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Au and Pt Nanoparticle Supported Catalysts Tailored for H₂ Production: From Models to Powder Catalysts

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Abstract

The use of metal nanoparticles (NPs), including Au and Pt, supported over oxides has been pivotal, and is ever increasing in enabling catalytic reactions which target the production of hydrogen. We review here the most recent works pertaining to the fundamental understanding of the structure, morphology, growth, characterization, and intrinsic phenomenological properties of Au- and Pt- based catalysts that influence the reactivity and selectivity to target hydrogen production. We draw on surface science and theoretical methods of model and powder catalysts using high resolution imaging, spectroscopy, scattering experiments, and theoretical studies. Based on these insights we identify key aspects of studies of supported metal nanoparticle (NP) catalysts for several reactions. The main focus of this review is on the intersection of catalytic chemistry related to the water-gas shift (WGS), oxygenate steam reforming (OSR), and solar-assisted reactions (SAR).

Keywords

Gold; platinum; supported catalyst; water-gas shift; steam reforming; water splitting.

1. Introduction

Heterogeneous catalysis makes use of a large range of noble metal-based catalysts that are essential for achieving industrially and commercially relevant applications specific to the ever emergent H₂ economy. Whether in the production of H₂ from reforming reactions (methane, syn gas, biofuels) or in the consumption of H₂ in fuel cells, NH₃ synthesis, hydrogenation, or methanation, we find Pt, Au and other noble metals used extensively as the active ingredient. As a result, the role of metals such as Pt and Au has been the intense focus of numerous scientific studies targeting the catalytic conversion of reactants directly to H₂. These studies have evolved over time with the generation of many fundamental aspects specific to the structure, chemical nature, morphology, and the chemical behavior of these materials under reaction conditions, which gives rise to the tailoring of key steps in the catalytic process leading to H₂. Though some features are ubiquitous to fundamental material properties of Pt or Au, it is now possible to influence or steer many reactions by the use of novel catalysts that can be designed to specifically target the most essential steps leading to conversion. Deactivation of reactions can also be carefully mitigated by ensuring that sufficient concentrations of the active agents are protected from the harsh conditions of a reaction.

The water-gas shift reaction (eq. 1), oxygenate steam reforming (eq. 2), and solar-assisted reactions, including solar water splitting (eq. 3) and photocatalytic methanol reforming (eq. 4), are well established processes utilizing water in the feed to produce hydrogen-rich gas with high efficiency. Although Au- and Pt- supported oxide catalysts dramatically enhance the (photo)catalytic activity, the nature of active phase, in terms of size, geometry, electronic structure, in these metal/oxide systems, as well as the influence of metal $\leftrightarrow$ support interactions are still ambiguous. In this review, we highlight the latest discoveries pertaining to these metals and discuss the importance of morphology, metal/support interactions, and redox states that distinguish Pt and Au from each other, and other metals, in the manifest of unique selectivity and activity.

This review is divided in two sections. The first part describes studies using model systems. Surface science and density functional theory (DFT) models can provide invaluable insights into the intrinsic phenomena that prevail during a heterogeneous catalytic process. In the fundamental investigation of Pt and Au materials numerous studies of well-defined metal surfaces (*i.e.* Pt(111), Au(111)) and supported metal NPs (*i.e.* Pt/CeO_x, Pt/TiO₂, Pt/CeO_x/TiO₂, Au/CeO_x, Au/TiO₂, Au/MgO) have provided ideal benchmarks for looking at individual steps that pertain to the conversion of oxygenated molecules to H₂. Challenges exist in the transfer of knowledge obtained at model conditions to those applied to more complex powder catalysts under reaction conditions. However, an ever increasing range of methods and tools from *in situ* microscopy, spectroscopy and scattering, as well as time-dependent DFT methods can help bridge what has come to be known as the ‘materials and pressure’ gaps. The results of these studies can explain data for complex systems and help to predict and enable new directions in the design and understanding of high-surface-area powder catalysts. The second part of the review is focused on the rational design of real powder catalysts, paying particular attention to their synthesis, characterization and catalytic performance.

2. Surface science and DFT models

Here we begin reviewing recent surface science investigations of Pt and Au model catalysts, paying specific attention to the growth, morphology, and oxidation state of the materials, before taking a closer look at the active site identification at the atomic level and with individual probe molecules. The use of models to interpret and unravel catalytic processes is an important strategy in reducing the complexity of high surface area powder catalysts and the multitude of cascading transformations that occur at steady state [1-2]. The ability to reduce the structural model down to the atomic level detail and mechanisms down to individual chemical activation steps is insightful and also critical. The use of single crystal and thin film substrates has been particularly versatile as benchmarks in these studies that can extend to mono-metals [3-6], bi and tri-metallic

[7-9], oxides [10-12], mixed oxides [13-15], inverse catalysts [16-19], carbides [20-25], sulphides [21,26-28] and nitride [20,22,29,30] based catalysts.

One of the most extensively studied systems is the ceria-based model, a catalytic powerhouse material, where the bulk, nano, and supported nature of a very commonly used support can readily be investigated. To mimic ceria substrates, ceria films are grown on metals in UHV. The deposition of cerium in an oxygen background leads to the formation of atomically flat ceria thin films on bulk single crystals. In one common procedure, ceria (6 monolayers (ML)) was vapor-deposited onto well-cleaned Ru(0001) substrates at elevated temperatures (790 K) in an oxygen environment (1×10^{-7} mbar O_2), and subsequently annealed to 980 K in 4×10^{-7} mbar O_2 [31,32]. Au or other metal NPs were then deposited at 300 K in ultra-high vacuum (UHV) onto the ceria films *via* electron beam assisted evaporation from a W crucible or wire. On ceria, Au NPs were preferentially located in order of the following positions: terrace point defects, step edges, and finally, at high Au coverages, on flat terraces [32].

Figure 1. Pt and Au catalysts outperform other metals at lower coverages for the water gas shift reaction when supported on ceria. Reprinted with permission from Bruix *et al.* [34]. Copyright (2012) American Chemical Society.

Before testing for WGS activity, the ceria-supported nanoparticles were annealed to the WGS reaction temperature after the deposition of Au at room temperature (RT) [33]. $\text{CeO}_2(111)$ [34] and $\text{Au}(111)$ [33] are inactive toward the water-gas shift reaction while the $\text{Pt}(111)$ surface exhibits a greater activity than the model system standard ($\text{Cu}(111)$), but is rapidly poisoned by carbon deposits [35]. Maximum WGS activity (20 torr CO, 10 torr H_2O , 625 K) was achieved on $\text{Pt/CeO}_2(111)$ with 0.2 ML Pt coverage on ceria, which corresponds to Pt NPs <1.7 nm in diameter, and <0.4 nm in height [34]. The smaller Pt NPs that resulted from low coverages of Pt exhibited a lower density of states near the Fermi level for the Pt 5*d* states, as compared to the larger Pt coverages, which had a lower WGS activity and a density of states that appeared more metallic-like (shown in **Figure 1**) [34]. This result indicates a decrease in activity as the Pt NPs become more bulk-like or metallic. $\text{Pt/CeO}_2(111)$ outperformed other metal/ceria WGS catalysts, including Au, Cu, and Ni [34]. While the Pt/CeO_2 system was more active for the WGS than Au/CeO_2 , the Au system showed greater activity than Pt when the metal coverage was > 0.5 ML, and importantly, Au/CeO_2 model catalysts are more active for hydrogen production via the WGS reaction than the industrial standard, Cu/ZnO , as depicted in **Figure 2** [33]. As shown in **Figure 1**, the greatest WGS activity for $\text{Au/CeO}_2(111)$ occurred with 0.4 - 0.5 ML of Au coverage [34]. The dispersion of Pt NPs is enhanced when ceria is partially reduced ($\text{CeO}_{1.88}(111)$), due to the increase in the number of terrace oxygen defects which can act as preferential nucleation sites for NP growth [36].

Figure 2. Au/ceria is more active for the WGS reaction than the industrial standard, Cu/ZnO. Reproduced from Rodriguez *et al.* [33]. With permission of Wiley.

In comparison with another reducible oxide TiO₂, Au behaves uniquely upon interaction with the support. The growth and diffusion of Au NPs supported titania have been well-investigated in recent studies. The deposition of Au on TiO₂(110) at room temperature resulted in Au island nucleation at step edges, and with increasing coverages of Au, 3D island growth occurred as indicated in scanning tunneling microscopy (STM) images in **Figure 3** [37]. Metallic NPs deposited on clean TiO₂(110) at room temperature under UHV conditions are highly dispersed across terraces and step edges until exposed to an oxygen background (5×10^{-7} mbar) at 1000 K. Upon oxidation at elevated temperatures, the particles migrated, and the sintering of the particles and the degree of diffusion were related to the binding energy of the metal particle to the substrate using DFT calculations [38]. As seen in **Figure 4**, Au atoms have the greatest mobility on TiO₂(110) due to the largest average height (12.7 ± 4.3 Å) and the lowest density (3.02×10^{12} clusters/cm²) of their clusters compared to Pt. The DFT calculations of metal atoms on TiO₂ surface demonstrate that the metal atoms bind preferentially at the oxygen vacancies where the binding of Pt is much stronger than Au, so that the growth of surface defects is crucial for nucleation of Au and Pt clusters [38,39]. Also, the calculated oxygen binding energies on (111)

surfaces of Au and Pt imply the metal-titania binding energies are correctly predicted by the admetal-oxygen bond strengths.

