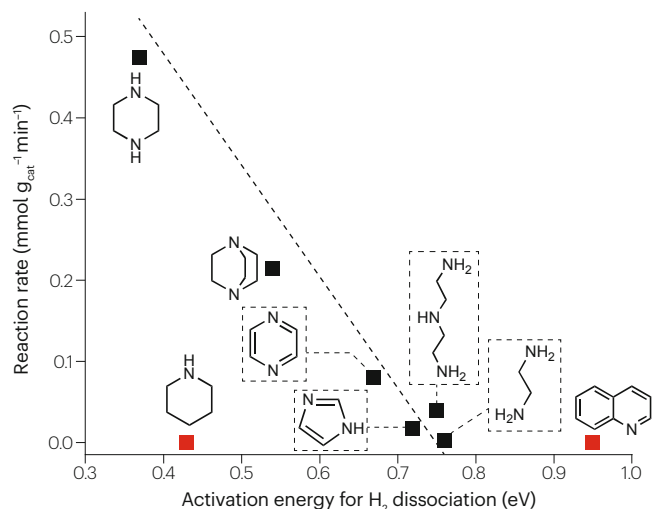
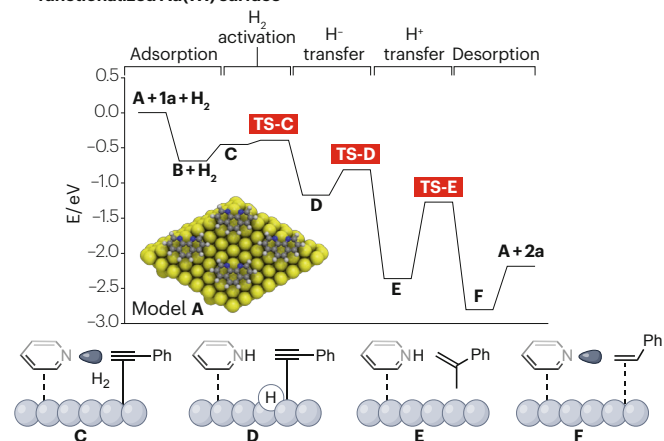
**a** Catalytic hydrogenation of phenylacetylene into styrene and ethylbenzene**b** Reaction course with Au/SiO<sub>2</sub> catalyst and piperazine**d** Reaction course with Au@N-doped carbon/TiO<sub>2</sub> catalyst**c** Experimental reaction rates vs computed activation energies for H<sub>2</sub> dissociation at the N ligand–Au(111) interface**e** Computed reaction energy profile for hydrogenation on phenanthroline-functionalized Au(111) surface

