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1 Strategies to improve hydrogen activation on gold catalysts

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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 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
42 discovered that gold (Au), typically considered inert, can catalyze the activation of H₂ and other
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
47 dispersed metallic nanoparticles. One such catalytic system is Au nanoparticles (Au NPs)
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 low-
50 coordination surface sites which offer improved catalytic properties over conventional Au
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
54 physical and chemical properties of Au are fundamentally altered.¹³ 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.¹³ 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 chemistry¹⁴⁻¹⁶. 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 reactions¹⁷⁻¹⁸.

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^{2,19-21}. 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 H₂ splitting on Au NPs^{2,19-22}. 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 NPs²³. The main challenge in using Au for hydrogenation
79 reactions is its low efficiency in dissociating H₂ 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* 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
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 H₂ 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^{18, 25-27} and the
98 enhancement of existing systems²⁸⁻³⁰ 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 H₂ activation, hydride formation,³¹ 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 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
114 nanoparticles. Another problem is the deactivation of the catalyst from structure degradation,
115 leaching, and carbon deposition³⁴. 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 reactions¹⁵⁻¹⁶. 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 particles²³. 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 activity³⁵.

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
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 experimentally³⁵. 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 products³⁵.
139 Conversely, the triple C–C bonds of alkynes are preferentially adsorbed and are subsequently
140 activated on Au³⁵. 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 hydrogenation³⁵. This high
142 chemoselectivity of supported small Au nanoparticles enabled the hydrogenation of α,β -
143 unsaturated aldehydes to the corresponding unsaturated alcohols³⁹⁻⁴⁰, and the deprotection of
144 epoxides via deoxygenation to the corresponding alkenes⁴¹, 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 hydrogenations²⁴. In this context, several strategies have been
150 developed to enhance the rate of H₂ 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 ligands⁴² (**Figure 1a**) or at the metal-
153 support interface in case of strong metal support interactions (SMSI)⁴³ (**Figure 1b**). H₂
154 dissociation could be also induced by hot electrons generated by plasmon enhancement⁴⁴
155 (**Figure 1c**) or at single Au atoms (**Figure 1d**)⁴⁵, 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/SiO₂) exhibited a substantial increase of activity in the presence of
164 various nitrogen-containing ligands⁴². 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 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
182 affected the stability of the Au surface⁴². Piperazine was selected as the best ligand, among
183 nineteen amines tested, to promote the catalytic hydrogenation of alkynes on Au NP catalyst⁴².
184 The Au-ligand catalytic system can be considered a frustrated Lewis pairs (FLP) analogue⁴⁶.
185 Other studies in the literature showed similar observations when combining Au NPs either with
186 other nitrogen-containing⁴⁷⁻⁴⁸ and phosphorous-containing⁴⁹ 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/TiO₂) showed an enhanced catalytic activity (**Figure 2c**) when compared to uncoated
194 Au/TiO₂ for alkyne semihydrogenation⁴⁷. 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 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 an 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
206 species A. The mechanism illustrates the major role of N-heteroatoms on the H₂ activation.
207 In another example, verified by DFT calculations, Lewis bases, such as NH₃, 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 Au₃₈ cluster) were able to generate hydrides (H*) and protons (NH₄*)

210 through heterolytic H₂ dissociation. The generated hydride and proton can then be concertedly
211 transferred to CO₂ to produce formic acid in all four Au models⁵⁰. The cooperation between Au
212 and adsorbed basic ligands has also been employed in the hydrogenation of other organic
213 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
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)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
235 enhance this heterolytic process^{43, 56}. An illustration of this concept can be observed in the case
236 of TiO₂(110), where the presence of low coordinated O₂ 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 support⁵⁶.

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– C₃N₄) dissociate H₂
241 homolytically⁴⁵. The catalyst was suggested by DFT to be composed of Au^{δ+} (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 H₂ 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 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
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%)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
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 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
261 tensions of the metal and support during the encapsulation process⁵⁷. Typically, the metal has
262 a higher surface tension than the TiO₂ 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 SMSIs⁵⁷. Recent discoveries of SMSIs in TiO₂ supported Au
265 catalysts have challenged the previously reported surface tension of TiO₂ (1.3–1.9 J m⁻²) and
266 raised questions about its potential overestimation⁵⁸. This opens up the possibility that Au may
267 possess a higher surface tension than TiO₂, allowing it to be wetted by TiO₂, 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 TiO₂⁵⁷.

