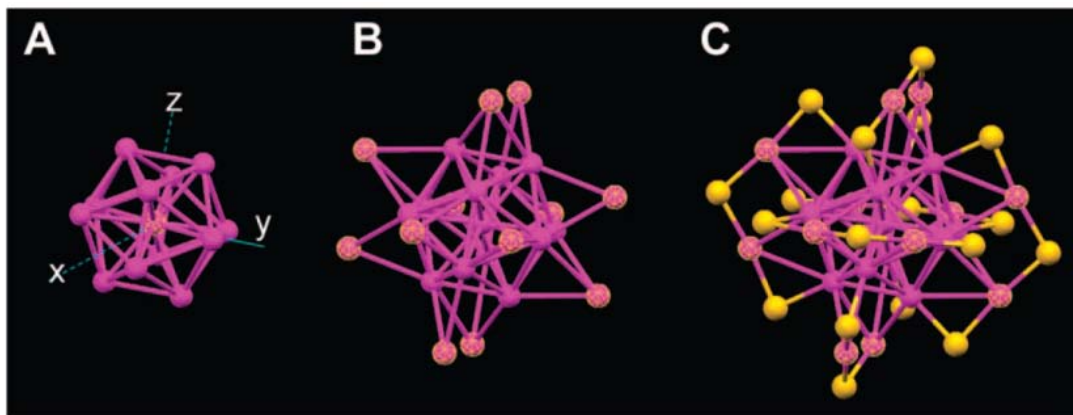


**Atomically Precise Au<sub>25</sub>(SR)<sub>18</sub> Nanoparticles as  
Catalysts for the  
Selective Hydrogenation of  $\alpha,\beta$ -Unsaturated  
Ketones and Aldehydes**

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- ❖ Gold nanoparticles - catalyst for selective oxidation and hydrogenation
- ❖ Origin of the catalytic properties –polydispersity-Observed catalytic properties reflect ensemble average.
- ❖ Polydispersity and unknown surface structure preclude the precise correlation of particle structure and electronic properties with their catalytic properties.
- ❖ Atomically precise, gold nanoparticles have been synthesized.
- ❖ Known crystal structures: correlation of particle structure with catalytic properties and an identification of catalytically active sites on the particle are possible



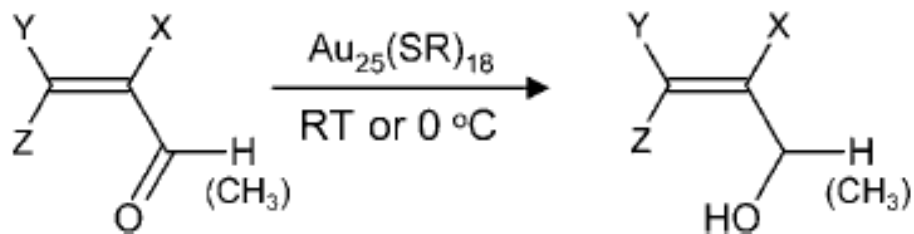
- electron-rich  $\text{Au}_{13}$  core may facilitate the adsorption and activation of the  $\text{C}=\text{O}$  bond
- owing to the low coordination, the exterior-shell Au atoms may provide a favorable environment for the adsorption and dissociation of  $\text{H}_2$ .
- $\text{Au}_{25}$  particles may be new catalysts for the hydrogenation of the  $\text{C}=\text{O}$  bond in ketones or aldehydes

$\text{Au}_{25}$  as catalyst for selective hydrogenation of  $\alpha,\beta$ -unsaturated ketone to  $\alpha,\beta$ -unsaturated alcohol  
The resulting unsaturated alcohol products are valuable intermediates for the production of perfumes and flavors.

conventional supported gold nanoparticle also act as catalysts for this reaction-side products—saturated ketones from C=C hydrogenation as well as saturated alcohols from further hydrogenation—have been reported.

In this work, ultrasmall  $\text{Au}_{25}(\text{SR})_{18}$  particles (0.97 nm metal-core diameter) can catalyze the hydrogenation of the C=O bond in  $\alpha,\beta$ -unsaturated ketone or aldehydes with 100% chemoselectivity for  $\alpha,\beta$ -unsaturated alcohols.