Figure 3. STM images showing coverage dependence of Au on $\text{TiO}_2(110)$: (a) 0.013 ML Au; (b) 0.08 ML Au and (c) 0.2 ML Au. Reprinted with permission from Spiridis *et al.* [37]. Copyright (2001) Elsevier.

Figure 4. STM images of 0.25 ML of (a) Au and (b) Pt supported on $\text{TiO}_2(110)$, after RT-deposition. Reprinted with permission from Galhenage *et al.* [38]. Copyright (2013) American Chemical Society.

The oxidation state of the $\text{TiO}_2(110)$ substrate plays a large role in the dispersion of NPs deposited at room temperature. Upon cleaning via Ar^+ sputtering and UHV-annealing cycles, the $\text{TiO}_2(110)$ surface contains oxygen vacancies and is in a reduced state. After oxidation (exposing the surface to O_2), the surface contains little to no oxygen vacancies, whereas after hydration (exposure to water), the surface is hydroxylated. The degree of oxidation of the $\text{TiO}_2(110)$ substrate affects the diffusion rates for the metal particles at elevated temperatures [38]. For both Pt and Au, the particles diffused less on the oxidized TiO_2 as compared to reduced TiO_2 , due to a larger barrier to diffusion, resulting in smaller cluster size, and a greater cluster density [38]. Interestingly, the hydroxylated surface exhibited a decreased barrier to Au diffusion on the hydrated surface as compared to the others (**Figure 5**), as indicated by the presence of fairly large Au clusters predominately on the high-coordination step edges, rather than small, well-dispersed clusters across terraces of reduced and oxidized TiO_2 . Complementary DFT calculations predict the adhesion strength (and therefore the diffusion energy) of the NPs is related to the bond strength between the metal and the substrate [38,40]. These results identify that the metals interact uniquely with redox states of the support and are strong indicators of metal-support interaction. In light of the experimental and computational findings, Au NPs dispersed on reducible oxides are better catalysts than those supported on nonreducible ones since reducible oxides are more capable of forming O-rich Au-support interface where the adhesion of Au oxide (or cationic Au) and support is much stronger.

Figure 5. (a) STM images of reduced-, hydrated- and oxidized-TiO₂(100) surface before and after 3% ML Au exposure at RT (bridging oxygen vacancies O_{br} in square, H adatoms on O_{br} sites in hexagon and oxygen adatom O_{ot} in Ti troughs in circle). (b) DFT-based adhesion potential energy profiles for Au₁ cluster diffusion on stoichiometric-, hydrated-, reduced-, and oxidized-TiO₂(110). The minima at which Au₁ is trapped at the point defects on *r*- and *o*-TiO₂(110) are indicated (arrows; vac. means vacancy). Au₁ diffuses along the O_{br} rows on *s*- and *o*-TiO₂(110), whereas, on *h*- and *r*-TiO₂(110), Au₁ diffuses along the Ti troughs. Reproduced from Matthey *et al.* [40]. With permission of AAAS.

Mixed oxides are a growing area of investigation with the ability to obtain new chemistries where mono-oxides were not able to achieve. To prepare mixed oxide substrates for instance in the case of CeO_x/TiO₂, cerium is deposited onto TiO₂(110) in an O₂ environment (1x10⁻⁷ torr) at 600 K [41-43]. TiO₂ imposes on CeO₂ NPs nontypical coordination modes with a subsequent alteration in relative stability of Ce³⁺/Ce⁴⁺ states, resulting in remarkable catalytic activity enhancement [41,42]. Pt NPs 1-2 atoms high formed after the evaporation of metallic Pt on to the substrate at 300 K [34]. The STM image in **Figure 6** shows features related to the individual

counterparts of the catalyst. The position (a) represents ceria “wires” on the $\text{TiO}_2(110)$ substrate, meanwhile region (b) shows the position of Pt NPs on top of ceria and region (c) indicates Pt NPs residing directly on the $\text{TiO}_2(110)$; all of which were characterized by their respective topographic heights in the STM image. This provides a versatile and complex Pt/ CeO_x / TiO_2 catalyst that shows good activity for the production of H_2 . The activity for the WGS reaction (20 torr CO and 10 torr H_2O) was greatly enhanced for Pt NPs supported on titania when ceria was added to the $\text{TiO}_2(110)$ surface, as shown in the right panel of **Figure 6**. The greatest activities were achieved on the catalysts containing miniscule coverage of Pt (< 0.3 ML) and 11% CeO_x [34]. The Pt $\leftrightarrow$ CeO_x interactions where small Pt clusters electronically perturbed by interactions with ceria are much stronger, enabling the admetal to adsorb water and fully dissociate. The DFT calculations show that the corner atoms of Pt_8 in contact with $\text{CeO}_2(111)$ surface or with $\text{Ce}_{40}\text{O}_{80}$ NP are strongly bound to oxygen sites of support with a net Pt $\rightarrow$ ceria charge transfer, therefore enhancing the ability to cleave O-H bonds and eventually yielding H_2 and CO_2 *via* the WGS reaction (**Figure 7**) [34,42,44,45]. This is not the case of the Au admetal (0.15 ML) where the catalytic activity of Au/ CeO_x / $\text{TiO}_2(110)$ was somewhat lower than Pt/ CeO_x / $\text{TiO}_2(110)$ [41,42]. The theoretical calculations indicate a very weak interaction of Au (with larger average height and diameter) with $\text{TiO}_2(110)$ and a negligible charge transfer while stronger electronic perturbation is observed for $\text{CeO}_2(111)$ support [40-42,46-48].

Figure 6. STM images of $\text{CeO}_x/\text{TiO}_2(110)$ under O_2 atmosphere (a) at RM and (b) after heating to 600 K and subsequent annealing at 900 K. (c) STM image of ~ 0.15 ML of Pt deposited on $\text{CeO}_x/\text{TiO}_2(110)$ at 300 K; and (d) submonolayer coverages of CeO_x on TiO_2 enhance the hydrogen production over Pt NPs compared to larger CeO_x coverages, no ceria, and the industrial standard of Cu/ZnO. Reproduced from Park *et al.* [42] and Bruix *et al.* [34]. With permission of American Chemical Society.

Figure 7. DFT-calculated structures for adsorbed H₂O, transition state (TS), and adsorbed HO + H along with the corresponding energy parameters [E_{ads} , $\Delta E(\text{TS})$, E_{reac}] for water dissociation over Pt(111) surface, free Pt₇₉ cluster, Pt₈ cluster, Pt₈ clusters deposited on CeO₂(111) surface, and Pt₈ clusters deposited on Ce₄₀O₈₀ NP. Pt, O, Ce and H atoms are in blue, red, cream and white spheres, respectively. Reproduced from Bruix *et al.* [34]. With permission of American Chemical Society.

In addition, comparisons in the behavior of metal NPs with different supports can be studied. Among popular oxide materials, MgO is critical in the investigation of the effect of hydroxylation on the surface upon NP stabilization. Freund and coworkers investigated the structure and stability of Au NPs on MgO(001), paying particular attention to the effect of the presence of hydroxyl groups [49,50]. MgO(001) thin films (10 ML) were grown on Ag(001) substrates by depositing Mg in an O₂ background (1×10^{-6} mbar) at 573 K. In order to produce the hydroxylated MgO surface, water was dosed directly onto the surface at RT at a local pressure of 1×10^{-3} mbar, resulting in a hydroxyl coverage of 0.4 ML. The hydroxyl groups enhances the stability of the Au NPs anchored onto the surface, due to the formation of strong Au-O interfacial bonds, thereby oxidizing Au NPs to small Au_xO_y aggregates and hampering diffusion and sintering of Au at elevated temperatures. Post-annealed Au NPs on MgO, on the other hand, exhibited larger particles with a smaller density, as shown in **Figure 8**.

Figure 8. STM images show the Au NP size and dispersion on MgO(001) vs. hydroxylated MgO (MgO_{hydro(l)}) at two coverages. 0.04 ML of Au on MgO (a) and hydroxylated MgO (b);

0.2 ML of Au after RT deposition on MgO (d), hydroxylated MgO (e), 0.2 ML of Au after annealing to 600 K to demonstrate thermal stability on MgO (g) and hydroxylated MgO (h); and each respective NP size dispersion is shown at the bottom panels (c, f, i). Reprinted with permission from Brown *et al.* [50]. Copyright (2011) American Chemical Society.

Beyond simply the morphology, the chemical nature of the as-prepared metal NPs is important. **Figure 9** shows the corresponding X-ray photoelectron spectroscopy (XPS) spectra in which both MgO and the hydroxylated surface are covered by 0.4 ML Au. The Au NPs on MgO remain in their metallic state (Au 4f_{7/2} peak is located at 84.0 eV) in **Figure 9a(i)**, whereas the Au NPs are oxidized on the hydroxylated surface (the Au peak is shifted to higher binding energies) in **Figures 9a(ii)** and **9a(iii)**. **Figure 9b** shows the O 1s region of the XPS spectra, indicating the presence of OH groups on the surface after the exposure to water at RT. The alteration in chemical nature of Au NPs can be attributed to chemisorption of hydroxyl groups stemming from direct interaction between water and small Au NPs and/or from spillover of hydroxyl groups from MgO support [50].

Figure 9. XPS spectra of (a) Au 4f and (b) O 1s spectral regions for 0.04 ML Au (i) deposited at RT on 13 ML MgO(001)/Ag(001) and (ii) after subsequent hydroxylation at 1 mbar of D₂O. (iii) Spectra obtained after deposition of 0.04 ML Au on hydroxylated (1

mbar of D₂O) 13 ML MgO(001)/Ag(001). Reprinted with permission from Brown *et al.* [50]. Copyright (2011) American Chemical Society.