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
285 adsorption configuration of C–Au further influences the chemisorption process due to its
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
289 and Au/SiO₂ catalysts⁵⁹. Additionally, there may be a continuous exchange of C atoms between
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
292 chemoselectivity to 3-vinylaniline was observed⁵⁹. 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 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
301 an alternative strategy to activate H₂^{23,44,60}. 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 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
320 and temperature, showcasing the process' reversibility⁶⁰. For a direct comparison of H₂
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
331 participating in the process.⁶⁰ 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 again²³. The measured LSPR shifts was of
340 about 0.02 nm during H₂ adsorption (as measured by Transmittance Anisotropy

341 Spectroscopy)²³. 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 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
349 in Au nanoparticles decreases²³. This enhanced comprehension of the chemisorption
350 mechanism of H₂ onto Au NPs is anticipated to facilitate advancements in the fabrication and
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
354 chemical reactions governed by mechanisms involving plasmonic effects and hot electron
355 transfer may also be advantageous⁶¹⁻⁶³. 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 H₂ were vital for high yields and the plasmon decay substantially lowered the energy barrier for
359 hydrogen dissociation⁶⁰. Moreover, the dissociation of H₂ 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 SiO₂ catalysts⁶⁴.

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 SiO₂ and TiO₂ 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 activities⁶⁵ were attributed to the charge transfer at the
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*

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 catalysts⁶⁶⁻⁷¹, 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 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
398 MgO surface induced high activity and selectivity in ethene hydrogenation⁷⁹. 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 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
404 conditions⁸³⁻⁸⁴. 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 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 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 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
416 MOFs⁸⁵. In addition, after 10 catalytic cycles, the catalyst retained its original morphology and
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 °C⁸⁸. 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 atoms⁸⁹⁻⁹¹. 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 hydrogenation¹⁰⁴⁻¹⁰⁵. 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 shell¹⁰⁶. The optimal ensemble configuration for
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
453 catalytic hydrogenation of chloronitrobenzenethiol to chloroaminobenzenethiol (**Figure 5a**)
454 over Au–Pd catalyst was carried out¹¹⁰ (**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 conducted¹¹⁰. 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_{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
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**)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

472 on Pd, hydrogen atoms migrated to adjacent Au surfaces over relatively long distance of 15-30
473 nm¹¹⁰. 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^{104-105,}
478 ¹¹¹⁻¹¹². 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 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
493 reaction of the adsorbed H species on Au¹¹¹. 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 systems¹¹³. 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 halonitrobenzenes²⁶. As such, an
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
507 compared in terms of the selectivity to *para*-chloroaniline²⁶ (**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/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
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 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
522 structure are very active in this reaction¹⁰² (**Figure 6d**). SiO₂ 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 °C¹⁰² (**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 alloy¹⁰² (**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 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
546 from deactivation⁹⁶⁻⁹⁷.

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
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 catalysts¹¹⁴.

568 Another important challenge will be the use of hybrid catalysts mixing single atoms and
569 nanoscale particles¹¹⁵⁻¹¹⁷. 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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610 The authors contributed equally to all aspects of the article.

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902

903
904 **Figure 1.** Types of H₂ activation on heterogeneous Au catalysts and strategies to enhance H₂ dissociation on Au. (a) two different
905 types of H₂ 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 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 C₃N₄ 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. H₂ 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/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 H₂ 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^{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
924 with permission from ref 47, ACS.

925
926 **Figure 3.** Hot electron induced H–D formation at 23 °C on 1% Au/SiO₂ catalyst. (a) The rate of H–D formation was
927 continuously monitored in real-time under two conditions: with laser excitation (2.4 W/cm², active) and without laser excitation
928 (0.0 W/cm², 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/SiO₂. (c) H–D
930 formation rate for 1% Au/TiO₂ catalyst. In both cases the same reaction condition were applied with laser excitation of 2.4
931 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
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 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 (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⁻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 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 CO₂ 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 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 H₂ 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 H₂ 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)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 H₂, 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
1029 most common of which are: Au–Pt^{26,93}, Au–Pd⁹⁴⁻⁹⁸, Au–Ir⁹⁹, Au–Ag¹⁰⁰, Au–Cu¹⁰¹, Au–Ni¹⁰² and Au–
1030 SiO₂¹⁰³.