$\text{Au}_{25}(\text{SR})_{18}$  particles are catalytically active for hydrogenation reactions even at low temperatures (e.g.  $0^\circ\text{C}$ ), which is not possible with conventional Au nanoparticles.



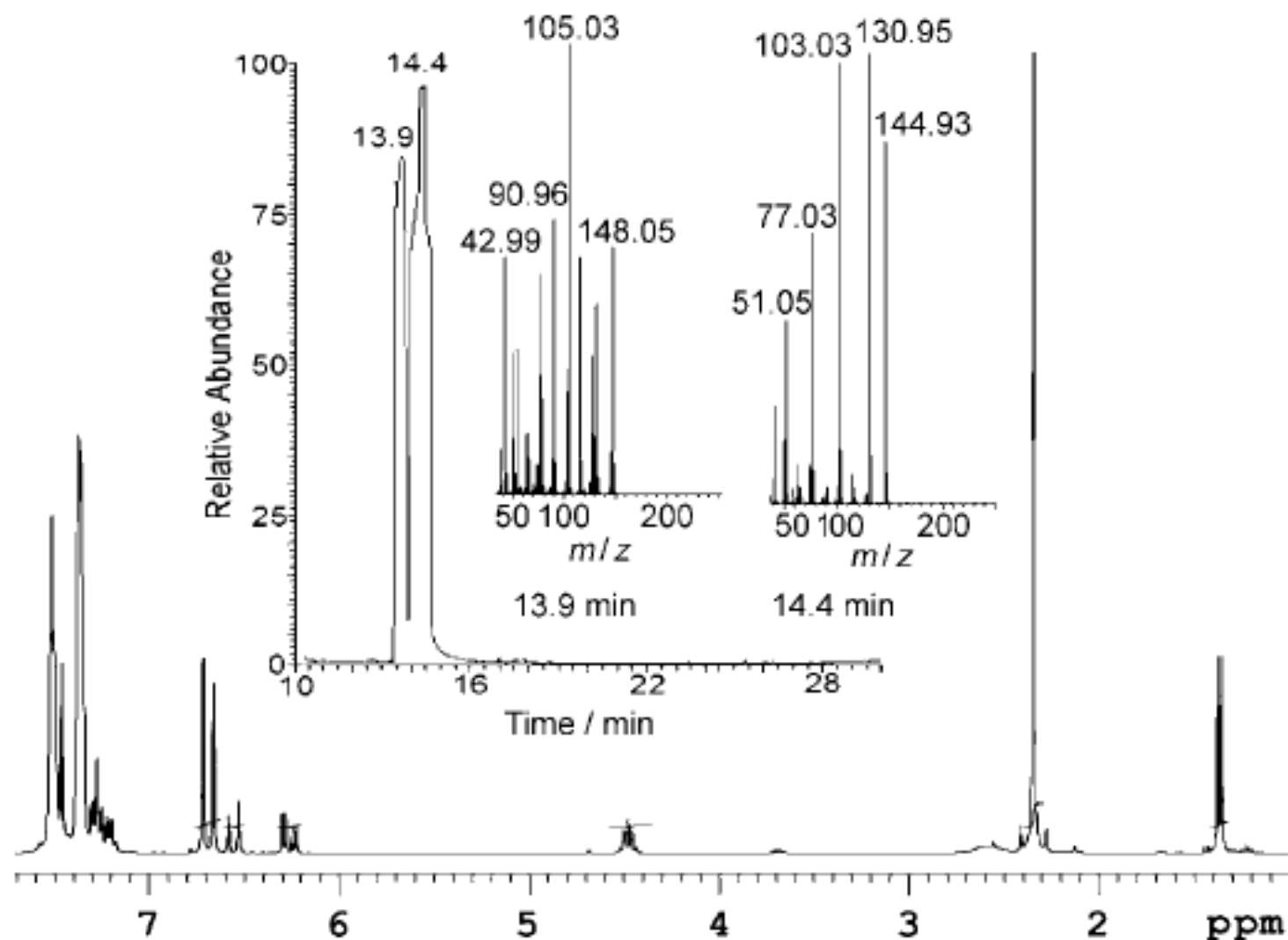
**Scheme 2.**  $\text{Au}_{25}(\text{SR})_{18}$ -catalyzed hydrogenation of a range of substituted  $\alpha,\beta$ -unsaturated ketones and aldehydes. X = H or  $\text{CH}_3$ , Y = H,  $\text{CH}_3$ , or Ph, and Z = H or  $\text{CH}_3$ .

