

Supporting Information

Reversible Control of Chemoselectivity in Au₃₈(SR)₂₄ Nanocluster-Catalyzed Transfer Hydrogenation of Nitrobenzaldehyde Derivatives

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Experimental

Synthesis of Au₂₅(SR)₁₈ nanoclusters: Au₂₅(SR)₁₈ nanoclusters were prepared according to a kinetically controlled method.^{s1} Briefly, 0.4 mmol HAuCl₄·3H₂O (dissolved in 5 mL nanopure water) was combined with a toluene solution of tetraoctylammonium bromide (0.48 mmol) in a 25 mL round bottom flask. The aqueous was removed by a syringe after the solution was vigorously stirred for 15 min. Then, phenylethanethiol (1.2 mmol) was added to the flask and the solution was stirred at a very low speed. After it turned to clear, 4 mmol NaBH₄ dissolved in 10 mL cold nanopure water was quickly added all at once. After aging overnight, methanol was added to separate the nanoclusters from TOAB and side-products. The Au₂₅(SR)₁₈ nanoclusters were collected after removing the supernatant.

Synthesis of Au₃₈(SR)₂₄ nanoclusters: Au₃₈(SR)₂₄ nanoclusters were made following the previously reported size-focusing method.^{s2} In a typical experiment, 0.5 mmol HAuCl₄·3H₂O and 2.0 mmol glutathione (GSH) were mixed in 20 mL acetone at room temperature under vigorous stirring, and then the solution was cooled to 0 °C. After 20 min, 6 mL cold nanopure water containing 5 mmol NaBH₄ was rapidly added to the suspension under vigorous stirring. The solution immediately turned black. After about 20 min, the clear acetone phase was discarded. Finally, the Au_n(SG)_m clusters solution was extracted by adding 6 mL water. For the size-focusing step, the above solution was mixed with 0.3 mL ethanol, 2 mL toluene and 2 mL phenylethanethiol. The diphasic solution was heated to 80 °C and maintained at this temperature for 40 h. The organic phase was washed with methanol and then Au₃₈(SR)₂₄ nanoclusters were separated from the precipitant by extraction with dichloromethane.

Synthesis of Au₅₂(SR)₃₂ nanoclusters: Au₅₂(SR)₃₂ nanoclusters were prepared following the previously reported method.^{s3} Briefly, 0.24 mmol HAuCl₄·3H₂O and 1.12 mmol HNO₃ dissolved in 0.075 mL nanopure water were added to 15 mL tetrahydrofuran containing 0.36 mmol tetraoctylammonium bromide. 2.93 mmol phenylethanethiol was added to the above solution after it was stirred for 15 min. The solution was stirred at a constant speed (900 rpm) until it turned to be colorless, and immediately a freshly made cold aqueous solution of NaBH₄ (3.36 mmol) was added. After aging overnight, the indissolvable was removed and the solution was concentrated. After cold water was added, the precipitates were collected and washed with methanol. Finally the Au₅₂(SR)₃₂ nanoclusters were isolated from the crude by the thin layer chromatography using CH₂Cl₂-petroleum ether as a developing solvent.

Synthesis of Au₁₄₄(SR)₆₀ nanoclusters: Au₁₄₄(SR)₆₀ nanoclusters were also obtained using the size-focusing method.^{s4} Briefly, 0.45 mmol HAuCl₄·3H₂O dissolved in 5 mL nanopure water and 0.52 mmol tetraoctylammonium bromide dissolved in 10 mL toluene were combined and vigorously stirred in a 25 mL round bottom flask. The aqueous layer was removed by a syringe and the toluene phase was cooled to 0 °C. Phenylethanethiol (1.35 mmol) was added to the flask under fast stirring. After it turned to clear, 5 mL cold nanopure water containing 4.5 mmol NaBH₄ was quickly added all at once. The solution turned immediately black and was stirred for 24 h. The black toluene solution was dried by rotary evaporation before methanol was added to separate Au nanoclusters (size mixed) from TOAB

and side-products. For the size-focusing step, 0.5-0.8 mL phenylethanethiol was added to 1 mL toluene containing 20 mg Au nanoclusters of mixed sizes, and the above solution was heated to 80 °C and maintained at 80 °C for 40 h under stirring. Methanol was added to precipitate the Au nanoclusters. The Au₁₄₄(SR)₆₀ nanoclusters was separated and obtained by extraction with dichloromethane.

Preparation of Au_n(SR)_m/oxide catalysts: Au_n(SR)_m/oxide catalysts were prepared by adding 500 mg oxide powder to 15 ml of dichloromethane containing 5 mg Au_n(SR)_m nanoclusters and then stirring at room temperature until complete evaporation of the solvent. The remaining solid was dried at 150 °C for 1.0 h under vacuum.