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

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Fig 1

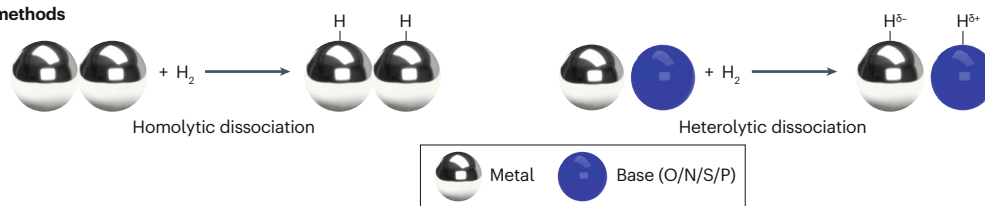
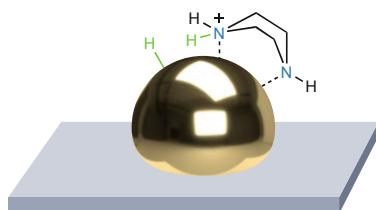
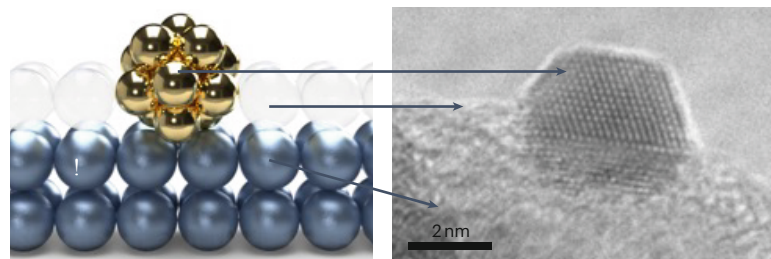
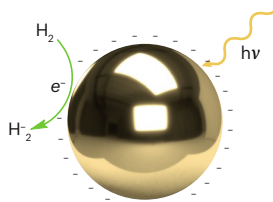
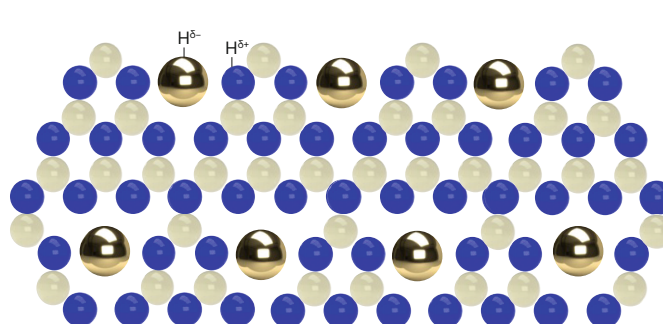
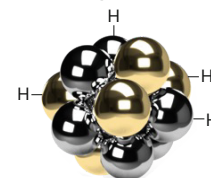
a H₂ activation methods**b** Ligand activation of H₂**c** Strong support-metal interaction (SMSIs)**d** Effect of hot electrons on Au properties**e** Au single atoms inside C₃N₄**f** Au alloys