The catalytic reaction was carried out at 08C (or room temperature) in the solution phase and initiated by introducing H<sub>2</sub> at atmospheric pressure.

Both free (unsupported) and oxide-supported Au<sub>25</sub>(SR)<sub>18</sub> catalysts were evaluated. The reaction product was analyzed by NMR spectroscopy and GC-MS. NMR analysis identified two components: the unsaturated alcohol product, and unconverted benzalacetone.

No saturated ketone or saturated alcohol product was detected by NMR spectroscopy. This is also consistent with GC-MS analysis. Only two species were detected by GC, and MS analysis shows that the first eluted species (13.9 min) has a mass signal at m/z 148 (assigned to the unsaturated alcohol), and that the residual benzalacetone (eluting at 14.4 min) shows a signal at m/z 145.

The conversion and selectivity are quantified on the basis of NMR and GC analysis. For the unsupported Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> catalyst, the conversion yield (3 h reaction time) is 22% with 100% selectivity for the unsaturated alcohol product



**Figure 1.**  $^1\text{H}$  NMR spectrum, GC trace (inset), and mass spectra (smaller insets) of the crude product arising from the hydrogenation of benzalacetone with the  $\text{Au}_{25}$  catalyst. Two species (unsaturated alcohol and residual starting material) are identified.

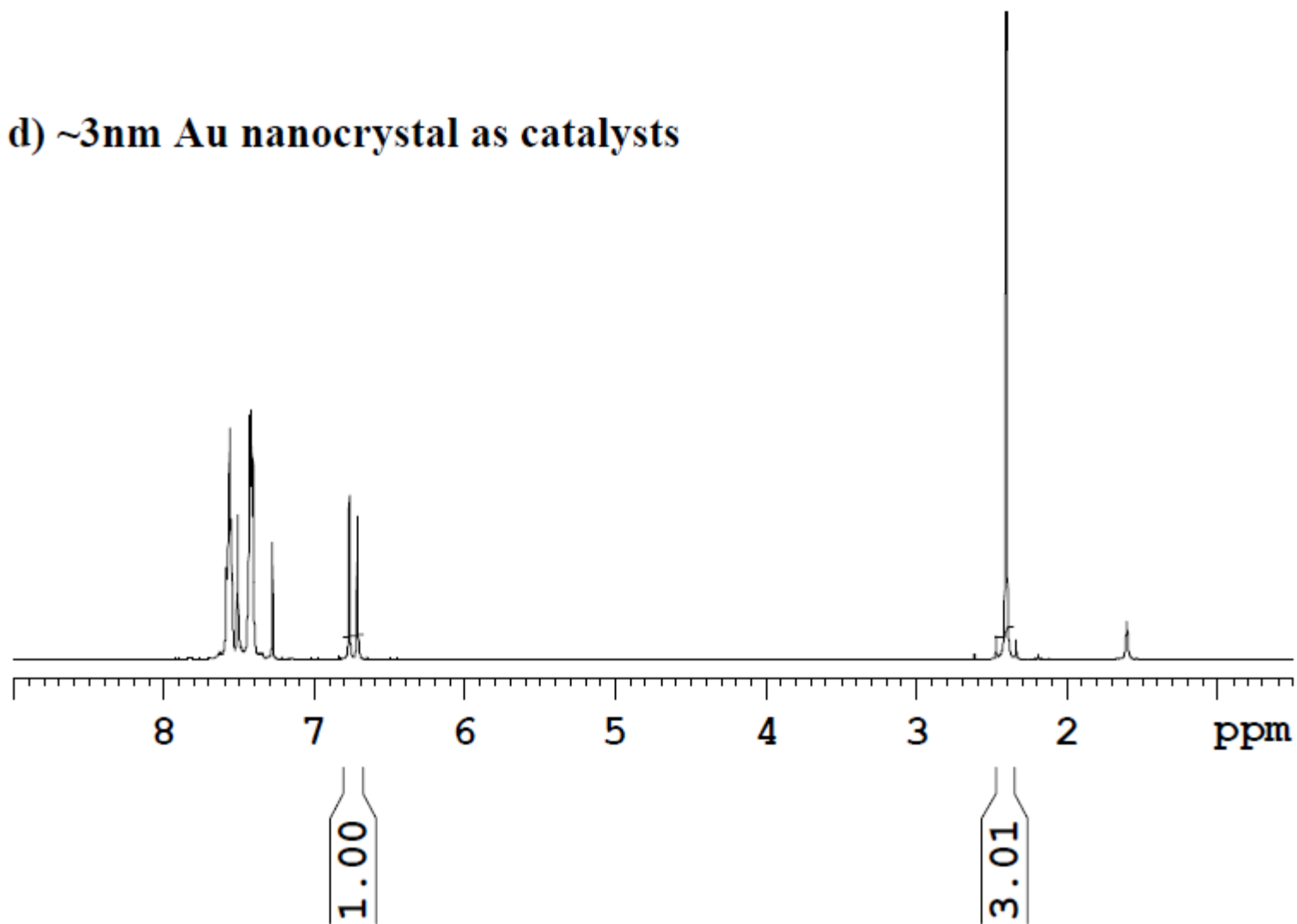
**Table 1:** The catalytic performance of Au<sub>25</sub>(SR)<sub>18</sub> catalysts for the selective hydrogenation of benzalacetone with H<sub>2</sub>.

