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# Heterogeneous gold catalysts for selective hydrogenation: from nanoparticles to atomically precise nanoclusters

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Gold nanocatalysts with different sizes (nanoparticles and nanoclusters) show different catalytic performances for various selective hydrogenation reactions. The recent breakthrough in a controllable synthesis of atomically precise gold nanoclusters provides unprecedented opportunities for understanding the catalytic behavior at the atomic/molecular levels. Herein, we review the progress in catalytic hydrogenation over gold nanoparticles and atomically precise gold nanoclusters in the last five years. We also compare the results obtained from different reactions so that a better understanding of their catalytic behavior can be obtained. Finally, we provide some future perspectives on gold nanocatalysis.

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# 1. Introduction

Bulk gold is known to be inert because of the absence of dissociation capability towards molecular oxygen and molecular hydrogen. The intrinsic catalytic reactivity of gold had been overlooked for a long time until the discovery that gold at the nanoscale showed unique catalytic activity for carbon monoxide oxidation at -76 °C.<sup>1</sup> Catalytic hydrogenation is one of the most important transformations in the chemical industry. This type of reaction was traditionally catalyzed by platinum group metals such as Pd, Pt and Ru. In recent research, gold nanocatalysts have increasingly gained attention for selective hydrogenation reactions due to the good activity and extraordinary selectivity of nanogold.<sup>2–6</sup>

It is generally accepted that the catalytic performance of gold nanocatalysts is critically related to particle size.<sup>7</sup> The supported gold nanoparticles with small sizes (*e.g.*, 2–5 nm) usually show robust catalytic properties, which originate from the interaction between small-size gold nanoparticles and CO molecules leading to the structure evolution of single gold nanoparticles and dynamic low-coordinated gold atoms under catalytic working conditions.<sup>8</sup> The Au nanocatalysts produced by conventional preparation methods, including co-precipitation, deposition-precipitation and sol precipitation methods,<sup>9–11</sup> are apparently more or less polydispersed in size, not to mention the lack of well-defined structures. These

issues result in major challenges in investigating the precise size-dependent catalytic properties, identifying the catalytic sites and determining the structure–property relationships of Au catalysts.

With the development of solution-phase synthesis techniques of nanomaterials and their characterization methodologies in the past few decades, the controlled synthesis of metal nanoclusters with a precise number of atoms (termed gold nanoclusters) has been successfully developed.<sup>12–16</sup> More importantly, the electronic properties of metal particles change drastically from nanoparticles to nanoclusters (Fig. 1),<sup>17,18</sup> which provides new opportunities for catalysis. Due to discrete electronic structures, gold nanoclusters (<2 nm) are expected to react differently with reactants than conventional nanogold, hence exhibiting unique properties. Besides, atomically precise gold nanoclusters have a well-





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defined size (*i.e.* a precise number of gold atoms) and also a well-defined atomic structure, which provide unprecedented opportunities for exploring the precise size-dependent catalytic properties and acquiring the structural insights into catalytic mechanisms.

Herein we review the progress about the catalytic hydrogenation research of gold nanoparticles and nanoclusters in the last 5 years. We hope that the critical review can be useful in achieving a better understanding of nanogold catalyzed selective hydrogenation reactions.

# 2. Gold nanoparticle catalysts

#### 2.1 Semihydrogenation of alkynes

Alkenes constitute one of the largest classes of industrially synthesized organic compounds. The semihydrogenation of alkynes is the simplest and most straightforward approach to producing alkenes and is also an essential process to remove alkyne impurities (<2%) from alkenes in the polymerization industry.<sup>19</sup> Compared with Pd-based catalysts that suffer from the problem of over-hydrogenation,<sup>20</sup> gold nanocatalysts display extraordinary selectivity in many hydrogenation reactions.<sup>3</sup>

Due to the limited capability to dissociate molecular hydrogen, gold nanocatalysts exhibit low activity in hydrogenation reactions. Nevertheless, an effective strategy to improve the activity of gold catalysts is to load gold nanoparticles on an appropriate support. For example, employing the functionalized graphene oxide (GO) as a support, highly dispersed Au nanoparticles with enriched low-coordination sites were prepared, endowing the Au/GO catalyst with 99% styrene selectivity and 99% conversion in the hydrogenation of phenylacetylene.<sup>21</sup> Rossi *et al.*<sup>22</sup> reported that N-doped-carbon modified Au/TiO<sub>2</sub> catalysts exhibited excellent activity and selectivity for the hydrogenation of various alkynes. The frustrated Lewis pair interface between gold and nitrogen can serve as a basic site to promote the heterolytic activation of H<sub>2</sub> and thus accounts for the observed properties.<sup>22,23</sup>