Fig 2

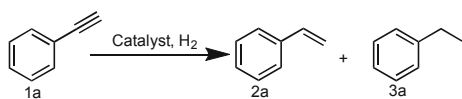
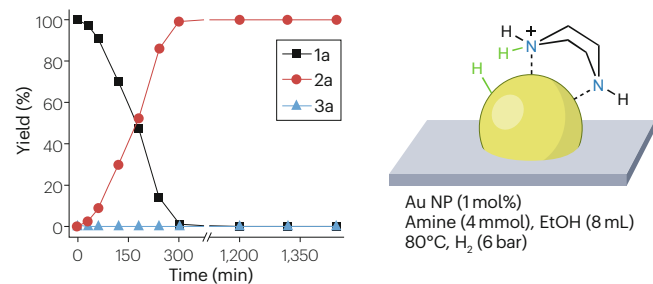
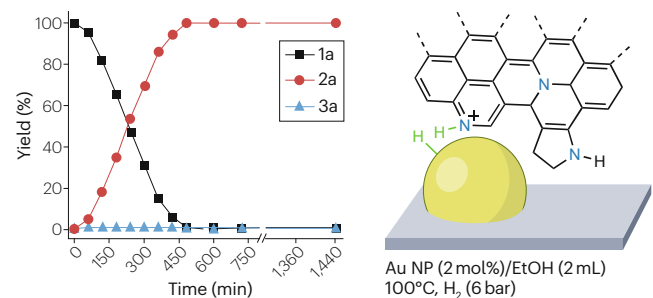
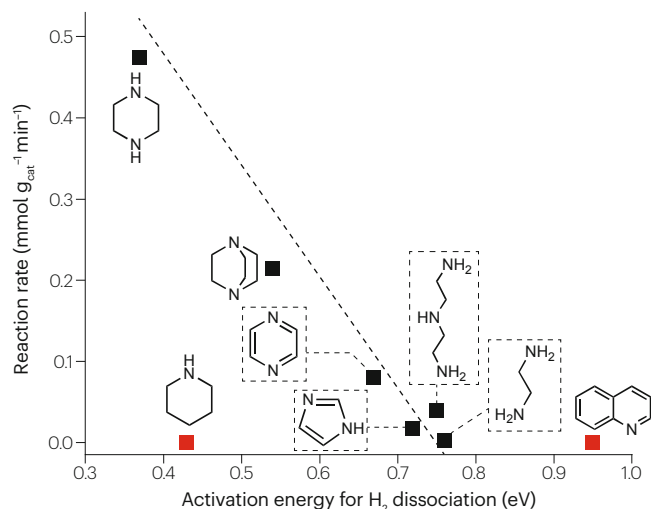
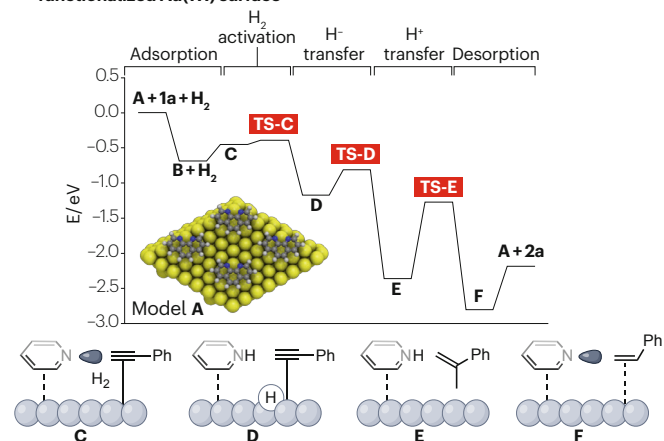
a Catalytic hydrogenation of phenylacetylene into styrene and ethylbenzene**b** Reaction course with Au/SiO₂ catalyst and piperazine**d** Reaction course with Au@N-doped carbon/TiO₂ catalyst**c** Experimental reaction rates vs computed activation energies for H₂ dissociation at the N ligand–Au(111) interface**e** Computed reaction energy profile for hydrogenation on phenanthroline-functionalized Au(111) surface