Entry	Catalyst	Conv. [%]	Selectivity [%]		
			UA <sup>[a]</sup>	SK <sup>[b]</sup>	SA <sup>[c]</sup>
1	Au <sub>25</sub> (SCH <sub>2</sub> CH <sub>2</sub> Ph) <sub>18</sub>	22	100	0	0
2	Au <sub>25</sub> (SC <sub>12</sub> H <sub>25</sub> ) <sub>18</sub>	20	100	0	0
3	Au <sub>25</sub> (SCH <sub>2</sub> CH <sub>2</sub> Ph) <sub>18</sub> /Fe <sub>2</sub> O <sub>3</sub>	43	100	0	0
4	Au <sub>25</sub> (SCH <sub>2</sub> CH <sub>2</sub> Ph) <sub>18</sub> /TiO <sub>2</sub>	40	100	0	0
5	Au <sub>25</sub> (SCH <sub>2</sub> CH <sub>2</sub> Ph) <sub>18</sub> /SiO <sub>2</sub>	19	100	0	0
6	Au nanocrystals <sup>[d]</sup>	0	–	–	–

Reaction conditions: 1 mg Au<sub>25</sub> nanoparticle catalyst (or 100 mg oxide powder loaded with 1 % wt Au<sub>25</sub>(SR)<sub>18</sub> particles), and 0.1 mmol benzalacetone in a mixture of toluene (5 mL) and ethanol (5 mL) stirred at 0 °C for 3 h under an atmosphere of H<sub>2</sub>. [a] UA: unsaturated alcohol. [b] SK: saturated ketone. [c] SA: saturated alcohol. [d] Nanocrystals are roughly 3 nm in diameter.

- Thiolate-capped Au nanoparticles ~ 3 nm in diameter are not catalytically active.
- Extraordinary catalytic performance of ultrasmall Au<sub>25</sub>(SR)<sub>18</sub> particles, should be related to their atomic packing structure and electronic properties.
- Effect of the type of thiolate on the Au<sub>25</sub>(SR)<sub>18</sub> particles (e.g. Aromatic thiolate vs. long-chain-alkane thiolate)-no significant differences were found in terms of the conversion yield and product selectivity.