The increase in catalytic activity can also be achieved by incorporating another element into the Au catalyst;<sup>24,25</sup> for example, single atom Pd deposited on the surface of Au nanoparticles enhanced the catalytic activity of Au by nearly 10-fold without affecting the high selectivity to 1-hexene for the hydrogenation of 1-hexyne.<sup>25</sup> The improved properties are attributed to Pd single atoms, as these atoms facilitate molecular hydrogen splitting, which leads to the availability of weakly bound atomic hydrogen on the otherwise inert gold surface.<sup>25</sup>

#### 2.2 Hydrogenation of carbonyl compounds

The chemoselective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes is an important kind of reaction because the resulting unsaturated alcohols are valuable chemical intermediates in the production of fragrances, pharmaceuticals and agrochemicals (Scheme 1).<sup>26</sup> Platinum group catalysts exhibited intrinsic selectivity for the C=C bond hydrogenation, while gold nano-



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Scheme 1 Chemoselective reductions of unsaturated carbonyl compounds to unsaturated alcohols.

catalysts showed high selectivity for the C=O bond hydrogenation, which resulted in their extensive use in this kind of hydrogenation.

The selectivity towards the C=O bond hydrogenation is linked to the size and morphology of Au nanoparticles and the nature of the support. In the diameter range of 1-5 nm, the supported gold nanoparticles above 2 nm exhibited higher activity and selectivity to allyl alcohol than those with less than 2 nm for the selective hydrogenation of acrolein.<sup>27</sup> The observed performance may originate from a quantum-size effect which generates a transition from the metal phase to the nonmetal phase and the change in the electronic properties of gold nanoparticles with different sizes;<sup>27</sup> on a note, very recently Higaki et al. have reported that the nonmetal-to-metal transition occurs between  $Au_{246}$  and  $Au_{279}$ ,<sup>18</sup> which is expected to promote the fundamental understanding of the quantum size effect in catalysis.<sup>15</sup> The higher activity and selectivity to allyl alcohol over gold nanoparticles with a higher degree of rounding were observed in the selective hydrogenation of acrolein.<sup>28</sup> Adding another element such as Cu and Ag to gold also dramatically improved the performance of gold nanocatalysts in the selective hydrogenation. The enhanced performance is related to the synergistic interaction between gold and the added element, which was beneficial for the activation of H–H, C=C and C=O bonds.<sup>29,30</sup>

Gold nanoparticles supported on a variety of supports showed different selectivities for the hydrogenation of the C=O bond in  $\alpha$ , $\beta$ -unsaturated aldehydes and ketones.<sup>31–33</sup> The encapsulation of small gold nanoparticles in the zeolitic imidazolate ZIF-8 framework endowed them with 95% selectivity to crotyl alcohol and prevented gold particle agglomeration in the hydrogenation of crotonaldehyde.<sup>34</sup> The enhanced selectivity was attributed to the small pores of ZIF-8 which permitted only the carbonyl group of crotonaldehyde to reach the Au nanoparticle surface. Zhang *et al.*<sup>35</sup> found that the synergistic cooperation of acidic and basic sites of the support should account for the preferential adsorption and activation of the C=O group over gold nanocatalysts.

#### 2.3 Hydrogenation of nitro compounds

Aromatic amine and its derivatives are key intermediates for the production of agrochemicals, pharmaceuticals, dyes and polymers. The catalytic hydrogenation of nitroarenes represents the most benign and cost-effective route. Since the important advancement that Au/TiO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> afforded >95% selectivity at high conversion in the chemoselective hydrogenation of 3-nitrostyrene,<sup>36</sup> gold nanocatalysts have attracted much attention.