Fig 3

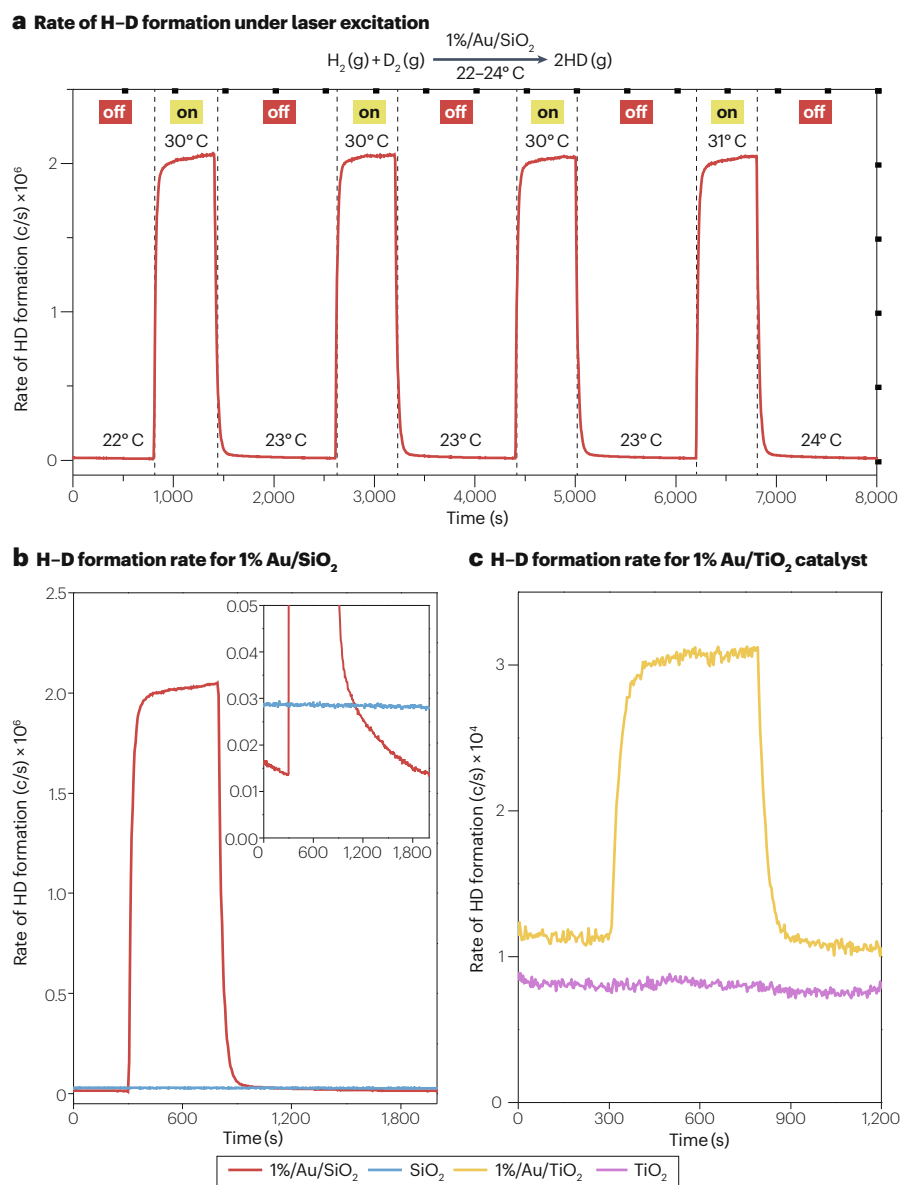
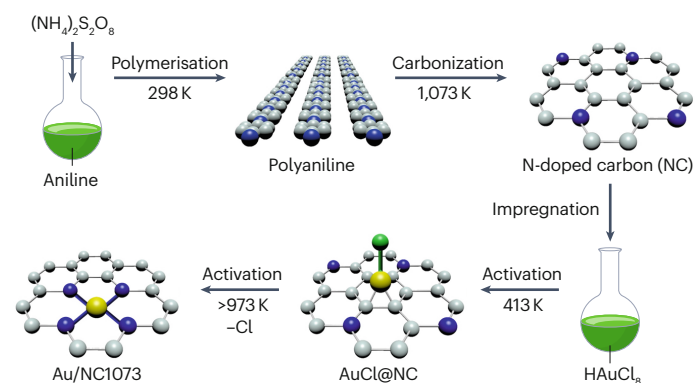
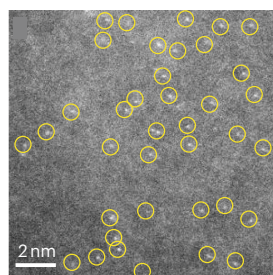


Fig 4

a Nitrogen-doped carbon (Au(III)/NC) synthesis and impregnation with 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