Furthermore, the reaction with common reactants can be titrated over these systems. For example, the adsorption of CO on MgO-supported Au clusters was imaged using STM and infrared-reflection-absorption spectroscopy (IRAS). The CO molecules preferentially adsorbed to the perimeter of the Au island, rather than on top of the particle, as shown in **Figure 10** [51]. Preferential binding sites of model catalysts can point to the active site of the material, and here CO is used as a probe molecule, as its adsorption and interaction with the surface is critical for the WGS reaction.

Figure 10. Adsorption of CO on Au/MgO model catalysts using STM: (a) CO imaged as a depression with a metallic tip; (b) CO imaged as a protrusion with a CO-terminated tip; (c) CO at the only perimeter of the Au island. Reprinted with permission from Lin *et al.* [51]. Copyright (2010) American Chemical Society.

Two-dimensional second derivative (d^2I/dV^2) maps correspond to the vibrational energy recorded at every point in a normal (topographic) STM image. A signal of ± 45 meV was monitored in order to investigate CO, as shown in **Figure 11**. Second-derivative images recorded at a voltage outside of the ± 45 meV optimal voltage for CO result in low-contrast images like that seen in **Figure 11b**, while the images recorded at ± 45 meV show high contrast at the

perimeter of the Au island, where the CO is adsorbed. Herein, the preferential CO binding to Au island perimeter can be assigned to either the low-coordinated boundary atoms or edge atoms as opposed to those enclosed in the Au island plane, or due to the localized electrons transferred from MgO/Ag at island perimeter [51,52]. The experimental observation is consistent with DFT calculations [53,54] where CO absorbs with lower binding energy (0.72 eV) to 3-fold coordinated edge atoms of negatively charged Au₁₂ island on MgO/Ag(001) and the increase in CO-Au repulsion due to the charge donation from CO 5σ into Au.

Figure 11. (a) STM topographic image of a Au NP supported on MgO with CO in the vicinity, imaging as depressions; (b) d^2I/dV^2 image at a voltage of -55 meV shows limited contrast, whereas voltages of (c) -45 meV and (d) +45 meV expose adsorbed CO at the perimeter of the Au island. Reprinted with permission from Lin *et al.* [51]. Copyright (2010) American Chemical Society.

Understanding the vital roles of structural, geometric and electronic properties of active phase, oxide support, metal-oxide interface and their interaction on the atomic and molecular levels, associated with theoretical calculations is fundamental to our better understanding of heterogeneous surface reactions on supported catalyst. As a consequence, the nexus between

surface science models and real-world supported catalysts is successfully established, hence not only providing new insights into the fascinating complex world of heterogeneous catalysis but also emerging mechanistic aspects to rationally design realistic, efficient supported catalysts.

3. Powder nanocatalysts

It is worth noting that atomic views of model and real catalysts can shed more light on critical active sites for catalysis, yet these measurements are not trivial to make. The intersection of surface science with catalysis aims to close the pressure and materials gap by understanding chemistry on an atomic scale of real catalysts under reaction conditions. Numerous reports have highlighted the advances made in imaging real catalysts under high pressure conditions by means of using aberration-corrected environmental transmission electron microscopy (ETEM) [55-59]. Perimeter sites, low-coordination corner sites, cationic gold and bilayers of gold have been proposed as the active species in literature concerning gold catalysis [55,57,60-62]. Yoshida *et al.* [56] observed a reconstruction of the exposed Au{100} facets on CeO₂ in the presence of 1 volume % CO in air environment, as seen in **Figure 12**. In the reconstructed surface, the Au atoms on the topmost surface layer form an undulating hexagonal lattice while those on the second topmost surface layer form a normal square lattice with slight distortion, allowing CO molecules to adsorb at higher surface coverages. Such *in situ* reconstruction accompanied with *ab initio* calculations is an important finding because it was thought that a flat facet of a Au NP cannot accommodate CO molecules in high density [63,64] due to the intrinsic weak adsorption of CO molecules and the repulsive intermolecular interactions.

Figure 12. Atomic view of a gold NP supported on ceria reconstruction under a vacuum and CO/air environment, imaged used aberration-corrected ETEM. Reprinted with permission from Yoshida *et al.* [56]. Copyright (2012) AAAS.

A combination of transmission electron microscopy (TEM) and physical modeling was also used to gain insight on the active site on an atomic scale of supported metallic NPs, citing that the catalytic activity is dependent on metal corner atoms in a NP, as highlighted in **Figure 13** [57-59]. The most essential factor influencing the adsorption and reaction properties of Au atoms is their coordination with other atoms [65]. The number of corner atoms does not increase as the particle size increases above 1 nm, indicating that the turnover rate is dependent on the number of particles rather than the size of the particles. Note that the number of particles will be maximized with smaller particles for any given gold loading.

Figure 13. Top panels show a high-angle annual dark-field/scanning transmission electron microscopy (HAADF/STEM) image of Au supported on rutile TiO₂, and the corresponding models of Au NPs. The truncated cubo-octahedral Au clusters contain 25, 119, and 331 atoms. Bottom panel reveals the comparison between the experimental H₂ production rates as a function of Au NP size with the models considering various active sites, of which the corner atom active site was the best fit. Reproduced from Williams *et al.* [57]. With permission of American Chemical Society.

Continuing studies with Pt supported on ceria also shows the strong relationship between corner atom sites and the catalytic activity. Careful steps were taken by the Cargnello *et al.* [59] to monitor structural changes to the size and shape (of which there were none) of the NPs due to the deposition and calcination processes *via* TEM. Post-mortem TEM images revealed that minimal sintering or coalescence of the particles occurred, indicated by the lack of change in size, cubo-octahedron shape, or distribution of the particles. Ceria-supported catalysts show a relationship between NP diameter and activity, revealing the importance of the atoms, perimeter

or corner atoms, at the metal-support interface, yet their model supports the theory that the corner atoms are the most catalytically active site due to their low coordination number compared to the other perimeter atoms [57-59], as shown in **Figure 14**. Such a conclusion is quite consistent with the observation from surface science models aforementioned.

Figure 14. Relationship between the activity and diameter of NPs, indicating the active sites are perimeter sites at the interface of CeO_2 support and NP. The similarity in slope between the model corner sites and the experimental data shows that the corner atoms are the most active site. Reprinted with permission from Cargnello *et al.* [59]. Copyright (2013) AAAS.

3.1. Synthesis approaches of NPs supported catalysts

Employing a suitable synthesis method to produce ultrafine, small Au and Pt NPs highly dispersed on the support is of the utmost importance for the high reactivity, selectivity and stability of supported catalysts. Isolated single atoms, subnano-sized metal clusters and nanosized particles have been elucidated to significantly improve the catalytic performance in different aspects: (i) strong metal-support interaction, (ii) intimate interfacial contact, (iii) quantum size effect, (iv) increased surface-to-volume ratio, (v) low-coordination environment of

metal centers, and (vi) band alignment [66-70]. Almost no activity was obtained over bulk Au catalysts whereas uniformly dispersed, ultrafine Au NPs smaller than 10 nm became highly active for H₂ and CO oxidation as well as other reactions as proven by surface science studies. It is attributed to the electronic states of the outer surface gold atoms composed about 40% of total atom content for hemispherical Au NPs of diameter 4 nm as well as the strong-metal-support interaction between Au and transition metal oxides [71,72]. Isolated Au single atoms supported on Fe₂O₃ are much more resistant to sintering than Au nanostructures due to the formation of strong covalent metal-support interaction, exhibiting ultra-stability and remarkable catalytic performance [72,73]. Similarly, size effect is crucial over Pt supported catalysts where isolated single Pt atoms anchored to the surfaces of Fe₂O₃ nanocrystallites exhibited excellent stability and high activity for CO oxidation arising from the partially vacant 5d orbitals of the positively charged, high-valent Pt atoms that help to reduce both the CO adsorption energy and the activation barriers for CO oxidation (shown in **Figure 15**) [74,75]. Otherwise, the sintering or agglomeration of Pt and Au NPs to form larger particles *via* either Ostwald ripening or coalescence dramatically suppresses the overall activity or selectivity of the catalysts over a period time under catalytic reaction conditions and even during catalyst synthesis.

It is noteworthy that the choice of a proper support plays a critical role in stabilizing the dispersed noble metal NPs and thus preventing such phenomena by means of the metal-support interaction and interfacial surface. Reducible oxides such as TiO₂, CeO₂ and Fe₂O₃ are considered active supports whereas non-reducible Al₂O₃, MgO and SiO₂ are declared to be inert or passive [71,72,75-81]. Among these supports, titania and ceria are most widely used in the catalytic production of H₂, particularly in the water-gas shift reaction at low temperature, oxygenate steam reforming and solar-assisted production, because of their oxygen storage capacity. The support might affect the shape of the noble metal NPs, resulting in faceting and possibly inducing defect sites [77,78,82]. The “junction effect” arising from the strong contact between support and noble metal NPs efficiently enhanced the catalytic activity since the electronic interaction between them reduced the enthalpy for oxygen vacancy formation, thus forming the catalytic active sites [83]. The metallic Au clusters in close contact with surface oxygen-vacancy defects of CeO₂ and the fast Ce⁴⁺ ↔ Ce³⁺ transfer are crucial in activity and stability improvement [78]. Similarly, the oxygen-vacancy F-center defects in or near the MgO surface plays an essential role in the activation of Au clusters by serving to anchor Au clusters

and to partially transfer the electronic charge from the substrate F-center to Au cluster, therefore promoting the catalytic activity [77,79]. By contrast, the charge transfer also occurs across the interface from Au to various oxide supports, *i.e.* CeO₂, TiO₂, ZrO₂, ZnO, Al₂O₃, to facilitate the catalysis reactions [78,80,81].