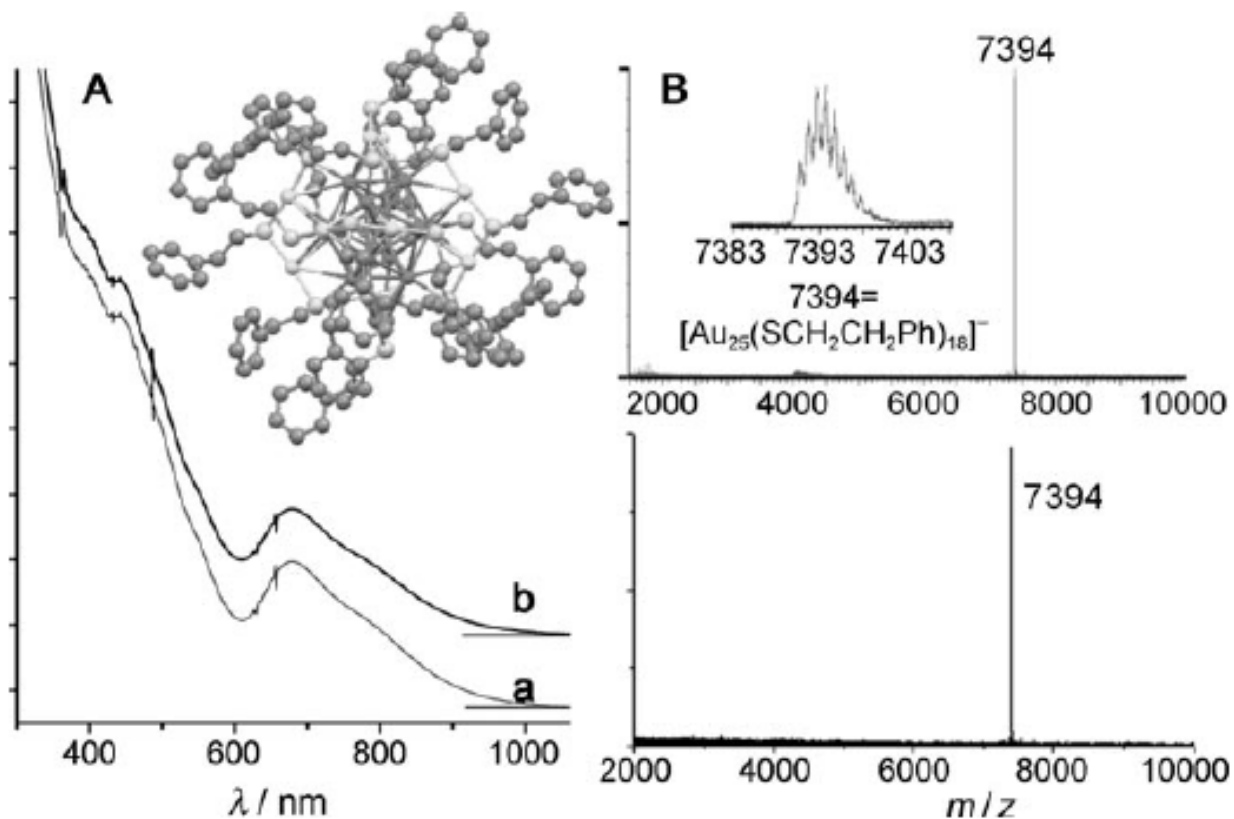
**d) ~3nm Au nanocrystal as catalysts**



- ❖ For real-world applications supported catalysts for the ease of recycling and reuse in catalytic reactions were used.
- ❖ Oxide-supported catalysts were prepared by soaking the oxide powder in a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{Au}^{25}(\text{SR})_{18}$  particles, followed by drying.
- ❖ The metal oxide (e.g.  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ) supported  $\text{Au}^{25}(\text{SR})_{18}$  catalysts show significantly higher conversion yields yet the same complete selectivity for the unsaturated alcohol.
- ❖ In contrast, the catalyst on the inert oxide support ( $\text{SiO}_2$ ) showed no enhancement in activity.
- ❖ Kinetic studies show that all the three supported catalysts provide maximum conversion at a 3 hour reaction time; the order of the reaction rate,  $\text{Au}^{25}/\text{Fe}_2\text{O}_3 > \text{Au}^{25}/\text{TiO}_2 > \text{Au}^{25}/\text{SiO}_2$ , is consistent with the order of the activity of the catalysts.
- ❖ In both free and supported catalyst systems, longer reaction times were found not to lead to any increase in the conversion indicating that an equilibrium is reached.