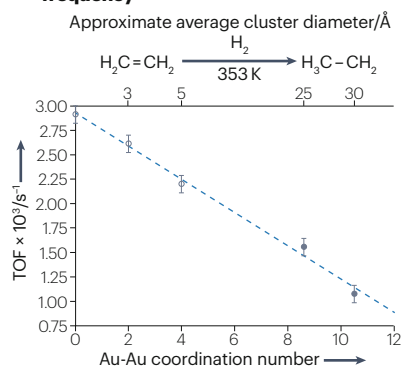
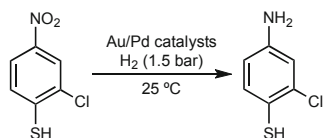
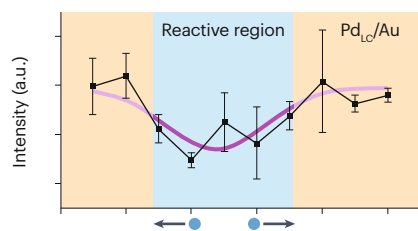
c Ethene hydrogenation turnover frequency

Fig 5

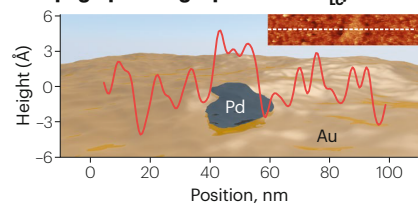
a Catalytic hydrogenation of chloronitrobenzenethiol to chloroaminobenzenethiol



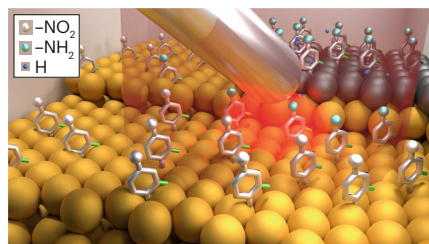
c NO₂ stretching bond (Raman) intensity in TERS line scan spectra on Pd₁₀₀/Au



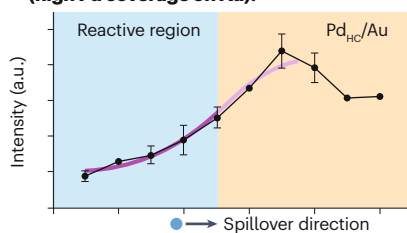
d Topographic height profile for Pd₁₀₀/Au



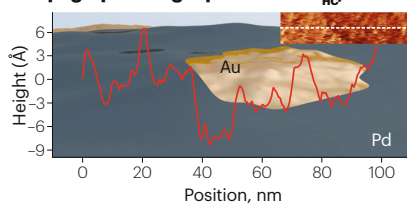
b STM-TERS illustration of an Ag tip investigating hydrogenation on Pd/Au



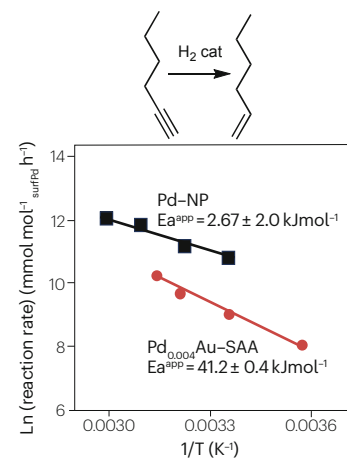
e NO₂ stretching bond (Raman) intensity in TERS line scan spectra on Pd₁₀₀H/Au (high Pd coverage on Au).