Gold nanoparticles positioned on the edge/corner sites of  $TiO_2$  afforded a TOF of 279 h<sup>-1</sup> with higher than 99% selectivity in the selective hydrogenation of 3-nitrobenzene.<sup>37</sup> The increased activity resulted from the unique absorption and activation of the nitro group compared to the conventional Au/ $TiO_2$ .<sup>37</sup> Gold nanoparticles loaded on  $TiO_2$  modified with the single-site Sn promoter showed a significant increase in catalytic activity and selectivity for the hydrogenation of substituted nitroarenes.<sup>38</sup> Due to a synergistic effect between Au and Ni, the AuNi<sub>3</sub>/SiO<sub>2</sub> catalyst gave a 93.0% selectivity to 3-vinyl-aniline and 90.8% conversion of 3-nitrobenzene under mild conditions.<sup>39</sup> Isolated Pd and Au nanoparticles supported on SiC were also reported to catalyze the hydrogenation of substituted nitroarenes to anilines, with high activity and selectivity under visible light irradiation at room temperature.<sup>40</sup>

Ligand-on gold nanoclusters were used as hydrogenation catalysts and precatalysts.<sup>41–43</sup> For instance, gold catalysts with well-controlled size (2.0 nm) were obtained through the calcination of cysteine-capped Au<sub>25</sub> nanoclusters on ZnAl–hydrotalcite (ZnAl-HT), giving excellent selectivity (>98%) to 3-vinylaniline at the complete conversion of 3-nitrostyrene over broad reaction duration and temperature windows (Fig. 2). The properties were unprecedented, which were closely related to the small size of Au nanoparticles and the nature of the oxide support derived from ZnAl-HT.<sup>42</sup> The types of divalent metal ions of HT affected the catalytic properties and hydrogenation pathways of Au/MAl-HT-300 (M = Ni, Zn and Mg).<sup>43</sup>



Fig. 2 HAADF-STEM images of the catalysts: (a)  $Au_{25}/ZnAl-HT$ , (b)  $Au_{25}/ZnAl-HT-300$ , and (c, d)  $Au_{25}/ZnAl-HT-600$ . Reproduced with permission from ref. 42. Copyright 2017 Wiley-VCH.

# 3. Gold nanocluster catalysts

#### 3.1 Semihydrogenation of alkynes

Like gold nanoparticles, gold nanoclusters also exhibit good catalytic properties in the semihydrogenation of alkynes.44 For instance, both the spherical Au<sub>25</sub>(SR)<sub>18</sub> and rod-shaped Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(C=CPh)<sub>5</sub>X<sub>2</sub> nanoclusters supported on TiO<sub>2</sub> exhibited ~100% conversion of alkynes and complete selectivity to alkenes for the semihydrogenation of terminal alkynes under mild conditions, albeit the ligand-on catalyst showed no activity for internal alkynes as substrates.45 In contrast, the internal alkynes can be transformed into Z-alkenes over ligand-off Au<sub>25</sub> catalysts. Therefore, a unique activation pathway of terminal alkynes over ligand-on Au25 nanoclusters was presented,<sup>45</sup> in which the terminal alkynes underwent the deprotonation of the alkynyl proton, followed by interaction with Au25 via deprotonated carbon. This mechanism was supported by the FT-IR spectroscopic analysis of intermediates. With the available atomic structures, the open triangular Au<sub>3</sub> facet on the spherical Au25(SR)18 nanocluster and the waist sites of the rod-shaped Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(C=CPh)<sub>5</sub>X<sub>2</sub> (X = Br/Cl) nanocluster were identified to be the active sites (Fig. 3).<sup>45</sup>

In another report, two Au<sub>38</sub> nanoclusters  $[Au_{38}(L)_{20}(Ph_3P)_4]^{2^+}$ (L = -S-Ph-m-Me or  $-C \equiv C$ -Ph) were synthesized and characterized. X-ray crystallography revealed that they had the same kernel and surface structures, with the only difference being the L ligands (Fig. 4). Their kernels comprise face-centered cubic-type Au<sub>34</sub>, which is surrounded by four AuL<sub>2</sub> staple motifs, four Ph<sub>3</sub>P, and twelve bridging L ligands. The alkynylprotected Au<sub>38</sub> nanocluster (supported TiO<sub>2</sub>) delivered high conversion (>97%) and selectivity (>93%) for the semihydrogenation of terminal and internal alkynes, while the thiolated Au<sub>38</sub> showed a very low activity (<2%).<sup>46</sup> The drastically different catalytic performances are probably related to the different electronic structures of isostructural Au<sub>38</sub> nanoclusters modulated by different ligands, which are also confirmed by UV-Vis and <sup>31</sup>P-NMR.<sup>46</sup>



