

Hydrogenation Reactions

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ZnAl-Hydrotalcite-Supported Au₂₅ Nanoclusters as Precatalysts for Chemoselective Hydrogenation of 3-Nitrostyrene

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Abstract: Chemoselective hydrogenation of 3-nitrostyrene to 3-vinylaniline is quite challenging because of competitive activation of the vinyl group and the nitro group over most supported precious-metal catalysts. A precatalyst comprised of thiolated Au₂₅ nanoclusters supported on ZnAl-hydrotalcite yielded gold catalysts of a well-controlled size (ca. 2.0 nm)even after calcination at 500°C. The catalyst showed excellent selectivity (>98%) with respect to 3-vinylaniline, and complete conversion of 3-nitrostyrene over broad reaction duration and temperature windows. This result is unprecedented for gold catalysts. In contrast to traditional catalysts, the gold catalyst is inert with respect to the vinyl group and is only active with regard to the nitro group, as demonstrated by the results of the control experiments and attenuated total reflection infrared spectra. The findings may extend to design of gold catalysts with excellent chemoselectivity for use in the synthesis of fine chemicals.

unctionalized aromatic amines are important industrial intermediates for pharmaceuticals, agrochemicals, fine chemicals, dyes, and polymers.^[1] They are generally synthesized by chemoselective hydrogenation of the corresponding functionalized nitroarenes. Previously, we developed a rationally designed FeO_x-supported Pt single-atom and pseudo singleatom catalyst and found that it showed outstanding reactivity for hydrogenation of nitro groups, while the hydrogenation of other unsaturated functional groups was unavoidable when the reaction time was prolonged and/or the temperature was raised.^[2] This is a common problem for most catalysts because they are active for the reduction of the nitro group as well as for the hydrogenation of other unsaturated functional groups (for example, C=C, C=O, and so forth) existing in the same

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molecule.^[1,3] Generally, preferential activation of the nitro group can be promoted by modifying the platinum-group metal with other metals. For example, a RhIn/SiO₂ catalyst showed good catalytic performance under mild conditions.^[4] However, activation of the C=C bond in styrene was not easy to avoid over a prolonged reaction period, according to the results of the control experiment. Moreover, preferential activation of the nitro group could also be promoted by the addition of phosphorous additives.^[5,6] But the use of harmful modifiers would be detrimental to sustainable chemistry. Herein, we try to solve this problem by developing a monometallic catalyst that only activates the nitro group instead of other unsaturated groups.

Supported Au nanocatalysts are notable for their high selectivity in many catalytic redox reactions.^[7] Nitrostyrene, bearing nitro and vinyl groups in the same molecule, is one of the most important and typical functionalized nitroarenes for fundamental investigation. Notably, chemoselective hydrogenation of the nitro group is quite demanding in nitrostyrene because of the facile hydrogenation of the C=C bond. In 2006, Corma et al^[8] first reported that Au/TiO₂ and Au/Fe₂O₃ catalysts are much more selective for hydrogenation of 3-nitrostyrene to 3-vinylaniline than Pd/C and Pt/C catalysts. When the conversion of 3-nitrostyrene attained 98.5% and 95.2%, the selectivities to 3-aminostyrene were 95.9% and 95.1% over Au/TiO₂ and Au/Fe₂O₃, respectively. However, the selectivity at complete conversion of 3-nitrostyrene was not provided. Subsequently, Matsushima et al.^[9] and Shimizu et al.^[10] found that the performance of the Au catalysts were highly dependent on the particle sizes of Au. When the Au particle sizes were decreased to 2.7 nm for Au-BP(DR)^[9] and 2.5 nm for Au/Al₂O₃,^[10] the catalysts showed better activity than that with larger sizes. Nevertheless, at complete conversion of 4-nitrostyrene, the selectivity to 4-aminostyrene obviously decreased with prolonged reaction time (for example, from ca. 90% to ca. 60% within about 4 h.^[10] Although Au catalysts possess great potential when it comes to promoting high chemoselectivity, to date, no breakthrough has been made that attains excellent chemoselectivity in conjunction with 100% conversion of nitrostyrene.

Recently, atomically precise gold nanoclusters (Au NCs) have attracted intensive interest owing to their small and uniform size.^[11] Thiolated Au₂₅ NCs are one of the most typical Au NCs that have been applied to synthesize supported Au catalysts with well-controlled size. It has been reported that the thermostability of Au NCs depends highly on the nature of the support.^[12,7f-g] However, the role of the residual S and the origin of the stability of Au NCs has not yet been clarified. To date there have been no reports on

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supported thiolated Au NCs as precatalysts for chemoselective hydrogenation of functionalized nitroarenes to aromatic amines.