f Topographic height profile for Pd₁₀₀H/Au



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



h Selectivity profile

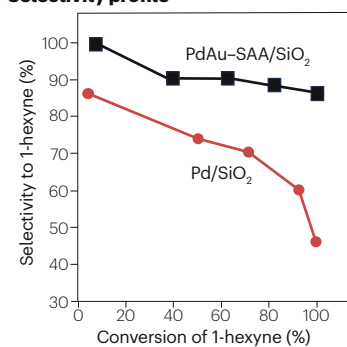
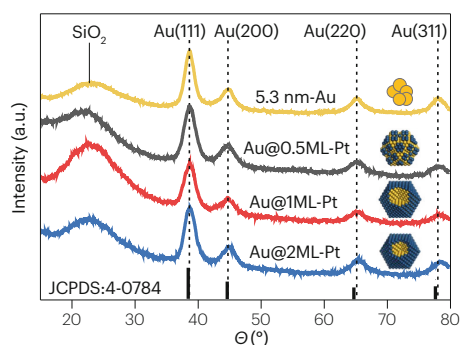
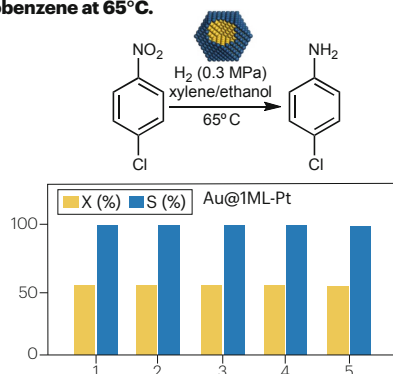
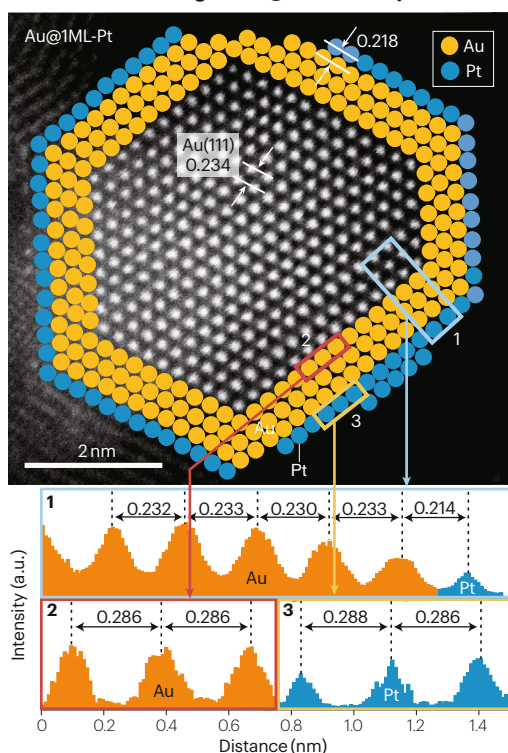
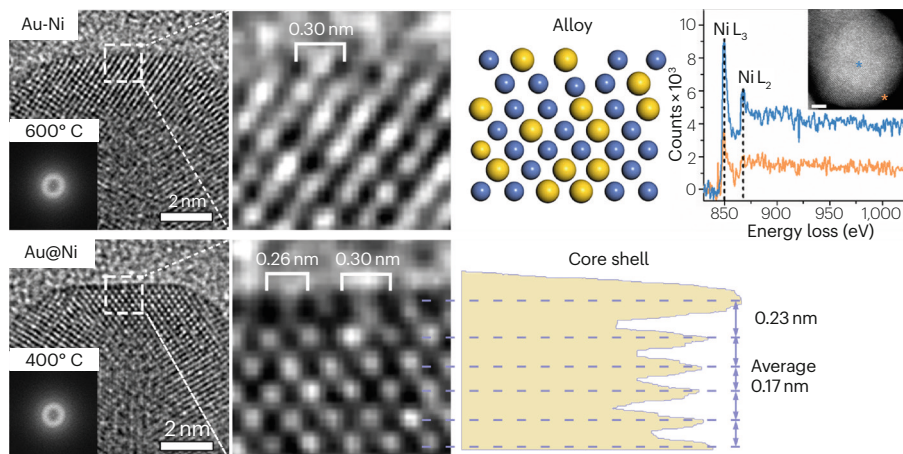
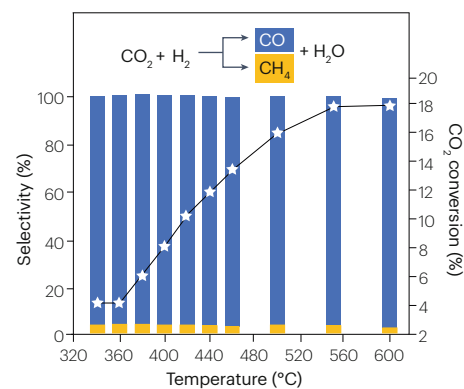
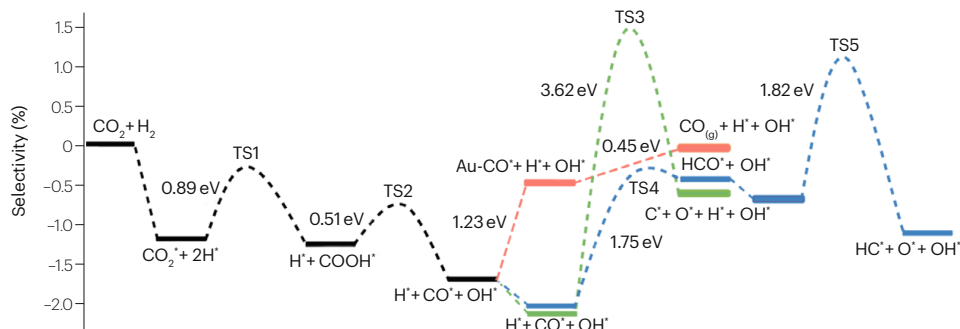
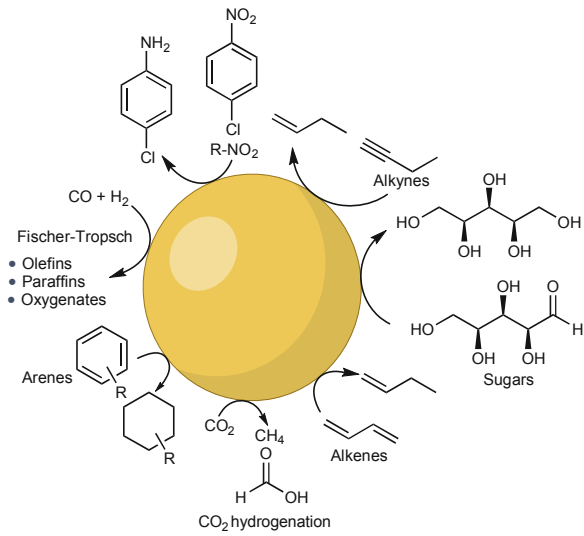