- ❖ When an additional benzalacetone was added to the mixture, a similar conversion (about 20% for unsupported catalysts and roughly 40% for supported catalysts) of the newly added reactants was obtained, indicating that the catalysts are not deactivated.
- ❖ Recyclability of the catalysts : six cycles



To confirm that the Au<sub>25</sub>(SR)<sub>18</sub> nanoparticles do not fragment during the catalytic reaction, the starting catalysts to those after reaction was compared by UV/Vis spectroscopy and mass spectrometry.



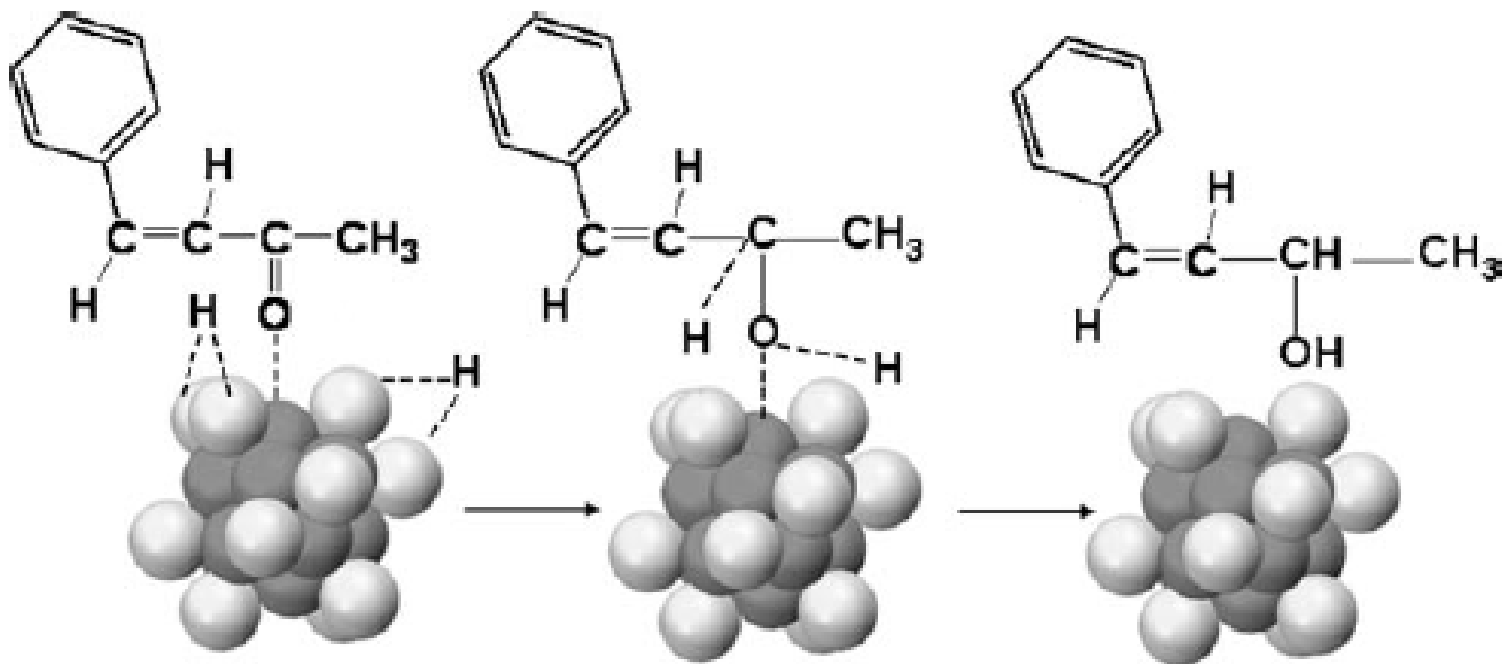
**Figure 2.** A) UV/Vis spectra of Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub> nanoparticles before (a) and after (b) the hydrogenation reaction, and b) after reaction; the inset shows the crystal structure of Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub>. B) ESI mass spectra of Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub> before reaction (upper panel) and after reaction (lower panel), respectively; The inset shows the isotope pattern of Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub>.