Preparation of NiAl-layered double hydroxide (NiAl-LDH): NiAl-LDH was prepared by a co-precipitation method as described in the literature.^{s5} A mixed aqueous solution of nickel nitrate and aluminum nitrate with a certain molar ratio of Ni to Al, and an aqueous NaOH solution were separately added to 50 mL distilled water under vigorous stirring. The pH of the solution was controlled at ~9.5 during the process. The resultant gel-like material was transferred to an autoclave and aged at 100 °C for 24 h. After washing with H₂O, an aqueous Na₂CO₃ solution was added to the slurry and stirred at 100 °C for 2 h. Finally, NiAl-LDH was obtained after being filtration, washing and drying.

Preparation of Au/NiAl-oxide catalysts: The Au/NiAl-oxide catalyst was prepared by the deposition-precipitation method. In a typical synthesis, 2.5 mL HAuCl₄ aqueous solution (0.024 mmol/L) was added to a suspension containing 1.00 g of NiAl-LDH under vigorous stirring. Then, 1 mol/L of NaOH solution was used to adjust the pH value to 10 and the reaction was allowed to proceed at room temperature for 6 h. Then, a solid was achieved after filtering, washing and drying. Finally, the solid was calcined at 400 °C for 2 h with a heating rate of 5 °C/min.

Characterizations: UV-Vis-NIR spectra of the samples were acquired on a UV-3600 with UV-VIS-NIR spectrophotometer (Shimadzu) at room temperature. Transmission electron microscopy (TEM) imaging of Au₃₈(SR)₂₄ nanoclusters was performed on a JEOL JEM-2000EX TEM operated at 200 kV. XAS measurements were performed at room temperature using the Sector 20-BM beamline of the Advanced Photon Source at Argonne National Laboratory. The end-station was equipped with a double-crystal Si(111) monochromator for wavelength selection. X-ray fluorescence yield XAS was employed using a 12-element Ge fluorescence detector to collect the data. Data processing was performed using the WinXAS software following the standard procedure. The product analysis of the control reaction was determined on A91 (GC) and Thermo Fisher-Exactive Orbitrap (HPLC-ESI-MS). Scanning transmission electron microscope (STEM) images were performed on a JEOL JEM2100F S/TEM in high-angle annular dark-field STEM mode at an operating voltage of 200 kV.

Evaluation of the catalytic performance: In a typical selective hydrogenation reaction, 4-nitrobenzaldehyde (0.05 mmol), potassium formate (0.25mmol), Au_n(SR)_m/oxide (100.0

mg, 1 wt % loading of nanoclusters) and H₂O (1.0 mL) were added to a reactor (Parr instrument company, series 4700, 22 mL capacity). The reaction mixture was kept at designated temperature as shown in Table 1. After the reaction, the mixture was extracted with ethyl acetate and then the crude product was obtained after the removal of the solvent. The conversion of 4-nitrobenzaldehyde and selectivity for 4-nitrobenzyl alcohol were determined by ¹HNMR (300 MHz) spectroscopic analysis.

The control experiment: 0.8 mmol 4-nitrobenzaldehyde, 5mL toluene and 0.1 g 0.1%Au/NiAl-oxide were added to a high-pressured reactor. Under vigorous stirring, the hydrogenation was carried out at 100 °C under the pressure of 10 atm H₂ for 4 h. After Au catalysts being separated by centrifugation, the chemical composition of the reaction solution was analyzed by ESI-MS and GC.

Evaluation for the selectivity for the use of HCOOK. To test the selectivity for the use of HCOOK, we have performed the following experiment. Reaction conditions: 60.0 mL pressured autoclave, 0.065 mmol 4-nitrobenzaldehyde, 0.25 mmol HCOOK, 0.1 g Au₃₈(SR)₂₅/CeO₂, 1.0 mL H₂O, 1.0 MPa Ar (0.0245 mol), 90 °C, 12 h. A 66% conversion of 4-nitrobenzaldehyde and ~100% selectivity to 4-nitrobenzyl alcohol were obtained according to our GC analysis. The molar amount of consumed 4-nitrobenzaldehyde was 0.0429 mmol. The GC peak area of as-generated H₂ (t=2.113 min, see Figure S11 below) was 1036.85, whereas the peak area of Ar (t=2.387 min) was 46097.95 (N₂ was employed as a carrier gas), determined by GC with TCD. According to the previous results, we calculated/obtained the relative molar correction coefficient for Ar to H₂ was 2.96. Based on the internal standard method (Ar as an internal standard substance), the molar amount of H₂ was 0.186 mmol. According to the references (*Chem. Eur. J.* 2009, 15, 11833-11836; *Catal. Lett.* 2016, 146, 1331-1339), the true selectivity for the use of HCOOK in the transfer hydrogenation was: $0.0429 \times 100 / (0.0429 + 0.186) = 18.7\%$, while the theoretical selectivity was: $0.0429 \times 100 / 0.25 = 17.2\%$.