**Fig. 3** Proposed mechanism for the ligand-on Au<sub>25</sub> nanocluster catalyzed semihydrogenation of terminal alkynes to alkenes using H<sub>2</sub>. Left panel: Au<sub>25</sub>(SR)<sub>18</sub> nanocluster. Right panel: Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(C=CPh)<sub>5</sub>X<sub>2</sub> (X = Cl, Br) nanocluster. Color codes: Au, green; S, yellow; C, gray; P, pink; and X, cyan. Hydrogen atoms are omitted for clarity. The areas marked in orange are the Au<sub>3</sub> active sites (left panel) and the waist active sites (right panel). Reprinted from ref. 45 with permission. Copyright 2014, American Chemical Society.



**Fig. 4** Crystal structures of  $[Au_{38}(PhC \equiv C)_{20}(Ph_3P)_4]^{2+}$  (A) and  $[Au_{38}(m-MBT)_{20}(Ph_3P)_4]^{2+}$  (B). Reproduced with permission from ref. 46, Copyright 2017 American Association for the Advancement of Science.

In comparison, the alkynyl-protected Au<sub>38</sub> nanocluster supported TiO<sub>2</sub> showed higher activity than the Au<sub>25</sub> nanoclusters, with the TOF being 11.9 h<sup>-1</sup> and 1.6 h<sup>-1</sup> (based on the Au loading) in the semihydrogenation of phenylacetylene, respectively.<sup>45,46</sup> Besides, unlike both the spherical and rod-shaped Au<sub>25</sub> nanoclusters exhibiting similar activities, the two isostructural Au<sub>38</sub> gave vastly different catalytic properties. These results indicate that the size of Au nanoclusters and their structure significantly affect the catalytic properties. It implies an important strategy for tailoring the catalytic performance of Au nanoclusters by designing and selecting the type of ligand.

#### 3.2 Hydrogenation of carbonyl compounds

When it comes to the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes, the complete selectivity for unsaturated alcohols can be obtained over thiolated-protected gold nanoclusters.<sup>47</sup> In addition to thiolated-ligated Au nanoclusters, other ligands such as tert-butyl(naphthalen-1-yl)phosphine oxide (SPO)-protected Au nanoclusters can be employed to efficiently catalyze the selective hydrogenation of a wide range of  $\alpha$ , $\beta$ -unsaturated aldehydes with different functional groups.48 The Au nanoclusters exhibited higher activity than Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub>, which was based on the TOF of cinnamaldehyde hydrogenation.47,48 It is likely that the weakly absorbed P-containing ligand promoted the exposure of Au sites and then increased the catalytic activity; however, the S-containing ligand with greater affinity for Au inhibited the catalytic properties.

The introduction of other elements into Au nanoclusters is a promising approach to modifying the catalytic performance.<sup>49–52</sup> For instance, Hayashi *et al.*<sup>53</sup> produced PdAu<sub>33</sub> and PdAu<sub>43</sub> by the co-reduction of Au and Pd precursors in the presence of PVP. Extended X-ray absorption fine structure (EXAFS) analysis showed that the single Pd atom was located at the exposed surface of the Au clusters, which is different from the structure of previously reported Pd doped Au nanoclusters, such as  $[PdAu_8(PR_3)_8]^{2+}$  (ref. 54) and PdAu<sub>24</sub>(SR)<sub>18</sub>,<sup>55–58</sup> where Pd is exclusively located at the central position. Single Pd atom doping into the Au nanoclusters remarkably enhanced the activity and the selectivity for the



Scheme 2 Chemoselective hydrogenation of nitrobenzaldehyde derivatives over Au<sub>99</sub>(SPh)<sub>42</sub>/CeO<sub>2</sub>.

hydrogenation of the C=C bond in the selective reduction of cinnamaldehyde,<sup>53</sup> whereas the central palladium atom in the  $Pd_1Au_{24}(SR)_{18}$  catalyst exhibited no increase in hydrogenation activity.<sup>58</sup>