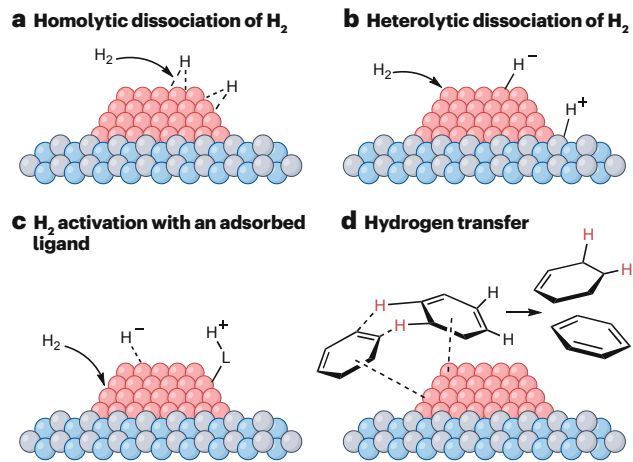
Fig 6

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**

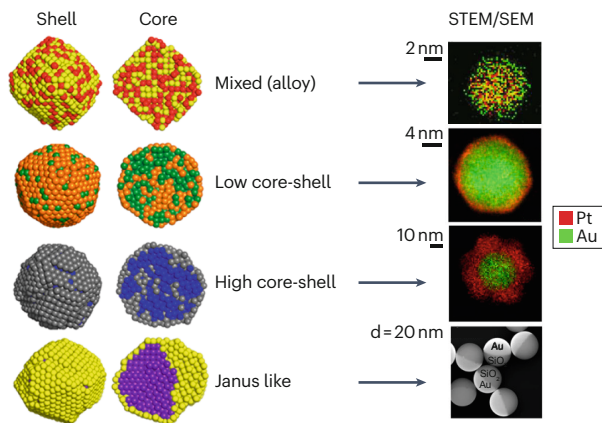
Box 1



Box 2



Box 3



GA