The catalytic properties of Au<sub>25</sub>(SR)<sub>18</sub> nanoparticles can be correlated with the particles atomic packing structure and electronic properties.

On the basis of the crystal structure of Au<sub>25</sub>(SR)<sub>18</sub> particles, a mechanism is proposed

The Au<sub>25</sub> particle possesses a core–shell structure. There are 20 triangular faces on the Au<sub>13</sub> icosahedral core. Only 12 facets are face-capped by the exterior 12Au atoms; thus, eight facets are left open.

These “hole” sites may act as active sites for C=O activation. A recent theoretical study suggests that the C=O group can coordinate to the surface atoms of Au<sub>13</sub> clusters, and charge-transfer results in a negatively charged Au<sub>13</sub> core.



**Scheme 1.** The proposed mechanism of the chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated ketone to unsaturated alcohol catalyzed by  $\text{Au}_{25}(\text{SR})_{18}$  nanoparticles. For clarity, the thiolate ligands are not shown. Dark grey: Au atoms of the core; light gray: Au atoms of the shell.

DFT calculations show a major difference in charge distribution on the Au<sub>13</sub> core and the Au<sub>12</sub> shell: the superatomic Au<sub>13</sub> core possess 8 valence electrons (1s<sup>2</sup>1p<sup>6</sup>) and is electron rich, while the exterior Au<sub>12</sub> shell is electron deficient as a result of electron transfer to sulfur of the thiolate ligand.

3 nm Au particles are crystalline with fcc packing and show a surface plasmon absorption band at 520 nm, indicating that the 3 nm gold core is already metallic, as opposed to the semiconducting Au<sub>25</sub> particles.

Discrete electronic structure of Au<sub>25</sub>(SR)<sub>18</sub> and its incomplete Au<sub>12</sub> exterior shell are responsible for the extraordinary selectivity and activity observed.

The eight uncapped Au<sub>3</sub> faces of the icosahedron should favor adsorption of the C=O group by interaction with the O atom of the C=O group in the unsaturated ketone; electron transfer between Au<sub>13</sub> and the O atom would activate the C=O bond.

Subsequently, the weakly nucleophilic hydrogen attacks the activated C=O group, leading to the unsaturated alcohol product.

Overall, the presence of the electron-rich gold core (Au<sub>13</sub>) favors the selective hydrogenation of the C=O bond over the C=C bond unsaturated ketone.

# Summary

- ❖ Catalytic capability of thiolate-stabilized, well-defined Au<sub>25</sub>(SR)<sub>18</sub> nanoparticles for the chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated ketones and aldehydes to unsaturated alcohols with complete (100%) selectivity is demonstrated.
- ❖ The core–shell structure of the Au<sub>25</sub>(SR)<sub>18</sub> particles (i.e. Au<sub>13</sub> core/Au<sub>12</sub> shell) and their unique electronic properties (i.e. electron-rich Au<sub>13</sub> core and low-coordinate (N=3) surface gold atoms) are thought to be responsible for the observed catalytic performance of Au<sub>25</sub>(SR)<sub>18</sub> nanoparticles.
- ❖ The atomically precise, ultras-small Au<sub>n</sub>(SR)<sub>m</sub> particles hold promise in their utility as a new type of gold nanocatalysts that offer high selectivity for certain reaction processes.
- ❖ An atomic-level understanding on how the crystal structure of the Au<sub>n</sub>(SR)<sub>m</sub> nanoparticles, the bonding effect of surface atoms, and the electronic properties affect the catalytic properties of gold nanoparticles will eventually aid in the design of nanocatalysts for specific reactions.