The chemoselective hydrogenation of the carbonyl group was preferred over thiolate-stabilized gold nanoclusters, even when the carbonyl group and nitro group co-existed in the same substrate.<sup>59</sup> Furthermore, hydrophobic Au<sub>99</sub>(SPh)<sub>42</sub> nanoclusters loaded on CeO2 gave rise to a higher conversion and ~100% selectivity for 4-nitrobenzyl alcohol in the chemoselective hydrogenation of 4-nitrobenzaldehyde. The catalyst also showed excellent stability and good versatility for a range of substrates (Scheme 2).<sup>60</sup> Afterwards, Li et al.<sup>61</sup> found that the addition of a Lewis acid (such as  $Cu^{2+}$ ,  $Ni^{2+}$  and  $Co^{2+}$ ) significantly improved the catalytic performance Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub> nanoclusters for the above chemoselective hydrogenations. The conversion of 4-nitrobenzaldehyde was increased from 13.4% to 90.1% at 50 °C, with the selectivity for 4-nitrobenzyl alcohol holding 100%, when Co(OAc)<sub>2</sub> was added as a Lewis acid.

Recently, we reported for the first time the transfer hydrogenation of nitrobenzaldehyde derivatives catalyzed by atomically precise gold nanoclusters (Au25, Au38, Au52 and Au144) using potassium formate as the hydrogen source.<sup>62</sup> In addition to the attainment of a complete selectivity for the hydrogenation of the aldehyde group, a size effect was also observed, and among the investigated sizes, Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> exhibited the highest catalytic activity.<sup>62</sup> It is worth noting that, with H<sub>2</sub> as the hydrogen source, no size dependence was found for the selective hydrogenation of 4-nitrobenzaldehyde using Au<sub>25</sub>(SPh)<sub>18</sub>/CeO<sub>2</sub>, Au<sub>36</sub>(SPh)<sub>24</sub>/CeO<sub>2</sub> and Au<sub>99</sub>(SPh)<sub>42</sub>/CeO<sub>2</sub> nanocluster catalysts.<sup>60</sup> The observed size dependence implies different catalytic mechanisms for the chemoselective reduction of 4-nitrobenzaldehyde due to different hydrogen sources (*i.e.*, H<sub>2</sub> versus HCOOK). What's more, a reversible control of the product selectivity by thiol ligands was discovered: the ligand-off Au<sub>38</sub> after thermal treatment showed the selectivity for the hydrogenation of the nitro group, and interestingly, the selectivity for the hydrogenation of the aldehyde group can be restored by treating the ligand-off Au<sub>38</sub> with thiol.<sup>62</sup> In combination with the previous results<sup>63,64</sup> and our testing of control experiments, there should be different adsorption modes of 4-nitrobenzaldehyde on the surfaces of ligand-on and ligand-off gold nanoclusters. The unexpected selectivity of the ligand-on nanocluster catalysts should originate from the preferred absorption of the aldehyde group of 4-nitrobenzaldehyde on the exposed gold atoms of Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub>.

#### 3.3 Hydrogenation of nitro compounds

For the reduction of 4-nitrophenol to 4-aminophenol by NaBH<sub>4</sub>, Au<sub>25</sub>(SR)<sub>18</sub> bearing shorter alkyl chains displayed better accessibility and activity than those bearing longer chains. The aromatic ligands led to an enhanced activity of Au<sub>25</sub>(SR)<sub>18</sub>, while amine group ligands exhibited a negative effect on the catalytic activity.<sup>65</sup> Thiolate ligands also modulate the catalytic active sites of Au<sub>25</sub>(SR)<sub>18</sub> nanoclusters and influence the reaction pathway for the hydrogenation of 4-nitrophenol.<sup>66</sup> It indicated that ligand engineering can be an efficient tool for tuning the catalytic properties of gold nanoclusters, as demonstrated in C–C coupling reactions as well.<sup>67</sup>

Tian *et al.*<sup>68</sup> reported a new structure of  $Au_{38}(SCH_2CH_2Ph)_{24}$ (denoted as  $Au_{38T}$ ) based on crystallographic analysis, which is completely different from that of the previously reported  $Au_{38}(SCH_2CH_2Ph)_{24}$  structure (denoted as  $Au_{38Q}$ ), although both nanoclusters have an identical composition. The  $Au_{38T}$ structure consists of an  $Au_{23}$  core which is composed of one icosahedral  $Au_{13}$  and one  $Au_{10}$  unit,<sup>68</sup> whereas  $Au_{38Q}$  is made up of a face-fused bi-icosahedral  $Au_{23}$  core.<sup>69</sup> In the reduction reaction of 4-nitrophenol with NaBH<sub>4</sub>, a 44% yield of 4-aminophenol was obtained over  $Au_{38T}$ , while no reduction occurred over  $Au_{38Q}$ . The high catalytic activity of  $Au_{38T}$  is related to its surface being not as densely protected as that of  $Au_{38Q}$ .<sup>68</sup> It indicates a structure–property relationship of gold nanoclusters and guides future work on how to control the nanocluster catalytic properties by tuning their structures.