Herein, we chose the thiolated Au₂₅ NCs as the precursor for synthesizing Au NCs with well-tuned size and ZnAlhydrotalcite (ZnAl-HT) as a precursor for the support used to stabilize the Au NCs against calcination. The catalyst calcined at the optimized temperatures showed excellent chemoselectivity to the 3-vinylaniline at 100% conversion of the 3-nitrostyrene in wide reaction period and temperature windows. This result is unprecedented for gold catalysts. Unlike the catalytic systems previously reported in the literature, $^{\left[1-3,13\right] }$ where the nitro group and the vinyl group were competitively adsorbed and activated, our results showed that C=C is hardly activated on our Au catalyst, leading to high chemoselectivity for hydrogenation of the nitro group. This work could provide useful methods for synthesis of Au NCs with well-controlled size, and catalyst fabrication with high chemoselectivity.

Cysteine-capped Au₂₅ (denoted as Au₂₅(Cys)₁₈) was synthesized by a NaOH-mediated NaBH₄ reduction method.^[14] The UV/Vis spectrum (Supporting Information, Figure S1) showed four peaks positioned at 440, 545, 670, and 780 nm, which suggested that the Au₂₅ NCs were successfully obtained. The as-prepared Au₂₅(Cys)₁₈ was deposited onto ZnAl-HT by an impregnation method with a Au loading of 1.1 wt %; the resulting catalysts were denoted as Au₂₅/ZnAl-HT-x (x signifies the calcination temperature). When the x values were between 300-500 °C, the catalysts showed excellent chemoselectivity (\geq 99 %) to 3-vinylaniline at 100 % conversion of 3-nitrostyrene (Figure 1). At the same time, the turnover frequency (TOF) also attained a plateau at the highest level. When the calcination temperature decreased to 200°C or increased to 600-700°C, the catalytic activity decreased correspondingly.

The Au₂₅/ZnAl-HT-300 catalyst was taken as an example to study the evolution of the product distribution during chemoselective hydrogenation of 3-nitrostyrene, as shown in Figure 2. The desired product (3-vinylaniline) presented



Figure 2. Evolution of the product distribution with reaction time over the Au₂₅/ZnAl-HT-300 catalyst.

a linear increase with reaction time, accompanied by a linearly decreasing concentration of 3-nitrostyrene. Until the substrate was completely converted, around the 200 min mark, other byproducts could hardly be detected. Even the reaction time was prolonged to 900 min with selectivity maintained at \geq 99%. Moreover, when the reaction temperature was raised from 90 to 135°C, a 98.1% selectivity to 3-vinylaniline was still attained with prolonged reaction time at complete conversion of 3-nitrostyrene (Table 1, entry 2). These results obviously show that the Au₂₅/ZnAl-HT-300 catalyst favored hydrogenation of the nitro group instead of the C=C bond. In contrast, severe over-hydrogenation of 3-nitrostyrene to 3-ethylphenylamine over the Au/TiO₂ catalyst (provided by the World Gold Council (WGC)) happened under the same reaction conditions (Table 1, entry 3,4). The chemoselectivity of our catalyst far exceeded those of supported Pt or Pd catalysts (Table 1, entry 5-7) when the conversion of the substrates was close to 100%. Although the rationally designed Ag@CeO₂ system could achieve high selectivity at complete conversion of the nitro compounds bearing C=C



Figure 1. The conversion, selectivity, and TOF values (line) over the Au₂₅/ZnAl-HT catalysts calcined at different temperatures. Reaction conditions: 3-nitrostyrene (0.4 mmol); Au catalyst (0.7 mol%); temperature 90°C; H₂ pressure (10 atm); reaction time 4 h. The TOF value was measured below 20% conversion.

Table 1: Hydrogenation of 3-nitrostyrene using different catalysts.



[a] Reaction conditions: 3-nitrostyrene (0.4 mmol), Au catalyst (0.7 mol%), reaction time 9 h, H₂ pressure (10 atm), [b] catalysts were provided by the WGC; [c] Reference [1b]; [d] Reference [8]; [e] determined by GC.

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bonds,^[15] the TOF value was much lower than that of our Au catalyst (5.2 h^{-1} vs. 69.2 h^{-1}).

To confirm this result, control experiments were conducted using an artificial mixture of nitrobenzene and styrene as the substrates (Supporting Information, Scheme S1). Over the Au₂₅/ZnAl-HT-300 catalyst, and even though the reaction temperature was raised to 135°C, styrene was hardly converted over a prolonged reaction period, while the nitrobenzene was completely converted to aminobenzene. On the contrary, styrene can be readily hydrogenated (64.1%) over a Au/TiO₂ (WGC) catalyst under the same reaction conditions. Both the nitro and vinyl groups can adsorb on the Au/TiO₂ catalyst, as reported by Corma et al. previously,^[13a] while the nitro group competed more favorably with adsorption of the vinyl group. Hence the C=C bond would be hydrogenated when the -NO2 group was approaching complete conversion. However, the nitro group and the vinyl group were not competitively adsorbed and activated on the surface of the Au₂₅/ZnAl-HT-300 catalyst; instead, only the nitro group could be activated while the vinyl group could not. This led to high chemoselectivity for hydrogenation of the nitro group over our Au catalyst.