Figure 15. (a, b) HAADF/STEM images showing single Pt atoms well dispersed on Fe₂O₃ support; and (c) proposed reaction pathways for CO oxidation on Pt₁/Fe₂O₃ catalyst. Reproduced from Qiao *et al.* [74]. With permission of Nature Publishing Group.

In addition, the oxidation state of active Au and Pt plays a crucial role in heterogeneous catalytic reactions. Numerous studies have pointed out the importance of metallic gold and platinum during WGS reaction [78,84-86]. Negatively charged gold sites ($\text{Au}^{\delta-}$) exposed at the surface of small clusters ($< 1 \text{ nm}$) were observed on the freshly reduced sample and under working conditions whereas they became neutral after WGS reaction [78]. On the contrary, the activity for the low temperature water-gas shift reaction was found to arise from the oxidized metal embedded in the support as opposed to the metallic NPs supported on the ceria [60]. Gold cations are keys for an active catalyst where the oxidized gold species, $\text{Au}_n^{\delta+}$, showed much lower activity for low temperature CO oxidation than that of well dispersed Au^0 NPs, while oxidized gold clusters were needed to activate the WGS reaction due to the formation of active oxidized $[\text{Au}_n\text{-O-Ce}]$ and $[\text{Au}_n\text{-O-Fe}]$ species on the surface and subsurface layers of the catalysts [81]. The isolated surface-type Au^{3+} ions are the most active sites not only for the WGS reaction but also for the hydrogenation of 1,3-butadiene and ethylene irrespective of supports due to their ability to activate carbon-carbon double and triple bonds [87-89]. The catalytic activity was also reported to be enhanced for alkali-promoted oxidized Pt atoms complexed with OH groups on alumina, silica and titania supports [90,91]. The atomically dispersed Pt-alkali- $\text{O}_x(\text{OH})_y$ species are explored to be the active sites, opening a new low-temperature reaction pathway. Similarly, stabilization of atomic, oxidized $\text{Au-O}(\text{OH})_x$ by alkali ions also catalyzes the low-temperature WGS reaction, and the activity is unaffected by the nature (*i.e.* the reducibility) of the support [92,93].

It is obvious that the nature of Pt and Au NPs, including the composition (mono- or bimetallic), particle size, geometry, dispersity and electronic environment, on the support plays an essential role in the structure-activity correlation, product selectivity and catalyst stability arising from the metal-oxide interaction as well as the alteration in electronic configuration. Reducible and non-reducible oxides, such as SiO_2 , TiO_2 , CeO_2 , Fe_2O_3 , ZrO_2 , Al_2O_3 , MgO , and mixed metal oxides have been widely used as supports due to their high specific surface areas, high thermal and mechanical stability, and earth-abundance [72,75,77,78,80,81,94]. The preparation method has been reported to significantly affect the performance of Pt- and Au-based catalysts [95-97]. Accordingly, the gold-based catalysts are only active when in a highly dispersed state whereas the pretreatment of Pt-based catalysts is an important factor. The loading of Pt, Au, and Pt-Au alloys on various supports have been conducted by several methods

including impregnation, deposition-precipitation, wet chemical reduction, photoreduction and polyol-assisted process. Chloroauric acid, gold chloride, gold acetylacetonate, nitrate (triphenylphosphine) gold (I), hexachloroplatinic acid, tetrammonium nitrate platinate, and platinum acetylacetonate are commonly used as metal precursors.

Figure 16. (a) Synthesis procedure of DP method to load Au NPs onto the oxide support; (b) TEM images showing the distribution of ultrafine, well-dispersed Au NPs supported on TiO_2 by DP method with different Au contents. Reproduced from Haruta [64] and Murdoch *et al.* [123]. With permission of Springer and Nature Publishing Group.

The impregnation techniques, including wetness impregnation [75,98-112] and incipient wetness impregnation (or dry impregnation) followed by drying are the most commonly used methods due to their simplicity and low waste streams [60,113-116]. The precious metal ions can be reduced to their metallic state by post-treatment in different atmospheres. However, large particle sizes (8-20 nm) result from sintering due to the weak interaction between the NPs and the support. Otherwise, deposition-precipitation (DP) is considered as one of the most successful techniques [64,65,78,96] to deposit highly dispersed, catalytically active noble metal NPs (NPs), particularly Au, on metal oxides with an isoelectric point (IEP) above 5 ($\text{IEP}_{\text{TiO}_2} = 6-6.5$, $\text{IEP}_{\text{CeO}_2}$

= 6.7-8.6, $\text{IEP}_{\gamma\text{-Al}_2\text{O}_3} = 7\text{-}8$, $\text{IEP}_{\text{MgO}} = 9.8\text{-}12.7$, $\text{IEP}_{\alpha\text{-Fe}_2\text{O}_3} = 8.4\text{-}8.5$). The precipitation method follows the principles of nucleation and growth using aqueous sodium hydroxide, ammonia, urea, and sodium carbonate as precipitating agents (shown in **Figure 16**) [56,57,64,65,73,80,81,96,97,117-126]. The gradual decomposition of urea or ammonia during the process results in a slower, more homogeneous precipitation, therefore minimizing the aggregation of precipitates and the loss of noble metal. The gold uptake during precipitation strongly depends on pH, temperature and specific surface area of the support. The deposition at a pH above the IEP of the support involves an increasingly negative charge of the support, inducing an electrostatic repulsion of gold-containing anions, thereby limiting the deposition of Au on the solid [97].

Another efficient approach is wet-chemical reduction by adding a reducing agent, *i.e.* sodium borohydride, hydrazine, ascorbic acid, oleyamine or citrate, to the metal precursor solution [127-138]. The adsorption of noble metal ions onto the support surface followed by the reduction induces highly dispersed metal NPs (Au, Pt, Au-Pt alloy) in intimate contact with the support [130,131,134,135]. Naldoni *et al.* [134] loaded Au and Pt NPs (3-4 nm) well dispersed on core (highly defective)-shell (stoichiometric) black TiO_2 (80% anatase – 20% rutile) nanocrystals by using aqueous sodium borohydride solution as reducing agent. Similarly, uniform dispersion of fine Au, Pt and Au-Pt alloyed NPs (2-3 nm) with 1 wt% of total metal content onto active TiO_2 was prepared by Wang *et al.* [135]. The formation of homogeneous alloyed-structure in the Au-Pt solid solution was obtained in which Pt metal, with a low heat of surface energy compared to Au, has a tendency to accumulate on the surface, inducing the Au@Pt core@shell structure. Several studies have reported the combinations of impregnation and reduction method, deposition-precipitation and reduction methods as well as reduction and impregnation methods to further control the size and shape of noble metal NPs [77,81,121,130,136-138]. For example, Naldoni *et al.* [131] combined the wetness impregnation and reduction by NaBH_4 to homogeneously grow spherical Au (3.6 nm) and Pt (2.9 nm) NPs over the whole TiO_2 surface with a narrow size distribution.

Figure 17. Top panel illustrates the synthesis protocol of $\text{Pt/CeO}_2\text{@SiO}_2$ core@shell nanospheres and Pt/CeO_2 hetero-nanocomposites by microemulsion-mediated method. Bottom panels show TEM images and high resolution TEM images of (a, b) $\text{Pt/CeO}_2\text{@SiO}_2$ and (c) Pt/CeO_2 hetero-nanocomposites. Reproduced from Zhou *et al.* [153]. With permission of American Chemical Society.

On the other hand, the polyol process using ethylene glycol solution of the metal precursor has been employed extensively to produce metal NPs supported on different oxides [139-141]. Such glycolate-metal complexes are decomposed by reflux or microwave radiation to yield *in situ* generated reducing species to produce colloidal metals which are subsequently captured by a support material suspended in the solution. Photoreduction or *in situ* photodeposition is also an appropriate and convenient process for the deposition of Au and Pt onto the surface of semiconductor support, particularly TiO_2 , through the generation of electron/hole pairs by UV irradiation that simultaneously oxidizes the sacrificial solvent or organic compound in the solution (*i.e.* alcohol, oxalic acid, glacial acetic acid) and reduces noble metal NPs [142-149]. Apart from the methods aforementioned, the deposition of Au and Pt has been conducted by other techniques such as flame spray pyrolysis, galvanic replacement, sonochemical method, microemulsion technique, direct ionic exchange and solution combustion method (**Figure 17**) [65,137,150-153].