# 4. Comparison of the catalytic behavior of gold nanoparticles and nanoclusters

In the catalytic hydrogenation reactions, the activation and dissociation of molecular H<sub>2</sub> are often the rate-limiting step.<sup>70</sup> For the adsorption and dissociation of H<sub>2</sub> over conventional gold nanoparticle catalysts, the low-coordinated gold atoms or the perimeter interface around the gold particles in contact with oxide supports was usually considered to act as the catalytic sites.<sup>21–23,71,72</sup> The type and nature of supports affect the size, morphology and chemical states of gold nanoparticles, thereby generating the significant effect on the activation of H<sub>2</sub>. The adsorption of nitrogen-containing bases on Au nanoparticle catalysts also promotes the activation of H<sub>2</sub> in some reactions.73,74 Gold nanoparticle-mediated hydrogenation reacfollow the Langmuir-Hinshelwood-like tions usually mechanism.73,74 The formed active hydrogen species should interact with the adsorbed substrate after the activation of H<sub>2</sub>, followed by the generation of the product.

It is reported that the exposed atoms of gold nanoclusters can provide a favorable environment for the adsorption and cleavage of molecular hydrogen.<sup>47</sup> Besides, ligands such as phosphines and alkynyls, which protect gold nanoclusters, can mediate and stabilize the structure of nanoclusters and cooperatively activate  $H_2$  with gold nanoclusters.<sup>46,48</sup> For instance,



**Fig. 5** Proposed mechanism for the hydrogenation of nitrobenzaldehyde catalyzed by  $Au_{11}(PPh_2Py)_7Br_3$  in the absence of amine additives. Color codes: Au, green; P, purple; and Br, cyan. The Ph\_2Py of other phosphine ligands is omitted for clarity. Reprinted from ref. 75 with permission. Copyright 2016, American Chemical Society.

Cano et al.<sup>48</sup> found that the heterolytic cleavage of molecular hydrogen occurred across the surface of Au nanoclusters and P-O groups of SPO, which was confirmed by a series of characterization and control experiments. Recently, Liu et al.75 synthesized diphenyl-2-pyridylphosphine-protected Au11(PPh2Py)7Br3 clusters, which exhibited excellent properties in the chemoselective hydrogenation of nitrobenzaldehyde in the absence of pyridine. On the basis of experimental and theoretical results, it was found that one PPh2Py ligand was first removed to expose the gold core atoms to reactants (Fig. 5). Then,  $H_2$ adsorbed onto the exposed gold atoms and was activated with the aid of the pyridine group of PPh<sub>2</sub>Py ligands on nanoclusters. The pyridine group abstracted a proton from H<sub>2</sub> to generate pyridinium (PyH<sup>+</sup>), leaving H<sup>-</sup> on the core (Au<sub>2</sub> site) for the ensuing hydrogenation. Finally, nitrobenzaldehyde adsorbed onto the surface of gold nanoclusters by the interaction of the -CHO group with PyH<sup>+</sup> and H<sup>-</sup>, followed by the formation of nitrobenzyl alcohol.75 This catalytic process not only avoided the use of toxic pyridine by efficiently introducing the pyridine group close to the gold surface to assist the reactant activation, but also confirmed that the cooperative interaction between gold nanoclusters and ligands played a crucial role in the activation of H<sub>2</sub>.