Further evidence for inertness to the vinyl group over our catalyst was provided by attenuated total reflection infrared spectra (ATR-IR) spectroscopy results, as shown in Figure S2 (Supporting Information); the asymmetric $v_{as}(NO_2)$ and symmetric $v_s(NO_2)$ IR vibration frequencies at 1526 and 1348 cm⁻¹ were observed when nitrobenzene was used as the

substrate. When nitrostyrene was applied as the only probe molecule, the IR bands at 1531 and 1350 cm⁻¹, attributed to v_{as} -(NO₂) and

 $v_s(NO_2)$,^[10,13a] clearly appeared while none of the vibrations of the vinyl group were observed. Further styrene adsorption experiments implied no v(C=C) was present (1630 cm⁻¹), and δ (=C-H) vibrations at 1416 cm⁻¹ appeared, which suggested that the surface of our catalyst could adsorb the nitro group rather than the vinyl group. Consistent with this result, after five reaction cycles over the Au₂₅/ ZnAl-HT-300 catalyst at 90°C the selectivity to 3-vinylaniline remained at \geq 99% when the conversion of 3-nitrostyrene was 100% (Supporting Information, Figure S3). Furthermore, we also applied the Au₂₅/ZnAl-HT-300 catalyst to other substrates (Supporting Information, Table S1) and found that it worked well for the hydrogenation of -NO2 with a wide scope of substrates. The above results indicated that the Au₂₅/ZnAl-HT-300 catalyst was capable of catalyzing the chemoselective hydrogenation of the functionalized nitroarenes to aromatic amines with high chemoselectivity.

The high-angle annular dark-field scanning transmission electron microscope

(HAADF-STEM) images clearly showed the distribution of Au particles on the Au25/ZnAl-HT catalyst calcined at different temperatures (Figure 3; Supporting Information, Figure S4). More than 500 Au particles in arbitrarily selected areas were measured for each sample. The Au NCs of the Au₂₅/ZnAl-HT catalyst before calcination were uniformly dispersed on the support with a mean diameter of 1.4 nm (Figure 3a). When the samples were calcined in a temperature range from 300 to 500°C, the average particle diameter grew slightly from 1.7 to 2.0 nm (Figure 3b; Supporting Information, Figure S4b,c). Even when the calcination temperature was raised to 600 °C, the particle diameter was increased only to 2.6 nm (Figure 3 c). The space lattice of Au (111) is 2.39 Å, which is very close to that of the support (101) with a space lattice of 2.44 Å (Figure 3d). This meant there was epitaxial interaction between Au and the support,^[16] which helped to enhance the thermostability of the Au NCs. This result was also in good agreement with the X-ray diffraction (XRD; Supporting Information, Figure S5) and UV/Vis (Supporting Information, Figure S6) measurements, indicating that Au₂₅- $(Cys)_{18}$ is a good precursor for controlling the particle sizes of the Au catalyst. When the calcination temperature was further raised to 700 °C, the average particle diameter of Au grew to 4.5 nm (Supporting Information, Figure S4d). Correspondingly, the catalytic activity dropped sharply (Figure 1). Thus, we speculated that the diameter of Au NCs was one of the most important factors that influence the catalytic activity of the Au₂₅/ZnAl-HT-x catalysts.



Figure 3. HAADF-STEM images of the catalysts: a) $Au_{25}/ZnAl-HT$; b) $Au_{25}/ZnAl-HT-300$; c-d) $Au_{25}/ZnAl-HT-600$.

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Because of the strong coordination between Au and S, it is difficult to remove S, which is thought to be poisonous to catalytically active sites.^[17] However, Jin et al. found that supported/unsupported Au NCs with specific amounts of Au atoms protected by S-containing ligands can perform catalysis directly.^[11c] The role of the protecting agents of the thiolated Au NCs is still controversial in the relevant literature. Herein, we studied the influence of organic ligands in the Au₂₅/ZnAl-HT catalyst on the catalytic performance. When we applied the Au₂₅/ZnAl-HT catalyst without calcination to the chemoselective hydrogenation of 3-nitrostyrene, no reactant was converted, which indicated that the organic ligands of $Au_{25}(Cys)_{18}$ might be detrimental to the reaction. At this time, the X-ray photoelectron spectroscopy (XPS) results showed that the binding energy (BE) of the Au $4f_{7/2}$ was 84.4 eV, indicating that Au was positively charged because of the interaction between Au and the thiol ligand (Supporting Information, Figure S7).^[12] Subsequently, we calcined the Au₂₅/ZnAl-HT catalyst at different temperatures from 200 to 700 °C. The BE of Au $4f_{7/2}$ decreased gradually with increasing temperature. After calcination at 300°C, the BE of Au $4f_{7/2}$ decreased to 83.6 eV, close to that of the final state 83.4 eV, which suggested that the thiol ligands on the surface of Au NCs were removed and the Au atoms on the surface were reduced to a metallic state.