Fig 3

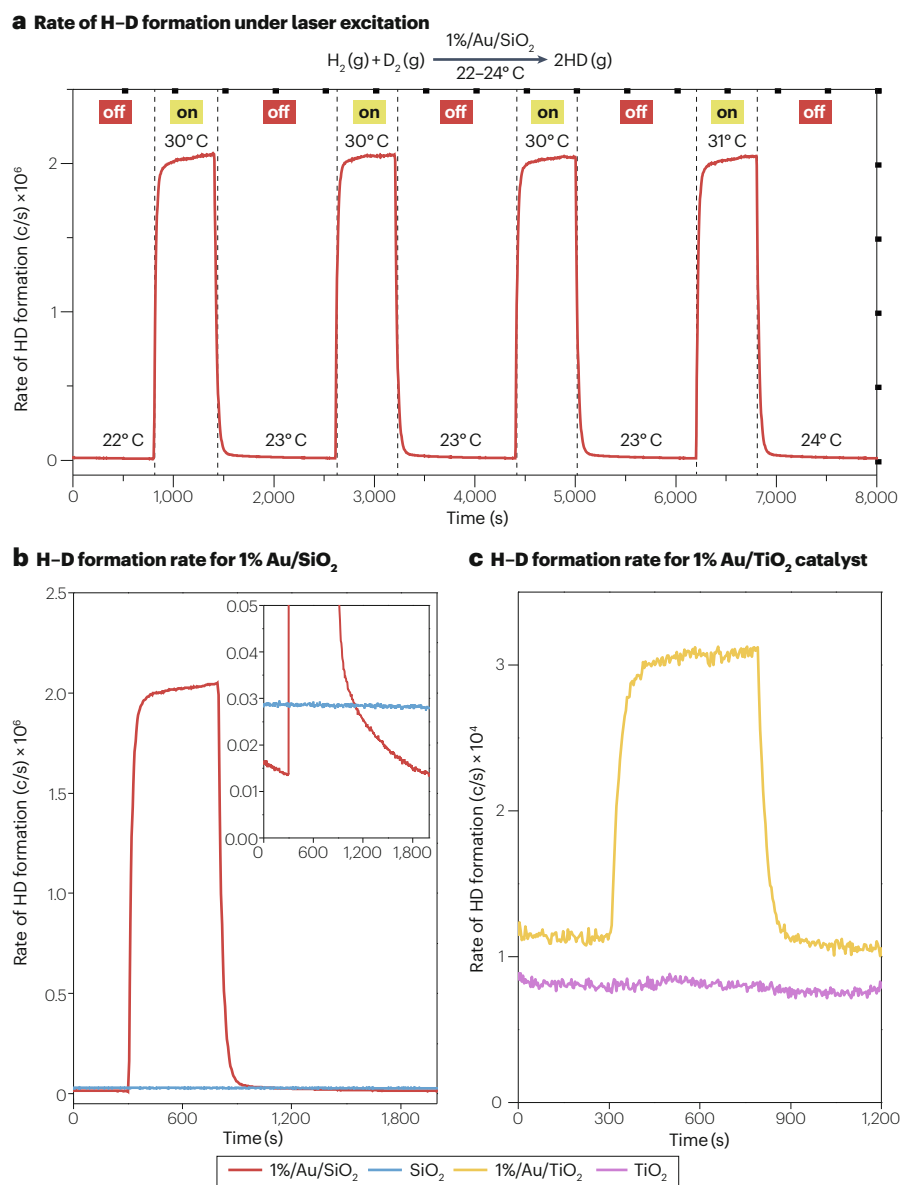
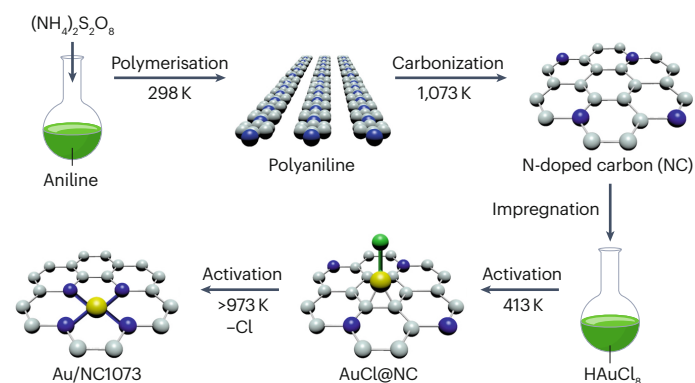
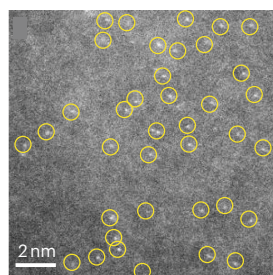


Fig 4

**a Nitrogen-doped carbon (Au(III)/NC) synthesis and impregnation with  $\text{HAuCl}_4$** **b HAADF-STEM micrograph of Au/NC1073 catalyst (Au SACs circled)**

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

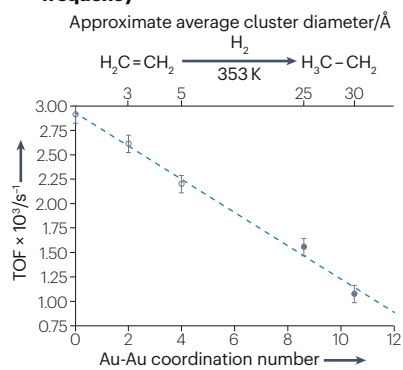
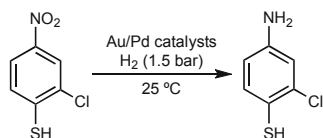
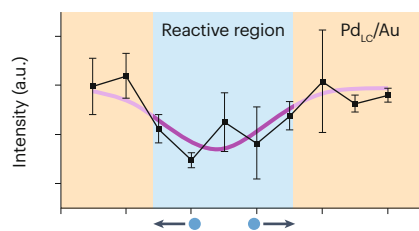
**c Ethene hydrogenation turnover frequency**