3.2. Structure-reactivity correlation and mechanistic insights

3.2.1. Water-gas shift reaction

The catalytic WGS reaction is one of the most important industrial processes to produce clean hydrogen. Among several classes of catalysts, noble-metal-support oxide catalysts, particularly Pt and Au based ones, are commonly studied. Burch [85] overviewed the advantages and drawbacks of gold catalysts by comparing that of platinum catalysts for the WGS reaction. Gold catalysts can offer some advantages in the low-temperature range (180-250 °C) where the platinum analogs are insufficiently active; and by contrast, the properly activated platinum catalysts exhibits much higher activity than that of gold at higher temperatures. Jacobs *et al.* [1113,120] have reported that it required approximately 20-times more of a 5% Au/CeO₂ catalyst to produce the same lightoff curve as found for a 5% Pt/CeO₂. Au reduction in H₂ was significantly hindered at low loadings where metal-support interaction between Au and ceria were the greatest. Similar behavior was observed in the study from Si *et al.* [124] where the strong interaction between Au and ceria-titania support efficiently prevented the massive agglomeration of Au NPs from sintering, resulting in only ~15% drop of conversion after 20 h under WGS conditions. Temperature-programmed reduction (TPR), *in situ* X-ray absorption near edge structure (XANES) and *in situ* diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS) studies showed that the extent of ceria reduction at lower temperatures over Pt catalyst was higher and deeper than in the case of Au, facilitating the formation of germinal OH groups (serving as the active sites) on the surface of ceria and therefore, yielding higher formate concentrations upon the addition of CO (as shown in **Figure 18**). They concluded that one should not select a Pt catalyst with a low Pt loading and test it in a low temperature shift range where the catalyst is not in an active state [113,120]. It is noteworthy that the enhanced activity of CeO₂ supported noble metal catalysts is frequently ascribed to the ability of ceria to undergo fast storage/release of oxygen cycles via a reversible conversion between Ce⁴⁺ and Ce³⁺ oxidation species [154]. These redox cycles imply a mechanism of oxygen vacancy formation that is indirectly correlated with the catalyst ability to activate oxygen species through electronic transfer and thus, to the catalytic activity in oxidation reactions. Apart from stabilizing small Au NPs, the presence of Ce³⁺ facilitated the dissociation of water during the WGS reaction that happens at the surface of oxide support or at the interface of oxide-gold [78,124,155]. It has also

been reported that Pt NPs exhibit identical function, assisting the dehydrogenation of the formate intermediate or dissociating H_2O to promote the decomposition of these mobile species [109,120].

The activity comparison between monometallic Pt and Pt-alloy structures has also been investigated extensively [109,156-158]. The intimate contact between Pt and second metal drastically promotes the catalytic reactions. In comparison with Pt-CeO₂ and Ru-CeO₂, the Pt-Ru alloyed catalyst with a mean particle size of 2 nm induced a small reduction in the intrinsic catalytic activity; meanwhile the alloyed structure was beneficial to the overall selectivity toward WGS reaction due to the prevention of C-O bond cleavage and subsequent hydrogenation of C to methane (**Figure 19**) [109]. Such alloying substantially inhibited the formation of gaseous methane and metal-bound formate species on the surface without diminishing the WGS activity or impacting the apparent activation energy.

Figure 18. (a, b) CO conversion at high and low space velocity conditions, respectively; and (c, d) intermediate determination by *in situ* DRIFTS during WGS over 2.5Au/ceria and 2.5Pt/ceria, respectively. Reproduced from Jacobs *et al.* [120]. With permission of Elsevier.

Castaño *et al.* [111] have evaluated the supports (γ -Al₂O₃, CeO₂/ γ -Al₂O₃, Ce_{0.8}Fe_{0.2}/ γ -Al₂O₃), the nature of the metal (Pt, Au), the dispersion, and the stream composition to find they each directly influence the WGS performance due to their modification of the materials' electronic properties. Stronger metal-support contact between NPs (Au or Pt) and CeO₂ and Ce-Fe solid

solution has been elucidated, in comparison with weaker interaction between γ -Al₂O₃ support and NPs, *via*: (i) the rearrangement of band gap structure due to the formation of partially reduced ceria (Ce³⁺ ions) and oxygen vacancies, and the presence of metal induced gap states; (ii) the broadening and shifting of the F_{2g} Raman signal to lower wavenumbers; and (iii) local morphology of Au and Pt NPs on Ce_{0.8}Fe_{0.2}/γ-Al₂O₃ where Pt atoms sit on oxygen vacancies and the partially filled *f* states of Ce³⁺ act as donors and 5*d* states of Pt as acceptor levels [111,154,155,158,159]. They also stated that at low temperature, gold catalysts are always more active than the corresponding platinum catalysts, but the reverse is true for temperatures above 200 °C [111]. It is very important that the solid solution support not only facilitates the electron transfer but also increases the number of oxygen vacancies, hence promoting the redox WGS mechanism [154]. Furthermore, Acerbi *et al.* [160] rationalized the electronic interactions at the interface occurring in noble metal/ceria/alumina systems (Pt, Pd, Rh, Ru, Ag, Au) using Nørskov's *d*-band center theory [161]. As shown in **Figure 20**, an inverse “volcano” type correlation between the *d*-band centers of noble metals and the enhancement in ceria reducibility was found. They suggested that the *d*-band center is a more effective electronic descriptor of the noble metal than the work function since it takes into account how the H₂ chemisorption is affected by the metal structure. Although the promoted reduction of surface ceria reduction is limited by H₂ dissociation on Au NPs and Pt to ceria reduction is limited by its affinity to O₂ as a non-dissociative reducing agent was used (*i.e.* CO in the WGS stream), both Au and Pt NPs could allow a promoted ceria reduction at lower temperatures. The differences in activity between Au and Pt catalysts may be explained by different reaction pathways where the adsorption/activation of CO, the creation of oxygen vacancies at the metal-support interface and the water dissociation are crucial [109,124,126,162-164].

Figure 19. WGS activity over PtRu-CeO₂ catalyst: (a) TEM image of PTRu-CeO₂, (b) CO conversion, and (c) *in situ* DRIFTS spectra. Reproduced from Xu *et al.* [109]. With permission of Elsevier.

As mentioned above, numerous reports have found that nonmetallic or oxidized Pt and Au species in nanosized support can play the role of active sites for WGS activity whereas Pt or Au NPs are spectator species [60,81,90-93,1098,114]. Ionic states of Au (+1, +3) and Pt (+2, +4) co-exist in clusters of atoms in which Au_n-O-Ce, Pt_n-O-Ce structures and surface Pt-O phases strongly bound to ceria support are stable after 15 h of WGS condition [60]. As a result, Au increases the concentration of reactive surface oxygen in ceria which occurs through partial lattice filling of vacant Ce sites with Pt^{δ+} or Au^{δ+}, creating additional oxygen vacancies on the surface of Ce⁴⁺-O₂ fluorite-like structure. Thus, the chemistry takes place on these atomically dispersed oxidized species and involves the neighboring OH groups. Otherwise, *in situ* Fourier

transform infrared spectroscopy (FTIR) study elucidated that the WGS reaction sites appear to be the sites at the boundary of very small Au clusters (< 1 nm) highly dispersed at the surface of defective ceria (CeO_{2-x}) [78]. The active sites could be located only on the supported Au NPs or on the perimeter of gold-oxide interface [82,84,86]. CO is mainly adsorbed on $\text{Au}^{\delta-}$ sites initially, and these Au clusters become Au^0 and partially $\text{Au}^{\delta+}$ in the presence of water as a consequence of water dissociation on ceria defects [78,86]. However, *in situ* time-resolved X-ray absorption spectroscopy (TR-XAS) and *in situ* time-resolved X-ray diffraction (TR-XRD) indicate that cationic $\text{Au}^{\delta+}$ species cannot be the key sites responsible for WGS activity in spite of Au^0 and Au^{3+} states in as-prepared catalyst [84]. The full reduction of gold oxide at the Au- CeO_2 interface and partial reduction of ceria support occur simultaneously under reaction condition, leading to the disappearance of $\text{Au}^{\delta+}$ and the generation of Ce^{3+} and oxygen vacancies.

Figure 20. Inverse “volcano”-type correlation between the temperature of the promoted reduction of surface ceria and the calculated center of the noble metal *d*-band in $\text{CeO}_2/\text{noble metal}/\text{Al}_2\text{O}_3$ and $\text{CeO}_2/\text{noble metal}/\text{SiO}_2$. Reproduced from Acerbi *et al.* [160]. With permission of Wiley.

3.2.2. Oxygenate steam reforming reaction

The use of oxygenated hydrocarbons or biofuels (*i.e.* ethanol, methanol, biomethanol, *n*-butanol, glycerol) for hydrogen production by steam reforming has been a great advantage over other processes due to the neutral of CO₂ - a greenhouse gas that causes the global warming. Steam reforming (SR) of oxygenated hydrocarbons is thermodynamically favorable at lower temperatures than non-oxygenated hydrocarbons because it is more exothermic [165-169]. In order to maximize the H₂ production, the formation of byproducts and carbon accumulation must be minimized during the SR reaction.

Several materials comprised of non-noble metal and noble metal supported catalysts have been developed for such a reaction and it is noteworthy that the nature of both the metal and the support is a key factor to enhance the catalytic performance of SR catalysts [98-102,104-106,108,115,116,128,165-173]. Noble metals, particularly Pt, as active phases deposited on metal oxide or mixed metal oxide supports have been widely studied [98-100,115,116,170-173]. Duan and Senkan [102] prepared libraries of catalytic materials comprised γ -Al₂O₃, SiO₂, TiO₂, CeO₂ and Y-ZrO₂ pellets impregnated with 42 elements from the periodic table at 4 different loadings (0.5, 1, 2.5 and 5 wt%) for ethanol SR reaction screening. They found that Pt/TiO₂ and Pt/CeO₂ were the most significant new leads, exhibiting the highest ethanol conversions (+90%) and hydrogen selectivities (~30%) at 300 °C among all 840 single component catalytic materials explored. In spite of much lower surface area, the competitive performance of Pt/CeO₂ compared to Pt/TiO₂ could be attributed to higher oxygen storage capacity of CeO₂, preserving the high dispersion of Pt during the repeated oxidation-reduction cycles. Additionally, the carbon deposition was also prevented after 5-6 h duration, stabilizing their catalytic activities. However, CH₄ (1.5 – 2%) and CO (0.5%) were also formed as byproducts over these supported Pt catalysts. Obviously, Pt promotes the reduction of ceria support, facilitating the generation of Type II bridging OH groups on ceria surface [171,173-177]. It can be ascribed to either vacancy formation, followed by dissociation of water, or by direct dissociation and spillover of hydrogen from Pt to the ceria surface. As illustrated in **Figure 21**, Jacobs and Davis [171] proposed that SR of methanol undergoes four steps: (i) dissociative adsorption of methanol to produce Type II methoxy species and adsorbed hydrogen; (ii) oxidative decomposition of methoxy groups by adsorbed water to liberate two hydrogen molecules and generate surface formate; (iii) water-

assisted decomposition of formate to hydrogen and unidentate carbonate; and (iv) decomposition of carbonate to carbon dioxide. The SR of ethanol proceeds *via* the dehydrogenation and dehydration reactions in which the former are promoted at the metal particles and metal-support interface [105,169].