However, according to thermogravimetric analysis (TGA) of Au₂₅(Cys)₁₈ (Supporting Information, Figure S8), the organic ligands were not removed completely between 300 to 500°C. It seems that the residual ligands did not suppress the catalytic activity after calcination in this temperature range. When the temperature increased to 600 °C most of the protecting agents were removed, while the activity of Au₂₅/ZnAl-HT-600 began to decrease (Figure 1). At 700 °C, the weight loss of Au₂₅(Cys)₁₈ reached 20.3%. At this time, both the activity and selectivity of $Au_{25}/ZnAl$ -HT-700 decreased dramatically. The above results indicate that the protecting agents, which are detrimental to the reaction on the surface of the Au NCs, might be removed preferentially with increased calcination temperature, as also suggested by the XPS results. Ligands that are relatively difficult to eliminate might position underneath the Au NCs interacting with the support and thus play a key role in stabilizing the Au NCs and promoting catalytic reactivity.

To further test the interaction of the residual organic ligands with Au, we studied the local coordination environment of Au by X-ray absorption spectroscopy (XAS). To obtain good signal-to-noise ratios, we increased the loading of Au to 9.2 wt %. The extended X-ray absorption fine structure (EXAFS) data fitting results are shown in Table S2 and Figures S9 and S10 (Supporting Information). Before calcination, neighboring Au atoms were observed at 2.77 and 2.97 Å with the coordination numbers (CN) 1.9 and 1.8, respectively. The Au-S interaction was the nearest neighbor of Au at 2.30 Å with a CN equal to 1.4. The data reflects a typical structure for thiolated Au₂₅ NC.^[12,18] When the calcination temperature was raised from 200 to 500°C, the CN of the Au-S bond decreased from 0.9 to 0.1, which suggested some residual protecting ligands were still present even after calcination at 500 °C. This characteristic also manifested in the mapping results (Supporting Information, Figure S11). Because the Zn^{2+} ion also prefers to interact with S rather than O,^[19] Au-S-Zn moieties may form, which enhance the interaction between Au and the support and promote the thermal stability of the Au NCs.

It is reported that the nitro group can be easily adsorbed on a basic surface.^[20] But the activity of the hydrogenation of the nitro group would be suppressed if the basicity of the surface was too strong (for example, MgO, MgAl-HT, and so forth). In contrast, the basic and acidic sites over the surface of Al₂O₃ could potentially promote the activation of the reactants.^[10] Herein, relatively weak basicity and acidity provided by ZnAl-HT-300-500 supports might play an important role in the selective hydrogenation of the nitro group. As was demonstrated by the ATR-IR result in Figure S12 (Supporting Information), ZnAl-HT calcined at 300 and 500 °C without deposition of Au adsorbed the nitro group instead of C=C. But the blank experiment showed that the support was not active for the hydrogenation of 3-nitrostyrene. This result indicated that the support itself could not catalyze the reaction. The active sites might be positioned at the perimeter between Au NCs and the support. Au atoms with low coordination numbers could activate hydrogen according to DFT calculations.^[13a] Herein, the activation of hydrogen might be highly dependent on Au NCs with a well-controlled size. Thus, the nitro group of 3-nitrostyrene adsorbed on the support could be activated and hydrogenated at the interfaces.

In summary, using a ZnAl-HT supported $Au_{25}(Cys)_{18}$ as a precatalyst we have obtained Au nanocatalysts blessed by useful performance: they were active only for the hydrogenation of the -NO₂ group but inert with respect to the C=C bond over wide reaction duration and temperature windows. The inertness of the catalyst to the C=C bond was verified by control experiments and ATR-IR results. The residual S and the epitaxial interaction between Au and the support contributed to high thermostability of Au NCs. The results of this study will inspire the design of efficient Au catalysts for the synthesis of fine chemicals.

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Conflict of interest

The authors declare no conflict of interest.

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ZnAl-Hydrotalcite-Supported Au₂₅ Nanoclusters as Precatalysts for Chemoselective Hydrogenation of 3-Nitrostyrene



Size-controlled gold nanocatalysts were prepared from a ZnAl-hydrotalcite-supported thiolated Au₂₅ precatalyst. Residual sulfur and epitaxial interactions between gold and the support stabilized the catalyst against high-temperature calcination, promoting complete conversion of 3-nitrostyrene into 3-aminostyrene with high selectivity for the nitro group.

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