Fig 5

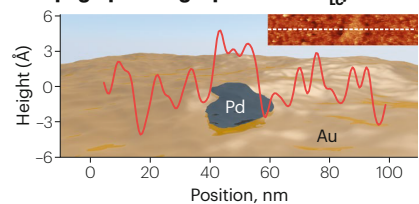
**a Catalytic hydrogenation of chloronitrobenzenethiol to chloroaminobenzenethiol**



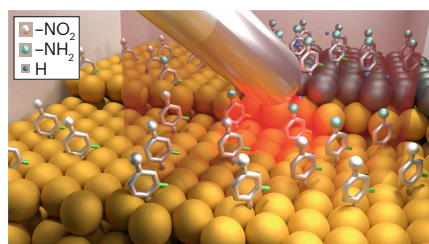
**c NO<sub>2</sub> stretching bond (Raman) intensity in TERS line scan spectra on Pd<sub>100</sub>/Au**



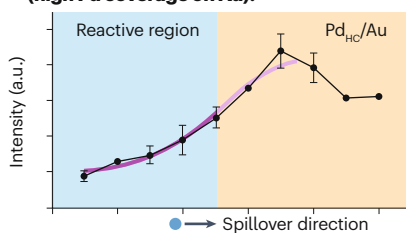
**d Topographic height profile for Pd<sub>100</sub>/Au**



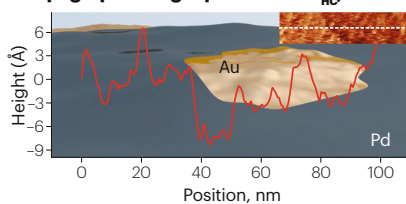
**b STM-TERS illustration of an Ag tip investigating hydrogenation on Pd/Au**



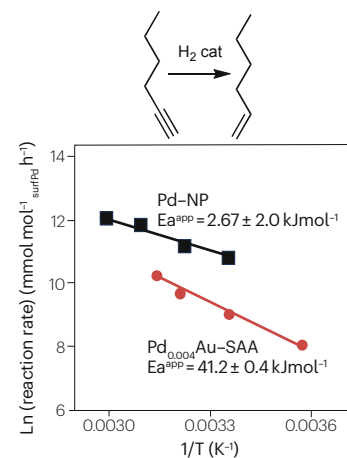
**e NO<sub>2</sub> stretching bond (Raman) intensity in TERS line scan spectra on Pd<sub>100</sub>H/Au (high Pd coverage on Au).**



**f Topographic height profile for Pd<sub>100</sub>H/Au**



**g Reaction rate for time-resolved hydrogenation of 1-hexyne over PdAu-SAA/SiO<sub>2</sub> v. monometallic Pd/SiO<sub>2</sub> catalyst**