Otherwise, it has been elucidated that Pt supported Al_2O_3 is much more effective at converting secondary liquid products, either by decomposition or reaction, to simple gas phase components (**Figure 22**) [116,172]. Accordingly, carbon monoxide is reacting with steam *via* the WGS reaction faster than it does with hydrogen *via* methanation, therefore reducing the carbon monoxide level but maintaining high hydrogen selectivity. The presence of coke in form of whisker carbon/carbon nanotube was observed but did not significantly deactivate under reaction conditions at 873 K possibly due to a higher H:C ratio of the deposit on Pt/ Al_2O_3 and/or the ability of ethanol to efficiently clean amorphous carbon from the surface. Comparing Pt with other noble metals, the H_2 and CO selectivities for SR of ethanol followed the order: $\text{Rh} \gg \text{Pt} > \text{Ru} \approx \text{Pd}$ as loaded on Al_2O_3 (seen in **Figure 23**) [100]. The order of $\text{Pt} > \text{Pd} > \text{Rh} > \text{Ru}$ was achieved from Erdöhelyi and Basagiannis's reports [104,105] where dispersed metallic Pt exhibited much higher activity and selectivity toward H_2 production and long term stability at low temperatures.

observed lower activities and selectivities towards CO_2 using $\text{Pt}/\text{Al}_2\text{O}_3$ compared to Rh and Ni catalysts, suggesting that the most selective catalyst in SR of ethanol should contain no WGS promoters. The support may promote the migration of OH groups toward the metal particles, catalyze the reforming reaction or stabilize the metals at high temperatures under steam [98,105]. It can be concluded that the different nature of both metal loading and oxide carrier can be drastically contributed to such differences in the catalytic performance.

Figure 22. (a) Ethanol conversion and (b-d) molar selectivity of gas products at different temperatures over $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. Reproduced from Bilal *et al.* [116]. With permission of Royal Chemistry Society.

Figure 23. Influence of reaction temperature on (a) ethanol conversion and (b, c) product selectivities (H_2 , CO and CO_2) obtained over different noble metals loading on $\gamma\text{-Al}_2\text{O}_3$ support. Reproduced from Liguras *et al.* [100]. With permission of Elsevier.

The addition of small amounts of Pt to Ni, Cu, or Co catalysts significantly lowers the formation of coke deposits by dehydrogenation of C_xH_y intermediates [178] and thus, increases the stability for the bimetallic catalysts [106,108,179-181]. Profeti *et al.* [115] investigated the catalytic activity of Ni/ $\text{CeO}_2\text{-Al}_2\text{O}_3$ catalysts promoted with noble metals (Pt, Ir, Pd and Ru) at low contents (0.3 wt%) for the SR of ethanol (at 450 and 600 °C) and glycerol (at 700 °C). The bimetallic systems containing Pt and noble metals efficiently decreased the reduction temperature of nickel surface species interacting with the support, owing to a hydrogen spillover effect. These noble metals also stabilized the Ni sites in the reduced state along with the reforming reaction, increasing the conversion of oxygenated hydrocarbons and H_2 yield, and suppressing the coke formation. Furthermore, the interaction between Ni and noble metal NPs may alter the electronic structure of the catalyst, arising from a shift in the d-band center that causes a change of the adsorption strength of reaction intermediates, thus facilitating the scission of C-C bond. Similarly, the presence of Pt caused an increase in the exposition of Ni metal atoms

on Al₂O₃ support (shown in **Figure 24**) [106]. Electronic interaction between Pt and Ni active phases in the bimetallic formulation induced higher activity in the C-C bond rupture of ethanol or C₂ intermediate molecules, revealing better stability and superior catalytic performance in ethanol steam reforming than Ni and Pt monometallic counterparts. Ethylene hydrogenation over Pt competed with ethylene dehydrogenation over Ni particles, minimizing the coke formation; meanwhile, the higher activity of Ni in the C-C bond breakage released hydrogen that allows Pt to hydrogenate the ethylene formed on Al₂O₃. Similarly, Ávila-Neto *et al.* [108] indicated that the fraction of metallic Co under reaction conditions was dependent on either the nature of the support (Al₂O₃, La₂O₃/Al₂O₃, CeO₂/Al₂O₃ and CeO₂/MgAl₂O₄) or the existence of Pt promoter. H₂ was activated on metallic Pt sites in lieu of oxygen vacancies in Co oxides, generating atomic hydrogen which migrates to the surface of CoO and Co₃O₄ by hydrogen spillover mechanism, and thus facilitating the reduction of Co²⁺ to Co⁰. Such controlling of Co²⁺/Co⁰ ratio was helpful to equilibrium the steps of ethanol activation and carbon oxidation, stabilizing the catalysts.

Figure 24. (a-c) *In situ* DRIFT spectra and (d-f) product distribution of ethanol steam reforming over Pt/Al₂O₃, Ni/Al₂O₃ and PtNi/Al₂O₃ (1% Ethanol/3% H₂O in a He flow of 30

mL/min, $T = 673\text{ K}$, $P = 1\text{ atm}$). Reproduced from Sanchez-Sanchez *et al.* [106]. With permission of American Chemical Society.

Reversely, the steam reforming activity of Pt is strongly affected by the addition of secondary metals such as Au, Pd, Ru, In, Fe, Rh [182-185]. Pt-Fe/ZrO₂ outperformed in methanol steam reforming reaction compared to other bi- and mono-metallic counterparts owing to the surface segregation of Fe due to its high affinity of Fe for oxygen during calcination, leading to Pt-rich core containing ~60% Pt⁰ content apart from surface Pt-oxide states like PtO and PtO₂ (Figure 25) [183]. However, Pt-Ru supported by γ -Al₂O₃ has been elucidated to be a highly efficient ethanol steam reforming catalyst [184]. Pt-Rh/CeO₂ is also an active catalyst for ethanol steam reforming because very small Rh clusters efficiently dissociated the terminal C-H bond and C-C bond, thus increasing H₂ selectivity [182].

Figure 25. (a) Relative decrease in activity of methanol decomposition with the concentration of Pt⁰ and PtO states for Pt-M catalysts (M = Au, Ru, Pd, Fe); (b) Illustration

of surface segregation phenomena over Pt-M alloys supported ZrO_2 where the oxygen affinity of M dominates its distribution onto the support (open and solid circles represent Pt and M atoms, respectively). Reproduced from Croy *et al.* [183]. With permission of Elsevier.

On the other hand, the fact that Au supported oxide catalysts have been elucidated to be active for either WGS or CO oxidation at low temperature has motivated the reactivity for ethanol reaction [186-188]. By means of XPS, FT-IR, temperature programmed desorption (TPD), Idriss and coworkers [186,187] have proven that the addition of Au onto CeO_2 efficiently suppressed the exclusive formation of surface acetaldehyde and acetate species as well as partially reduced CeO_2 surface even at ambient conditions, hindering the capacity of support to further oxidize ethanol in stoichiometric conditions. Moreover, Au NPs stabilized ethoxide species and favored the formation of CO_2 and H_2 . However, the DFT-computed higher dissociation barrier of the transition state for C-C, C-O, C-H and O-H bond cleavages for Au(111) (group 11) compared to Pt(111) (group 10) and other noble metals (*i.e.* Rh, Ir) suggests poor catalytic properties for ethanol steam reforming [189-191]. Also, much lower density of state (DOS) distribution near the Fermi level of Au(111) surface revealed relatively less active catalyst for redox reactions [190]. Considering both the computed results, (111) surface of Au is expected to be less efficient data explains in SR of ethanol, explaining why Au metal or Au supported catalyst has infrequently been reported in the hydrogen production from ethanol steam reforming [192]. However, Au catalysts work well in methanol steam reforming [171,194].

Taking into account the influence of the support, Pompeo *et al.* [75] found that the support with neutral character, like SiO_2 , favored the dehydrogenation and subsequent cleavage of C-C bonds towards glycerol steam reforming performance, exhibiting excellent activity levels to gaseous products, high selectivity to H_2 , and good stability, whereas the acidity-rich supports, such as $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 and $\text{Ce}_4\text{Zr}_1/\alpha\text{-Al}_2\text{O}_3$, promoted the lateral reactions of dehydration, dehydrogenation, hydrogenolysis and condensation, thus facilitating the catalyst deactivation due to coke formation and demonstrating low conversion to gaseous products (**Figure 26**). However, Gazsi *et al.* [195] observed the highest activity toward methanol steam reforming over the catalyst containing Au dispersed on CeO_2 support (H_2 yield of $\sim 97\%$), followed by MgO and TiO_2 support, and the lowest for SiO_2 ; meanwhile using an Al_2O_3 support favored the

dehydration reaction that yielded other products. It can be ascribed to the interface between Au NPs and partially reduced CeO_x where the electronic interaction occurred between reactive Au and n-type CeO_2 semiconductors. Similarly, loading platinum@zinc oxide core-shell NPs onto $\text{SiO}_2\text{-Al}_2\text{O}_3$ support led to comparable methanol steam reforming activity and selectivity for CO_2 as a conventional Pt/ZnO catalyst and much higher than those obtained over conventional Pt/ Al_2O_3 and Pd-based catalysts, owing to a Pt-Zn alloy formation upon reduction due to the intimate contact between these materials [128].