As mentioned above, both gold nanoparticles and nanoclusters afford nearly complete selectivity for alkenes in the semihydrogenation of alkynes.<sup>21–23,44–46</sup> Nevertheless, the conventional gold nanoparticles could not afford 100% chemoselectivity to the unsaturated alcohols<sup>3,27–35,76</sup> whereas ligandon gold nanoclusters delivered the complete selectivity in the selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes and ketones.<sup>47,48</sup> Zhu *et al.*<sup>47</sup> presented that the electron-rich Au<sub>13</sub> core of Au<sub>25</sub>(SR)<sub>18</sub> nanoclusters facilitated the adsorption and activation of the C=O bond, while the exterior shell acted as the catalytic sites for the activation of H<sub>2</sub>. They thought their unique electronic properties (*i.e.* electron-rich Au<sub>13</sub> core and low-coordinate surface gold atoms) are responsible for the moderate activity and complete selectivity for unsaturated alcohols in the chemoselective hydrogenation of  $\alpha$ , $\beta$ -unsaturated ketones and aldehydes. Subsequently, the mechanism about 100% selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated ketones to unsaturated alcohols on Au<sub>25</sub>(SR)<sub>18</sub> has been theoretically confirmed by first-principles density functional calculations.<sup>77</sup>

For the selective hydrogenation of a substrate containing a nitro group and a carbonyl group, the reduction of the group was preferred over ligand-on gold carbonyl nanoclusters,59-62,75 which is in striking contrast to the preferred reduction of the nitro group over conventional gold nanoparticles.<sup>36–40</sup> The new and unique catalytic properties of gold nanoclusters were possibly assigned to the preferential adsorption of the aldehyde group onto the surface gold atoms of  $Au_n(SR)_m$  nanoclusters *via* an insertion mode owing to the pocket-like active sites on nanocluster surfaces.59,77 In contrast, bare gold nanocatalysts typically exhibit flat (100) and (111) nanofacets, on which the reactant bearing both C=O and -NO2 groups adopts different activation modes. For further details, both experimental and theoretical works are still required to understand the atomic-level mechanism in future work. Nevertheless, it shows that ligand-protected gold nanoclusters are promising for the development of new types of catalysts with unique selectivity.

## 5. Conclusions & future perspective

Different gold species, including nanoparticles and nanoclusters, can serve as catalysts in the selective hydrogenation reactions. Many gold nanocatalysts exhibit excellent properties and recently some have even found their applications in the chemical industry.<sup>78,79</sup> It has been proven to be an effective strategy to develop Au nanocatalysts with high performance by controlling the nanogold size and morphology, incorporating another metal into the gold catalysts, depositing gold species on an appropriate support, and tuning the interaction between gold and the support.

However, the origin of the catalytic performance of gold nanocatalysts for selective hydrogenation reactions has not been sufficiently clarified. Identifying the catalytic sites and exploring the reaction mechanisms should be pursued in future research. Monitoring the dynamic characteristics of the catalytic hydrogenation process is pivotal for understanding the mechanism. More efforts should be focused on utilizing *in situ* or operando techniques, such as DRIFT-IR and EXAFS, to understand how the characteristics of gold nanocatalysts change under working conditions.<sup>80</sup>

Unlike gold nanoparticles with a size distribution and bare gold nanoclusters, gold nanoclusters with a precise number of atoms have their determined sizes and well-defined structures.<sup>12–16</sup> It provides a good platform to investigate the precise size dependence and achieve the fundamental insights into gold catalysis at the atom level. The controlled synthesis of gold nanoclusters offers new, exciting opportunities for the development of novel gold catalysts. Gold nanoclusters have also been demonstrated to be efficient pre-catalysts, which brings about gold nanocatalysts with high performance which are not achievable with the traditional preparation methods of gold catalysts, such as co-precipitation and depositionprecipitation.<sup>42,43</sup> In future work, a combination of experiment with theory should be pursued in order to reveal the catalytic mechanisms on nanocluster catalysts.<sup>81–83</sup>

Due to the high surface free energy, small-sized gold nanoparticles tend to aggregate into larger particles or detach from the support under harsh conditions, which leads to the decrease of activity and even deactivation. Therefore, it is one of the challenges to improve the gold catalyst stability. Recent efforts have been geared toward this direction; for instance, gold nanoclusters encapsulated in microporous silica were reported to maintain the average nanocluster size of ~1.6 nm after thermal treatment at 500 °C, delivering 99% conversion and 98% selectivity towards ethylene in the acetylene hydrogenation.<sup>84</sup>

Overall, we believe that the atomically precise, structurally characterized nanoclusters hold great promise in serving as unprecedented model catalysts and will significantly boost the fundamental studies in heterogeneous catalysis.<sup>44</sup>

# Conflicts of interest

There are no conflicts to declare.

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