**h Selectivity profile**

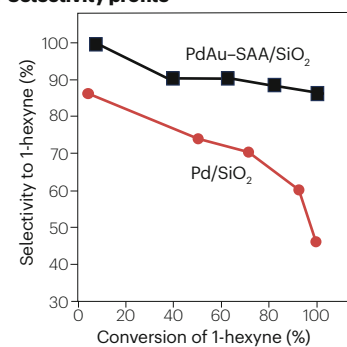
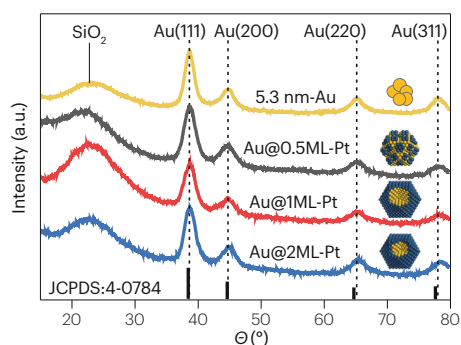
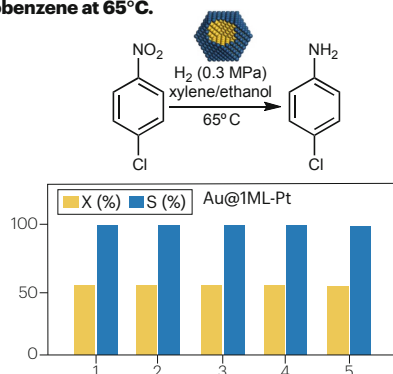
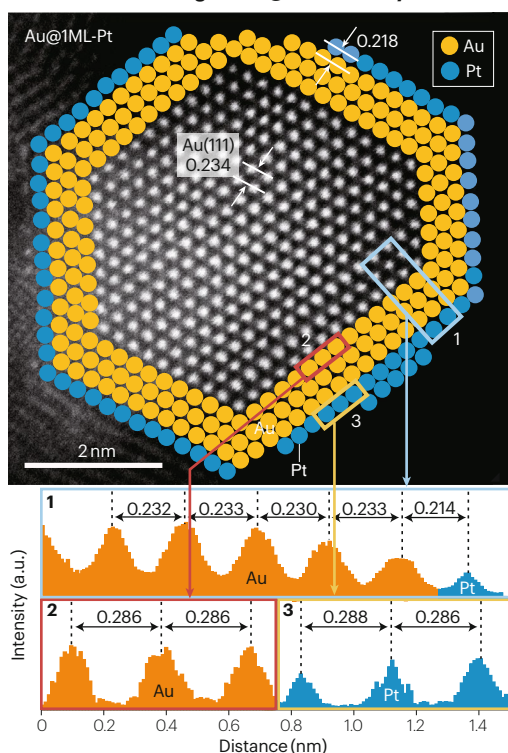
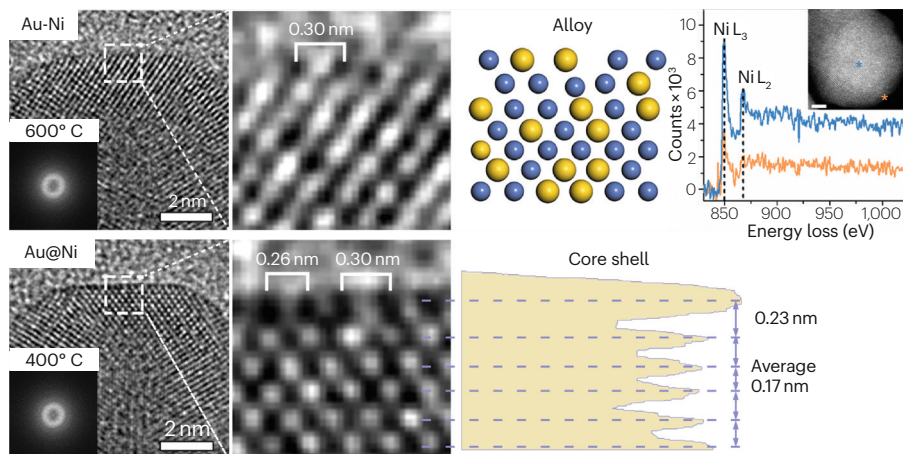
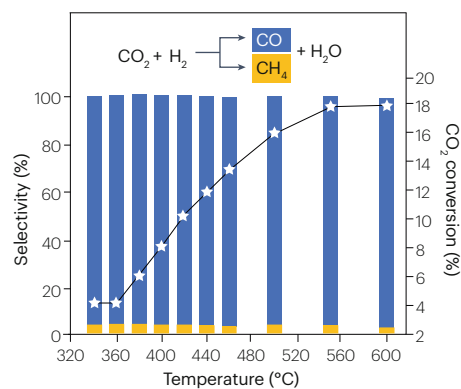
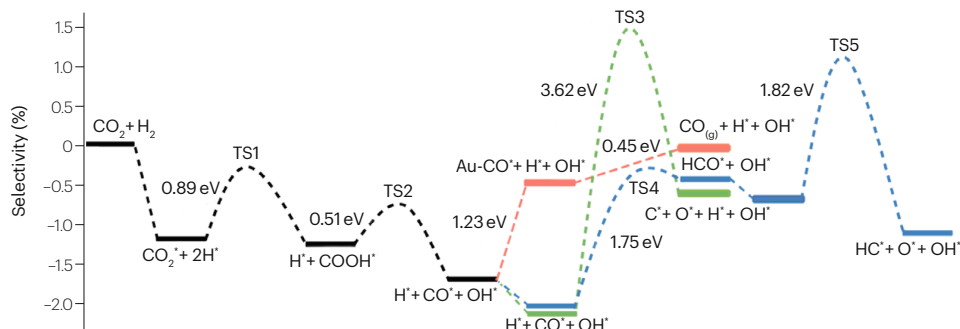
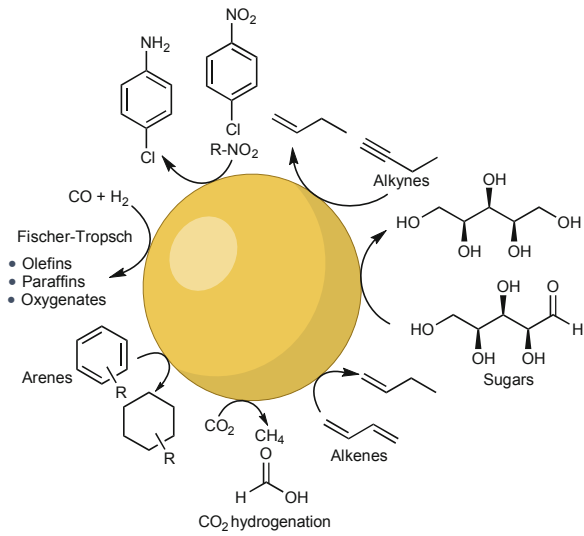