Figure 26. (a) Reaction pathways for H₂ production and (b) lateral products of glycerol steam reforming reaction over Pt based catalysts identified by gas chromatography/mass spectrometry (GC/MS). Reproduced from Pompeo *et al.* [75]. With permission of Elsevier.

3.2.3. Solar-assisted H₂ production

Figure 27. Schematic illustration of photocatalytic water splitting (WS) over TiO₂ photocatalyst loaded with Pt NPs.

Apart from the WGS and SR processes, H₂ can be photocatalytically produced from water, wastewater or chemical compounds; and TiO₂ is the most well-known photocatalyst for water splitting due to its nontoxicity, cheapness, stability, and earth-abundance. However, its wide band gap allowing the photoactivity only under UV region and the fast recombination of photoinduced electron/hole pairs significantly limits the performance of bare TiO₂. The deposition of Pt and Au NPs with larger work functions (Φ) (lower Fermi level) onto the surface of TiO₂ and other semiconductor oxides facilitates the efficient separation of charge carriers due to the trapping of photoinduced electrons to be involved in the reduction of hydrogen ions, the formation of a space charge layer at the metal-semiconductor interface [196], improving the charge separation and thus the photocatalytic hydrogen evolution (shown in **Figure 27**). The greater the difference between the work function of the noble metal ($\Phi_{Pt} = -5.93$ eV, $\Phi_{Au} = -5.31$ eV *versus* vacuum) [197] and of TiO₂ support ($\Phi_{TiO_2} = 4.2$ eV) [198], the higher the Schottky barrier with consequent increased efficiency of photoinduced electron transfer and trapping by the metal NPs, leading to higher H₂ evolution rate [137,199].

Figure 28. Proposed mechanisms and electronic transitions to explain the role of Au NPs in the photocatalytic water splitting with TiO_2 : (A) Au NPs acts as an electron trap that physically separates the excited electron used for proton reduction from the oxidation step that occurs on TiO_2 surface; (B) H^+ reduction occurs at TiO_2 sites but that the resulting hydrogen atoms need to migrate to Au NPs to recombine and produce H_2 product. Reprinted with permission from Joo *et al.* [133]. Copyright (2014) PNAS.

Figure 29. Schematic diagram of plasmon-induced charge separation and associated photochemistry at the metal/semiconductor heterojunction. Here the electron charge

separated in the metal is transferred to the semiconductor. Reprinted with permission from Zhang *et al.* [68]. Copyright (2012) American Chemical Society.

Alternatively, Joo *et al.* [133] proposed a new thinking about the reduction of protons on the semiconductor surface, not Au NPs. The reduced atomic hydrogen subsequently migrates to Au and recombines to yield H₂ as seen in **Figure 28**. Pt has been widely employed as a co-catalyst for H₂ production under UV light excitation due to its highest work function and low overpotential toward the reduction of protons to generate H₂ [95,137,198,199]. However, plasmonic Au NPs not only harvest visible light and convert the photons to free energetic electrons but also promote the solar-to-hydrogen conversion by increasing the separation of electron-hole pair driven by the plasmonic resonant energy transfer (PRET) which would occur between the electromagnetic, generated by surface plasmonic resonance (SPR), and the resonant electronic levels of semiconductors [68,131-134,200]. A diagram in **Figure 29** illustrates the model of SPR-induced charge carrier formation and subsequent charge transfer mechanism [68]. Increasing Au loading on anatase TiO₂ to optimal values results in the increased rate of H₂ production most likely due to a geometric rather than an electronic effect, particularly, a reduction in the available metal-support sites where both metal and support are needed for the photocatalytic reaction [121,123,145]. However, the lower activity and faster deactivation in H₂ production was observed on Pt-based catalysts compared to the equivalent gold catalyst due to a more rapid poisoning of the active sites which possibly stems from oxygen species strongly adsorbed on the surface of metallic NPs [107]. While Pt introduced ohmic contact, Au NPs underwent charging, storage and transport of interfacial electrons at the Au-oxide interface, inducing Fermi level equilibrium [107]. Additionally, the H₂ evolution rates from aqueous ascorbic acid solution over Au/TiO₂ under the light irradiation > 420 nm was three-times greater than Pt/TiO₂ due to SPR-enhanced charge separation as shown in **Figure 30** [145]. It is worth mentioning that the size of Au contributes differently to SPR-mediated enhancement *via* the different absorption and scattering efficiency. The greater SPR absorption over a wider wavelength range is pronounced for larger Au particle size, resulting in larger number of absorbed photons and higher activity [201]. However, too large NP size (> 40-50 nm) induces much stronger radiative scattering of resonant photons than the absorption and smaller one (< 20-30 nm) can create the energetic charge carriers, leading to surface plasmon decay [202,203]. The electron ‘spillover’ effect can occur for Au clusters smaller than 5 nm due to a reduction of

average electron density [201,204]. Otherwise, larger particle size reduces the available noble metal-oxide support sites for the necessary reaction [123].

Figure 30. (a, b) Comparison in H₂ production over Pt and Au photocatalysts under the irradiation of (a) UV-visible and (b) visible light ($\lambda > 420 \text{ nm}$); (c) proposed mechanism of plasmonic metal-semiconductor for H₂ generation under visible light excitation. Reproduced from Fang *et al.* [145]. With permission of Elsevier.

Naldoni *et al.* [134] studied the energy transfer mechanisms over Au and Pt loaded on core (highly defective)-shell (stoichiometric) black TiO₂ nanocrystals by means of cathodoluminescence (CL) spectroscopy. Pt NPs induced a dramatic quenching of CL signals compared to black TiO₂ due to the better separation of electron-hole pairs generated by the

electron beam whereas in the case of Au/TiO₂, the strong emission enhancement is associated with an increased density of charge carriers that recombine through radiative pathways (shown in **Figure 31**). The deposition of Au NPs (1 wt%) resulted in higher H₂ production rates in the photocatalytic methanol steam reforming compared to Pt NPs due to the synergistic effect between the intragap electronic states related to abundant oxygen vacancies of black TiO₂ and the interband transition of Au, and the SPR transitions under visible light as indicated in **Figure 32**. The superiority of Au-based catalysts for photocatalytic H₂ production compared to Pt ones is consistent with the literature [103,123].

Figure 31. (a, b) Structure and (c) CL spectra of Au supported black TiO₂ catalyst; (d, e) H₂ production rates obtained using the black TiO₂ support in photocatalytic methanol steam reforming. Reproduced from Naldoni *et al.* [134]. With permission of Royal Society of Chemistry.

However, such observations are in apparent contrast with previous studies where platinum is reported as a better co-catalyst than gold [131, 137]. Accordingly, the better performance of

Pt/TiO₂ was ascribed to the greater ability of Pt, with respect to Au, in acting as an effective electron sink, therefore limiting the electron-hole recombination to a larger extent. The more efficient the separation between photoinduced charge carriers, the more efficient are not only the conduction band electrons involved in the reduction path to produce H₂, but also the valence band holes initiated complete methanol oxidation to CO₂ [137]. The *in situ* electron spin resonance (ESR) spectroscopy demonstrated the easier electron transfer from Ti³⁺ to Pt, where the H⁺ reduction to H₂ occurs, than the others under UV-Vis irradiation due to less amount of Ti³⁺ active sites (following the order TiO₂ > Au/TiO₂ >> Pt/TiO₂) [131]. Nevertheless, excessive Pt loading (beyond the optimal content, 0.5 ~ 1 wt%) results in the larger aggregated particles and lower dispersity on the oxide support surface. It not only shields the active surface for light activation but also becomes the recombination centers that trap photogenerated electrons, hence diminishing the charge carrier separation and decreasing the photoactivity.

Figure 32. Schottky barrier formation at the n-type semiconductor/metal interface showing the transfer of Au hot electrons due to SPR excitation or interband transitions. Reproduced from Naldoni *et al.* [134]. With permission of Royal Society of Chemistry.