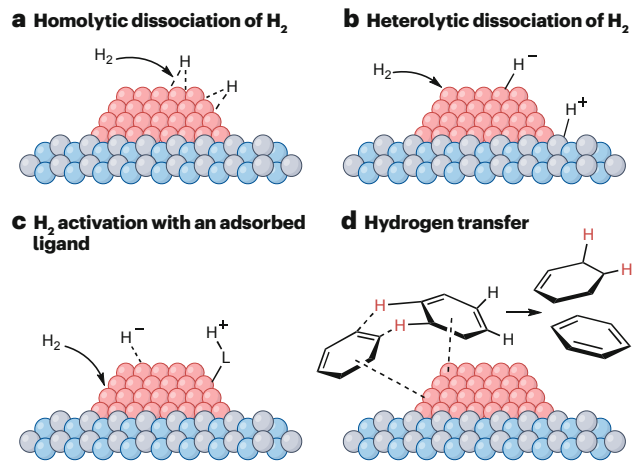
Fig 6

**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.****c HAADF-STEM image of Au@1ML-Pt catalyst****d Surface atom arrangement in Au-Ni bimetallic nanoparticle at 600°C and 400°C****e Selectivity and conversion profiles for the Ni-Au bimetallic catalyst****f Energy routes for CO2 hydrogenation on the alloyed Ni-Au surface**

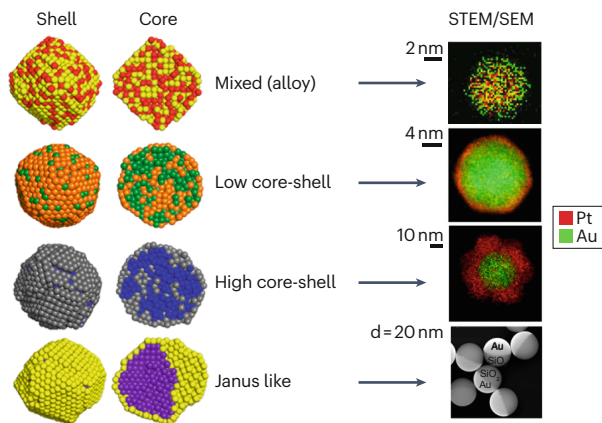
Box 1



Box 2



Box 3



GA