Recently, Wang *et al.* [135] have reported that the homogeneous Au@Pt core@shell structure showed a flattening of the Au SPR band in the visible light region due to the strong metal-metal interactions at the alloy interface. Au-Pt/TiO₂ catalyst produced 3550 μmole of H₂

within 3 h irradiation that is almost 2.4-, 1.7- and 9.8-fold increase compared to Au/TiO₂, Pt/TiO₂ and bare TiO₂, respectively. Such enhancement in photocatalytic activity is attributed to stronger interaction between Au-Pt and TiO₂ support, higher electron population on the alloyed structure and greatly improved photoinduced charge separation in the bimetallic system. However, Li *et al.* [130] have found that sub-nanometer, ultrafine particle size and high dispersion of PtO-clusters containing 6 - 10 Pt atoms on anatase TiO₂{001} nanosheets demonstrated remarkable hydrogen oxidation reaction suppression ability whereas its hydrogen evolution capacity is still comparable to that of metallic Pt cocatalyst (depicted in **Figure 33**). DFT calculations on Pt₈O₈/TiO₂(001) and Pt₁₂/TiO₂(001) indicate that the activation of O₂/H₂ to generate surface H^{*} and O^{*} is much more difficult on Pt-oxide compared with metallic Pt cluster on TiO₂(001) surface, thus indicating a higher suppression ability relative to Pt-clusters in dissociating the evolved H₂ into H⁺ and e⁻ reversibly or activating O₂ molecules (**Figure 34**). Parayil *et al.* [205] believed that Pt⁰ more efficiently accepts photogenerated electrons than oxidized platinum counterparts (PtO₂). However, if PtO₂ and TiO₂ are in close enough contact to create the heterojunction, PtO₂, a p-type semiconductor, works as electron trap to facilitate the electron propagation from conduction band of TiO₂ to PtO₂, prolonging the lifetime of charge carriers, minimizing the electron-hole recombination and hence improving the H₂ evolution activity. More importantly, such findings possibly pave the way for developing other highly-efficient heterogeneous Pt-based catalysts for clean energy and environmental applications. The existence of Au NPs on {001} facets of anatase TiO₂ nanosheets exhibited 64-fold improved efficiency of solar-to-hydrogen conversion arising from the SPR-mediated electron transfer path of energetic electron generated under visible light illumination ($\lambda > 420$ nm) coupled with the electromagnetic near-field effect [132]. A new Fermi level equilibrium is created due to the shift of Fermi level of Au and TiO₂ to more negative and more positive potentials, respectively, thereby allowing the transfer of high-energy plasmon electrons of Au NPs across an energy barrier to TiO₂ conduction band [206]. The *in situ* ESR spectra revealed that the plasmonic electrons are shallowly-trapped on surface Ti⁴⁺, which are not paired with single electron-trapped oxygen vacancies; therefore the electrons are more readily released [206].

Figure 33. (a) STEM image of PtO-clusters on TiO₂ nanosheets; (b, c) H₂ and O₂ evolution from water over PtO/TiO₂ and Pt/TiO₂ under UV-visible light irradiation ($\lambda > 300$ nm) and dark condition. Reproduced from Li *et al.* [130]. With permission of Nature Publishing Group.

Figure 34. (a) Illustration of photocatalytic H_2 evolution and back-reaction processes on PtO-clusters and metallic Pt NPs co-catalysts; and (b, c) standard Gibbs free energy profile of: (b) H_2 evolution reaction in aqueous solution on Pt_8O_2/TiO_2 , and (c) H_2 reacting with O_2 on Pt_8O_8/TiO_2 and Pt_{12}/TiO_2 surfaces in gas phase. Reproduced from Li *et al.* [130]. With permission of Nature Publishing Group.

The nature of the support has been of vital importance in the photocatalytic H_2 production activity. In this review, because of the complexity of abundant H_2 -evolved photocatalyst systems including transition metal oxides, mixed metal oxides, perovskites, spinels, ilmenites, nitrides, oxynitrides, sulfides, oxysulfides, only simple oxides and mixed metal oxides are mentioned. Murdoch *et al.* [123] found that Au NPs on TiO_2 anatase are about two orders of magnitude more active than those of a similar size on rutile support due to faster rate of electron-hole recombination for rutile, thus shorter lifetimes of photoinduced charge carriers [207-209].

Numerous studies have reported that the mixture of different TiO₂ polymorphs, *i.e.* anatase and rutile, anatase and brookite, brookite and rutile, titanate and anatase, gains advantage to the photocatalytic activity over its individual counterparts due to the formation of a large homo-junction area between two phases or the intimate contact in the interface of two phases (space charge region), efficiently promoting the charge separation [210-214]. Such a synergistic effect arising from the band alignment enhances the interfacial electron transfer rate in two aspects: (i) a passive electron sink and (ii) antenna effect. For instance, in case of the most famous commercial TiO₂ (Degussa P25) photocatalyst, the charge produced on rutile are stabilized *via* the electron transfer to lower energy anatase lattice trapping sites and very importantly, rutile acts as an antenna to extend the photoresponse into visible wavelength (**Figure 35a**) [210]. It almost coincides with the mechanism elucidated by Scanlon *et al.* [212] *via* the combination of theory and experiment as illustrated in **Figure 35b,c**. Kandiel *et al.* [143] demonstrated that a mixture of brookite nanorods and anatase particles in the presence of Pt NPs exhibited much greater H₂ generation rate than single anatase due to the facilitation of interfacial electron transfer across the brookite-anatase junction.

Figure 35. (a) Pathway of charge carriers in mixed-phase TiO_2 ; and (b) Total and ion-decomposed electronic density of states of anatase and rutile TiO_2 calculated using the HSE06 hybrid density functional. Reproduced from Hurum *et al.* [210] and Scanlon *et al.* [212]. With permission of American Chemical Society and Nature Publishing Group.

Figure 36. (a) TEM image, (b) H_2 evolution of Au/ZnO NPs, and (c) mechanism of H_2 generation on the surface of Au/ZnO NPs under visible light exposure. Reproduced from He *et al.* [216]. With permission of Royal Chemical Society.

Apart from TiO_2 , different transitional metal oxides and mixed oxides have been employed as the supports for photocatalytic H_2 production, such as Cu_2O , CeO_2 , ZnO , Fe_2O_3 , WO_3/SiO_2 , CeO_2/TiO_2 , TiO_2/ZrO_2 [10,112,142,147,149,215,216]. Recently, He *et al.* [216] synthesized Au/ZnO NPs template by yellow fluorescent glutathione-Au nanoclusters/zeolitic imidazolate framework-8 NPs, as seen in **Figure 36**. The great improvement in H_2 production could be ascribed to the role of Au NPs as a sink for the photoinduced electron storage and the Fermi level shift towards more negative potentials apart from the SPR effect. CeO_x-TiO_2 mixed oxides with different ceria contents and geometries are unravelled to be a potential candidate for water splitting due to the hierarchical heterogeneity at the interface as well as the strong interaction

between CeO_x and TiO_2 *via* the electronic perturbation [110,112]. The observation on powder catalysts is well consistent with our previous surface science studies [41-43]. Moreover, the presence of Pt NPs imposed a significant reduction of CeO_2 dispersed on TiO_2 , creating and stabilizing Ce^{3+} centers on the outermost surface or near the oxide-oxide interface that not only dissociated water but also acted as the hole scavengers, drastically enhanced the formation of electron/hole pairs and efficiently suppressing the surface charge recombination. Liu *et al.* [147] unexpectedly observed high H_2 generation onto $\text{Pt}/\text{WO}_3/\text{SiO}_2$ materials due to the quantum confinement effect of highly dispersed WO_3 NPs (2-4 nm) and the formation of the interface W-O-Si like species (**Figure 37**). Note that Pt/WO_3 has been considered as an efficient visible-light-driven O_2 evolution catalyst. SiO_2 is a high cation electronegativity support and in such composite materials, silica could be regarded as a positive center for WO_3 NPs, causing the distortion of adjacent WO_3 structure and altering the electronic band structure *via* the upshift of conduction band minimum for W-O-Si species, thus meeting the thermodynamic potentials for proton production. Metallic Pt dispersed on highly ordered mesoporous $\text{TiO}_2\text{-ZrO}_2$ possessing large surface areas and pore volume, narrow pore size distributions and abundant surface Lewis acid sites, exhibited good H_2 production performance due to the cooperative effect of large surface-to-volume ratio, porosity and crystallinity that induced the easier separation of electrons and holes [142].

Figure 37. (a) Photocatalytic H₂ generation activity over WO₃/SiO₂ composite under full-arc irradiation of Xe lamp; (b) XPS valence band; (c) Mott-Schottky plot and (d) electronic structure of WO₃/SiO₂ and its photoexcitation mechanism for H₂ evolution. Reproduced from Liu *et al.* [147]. With permission of Elsevier.

4. Conclusions and future outlook

In this review, we have identified and highlighted important studies that provide valuable insights into the role of supported metal catalysts of Pt and Au on the catalytic production of H₂ from numerous chemical conversion processes. There are many challenges to exploit the structural, electronic and chemical properties of nanostructured Pt and Au towards optimum conversion of reactants such as H₂O (WGS, SAR) and oxygenates (SR) to H₂. The key factors to bringing together convergent principles that are common to catalyzing these reactions is a fundamental understanding of the nature of the active state of the catalyst that facilitates H₂

production and an appreciation for the mitigation of deactivation. It is clear from numerous studies that this is a product of a combination of effects with a collective contribution of size, geometric, electronic and metal-support interactions for both Pt and Au catalysts.

In general, Pt is more reactive than Au, facilitating easier chemical activation processes; however, Pt is more prone to poisoning while Au remains inert due to various deactivation processes. In both materials, the role of the active state is specific to the nature of the reactants and reaction conditions, where the metallic state is more reactive than the oxide of both metals. Both Au and Pt do however exhibit structural instability through sintering under harsh reaction conditions but can be anchored onto the supports. Furthermore, the effect of the supports on these metals can be very specific to the reaction; however, it is clear that the chemistry of both metals can be tuned through the metal-support interactions.

With this in mind the ability to extended H₂ production further, we propose several key strategies:

- (i) The atomic control of catalyst geometry to optimize the presence and protection of active sites.
- (ii) The identification of electronic and support effects so as to selectively tune the reactivity.
- (iii) The determination of the reaction mechanism to steer appropriate pathways that can deliver products.
- (iv) The understanding of the deactivation processes that can prevent production of H₂ and formulate catalyst structure to prevent it.

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Graphical abstract