Internal standard experiment: 4-nitrobenzaldehyde (0.05 mmol), o-xylene (0.04mmol), potassium formate (0.25mmol), Au_n(SR)_m/CeO₂ (100.0 mg, 1 wt % loading of nanoclusters) and H₂O (1.0 mL) were added to a high-pressured reactor. The reaction was carried out at 100 °C for 12 h. After the reaction, the mixture was extracted with ethyl acetate and obtained by centrifugation. The conversion of 4-nitrobenzaldehyde and selectivity for 4-nitrobenzyl alcohol were determined by GC.

Supporting Figures S1-10 and Table S1:

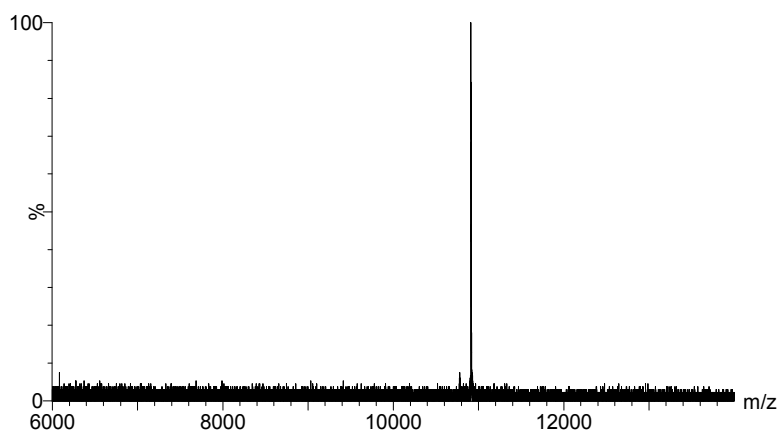


Figure S1. Electrospray mass spectrum of $\text{Au}_{38}(\text{SR})_{24}$ in solution (mono-caesium adduct).

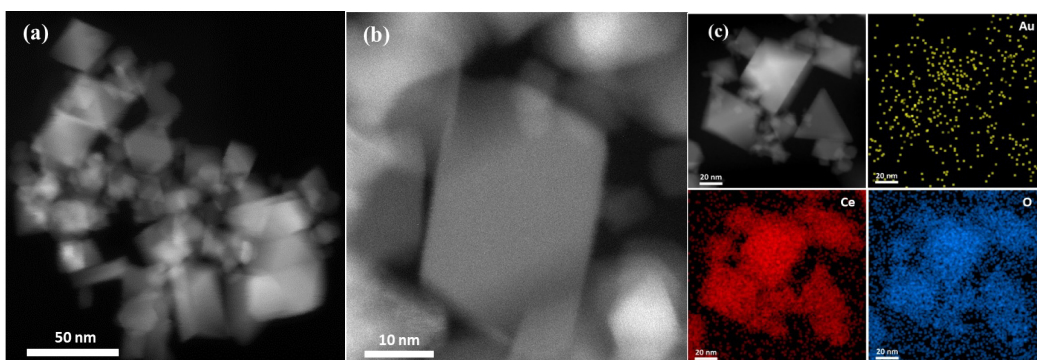


Figure S2. (a-b) Representative HAADF-STEM images of $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ before reaction; (c) HAADF-STEM image and the corresponding element maps showing Au (yellow), Ce (red), and O (blue).

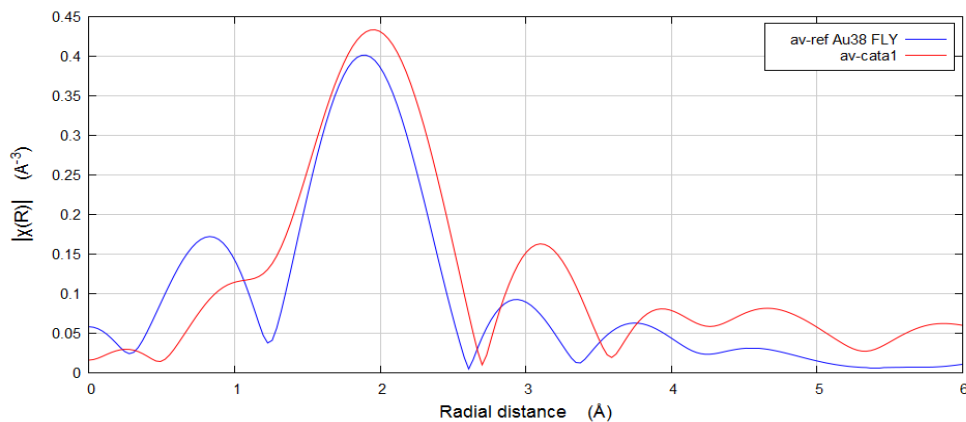


Figure S3. EXAFS spectra of unsupported $\text{Au}_{38}(\text{SR})_{24}$ (in blue) and $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ (in red) catalysts after the thermal treatment at 150 °C.

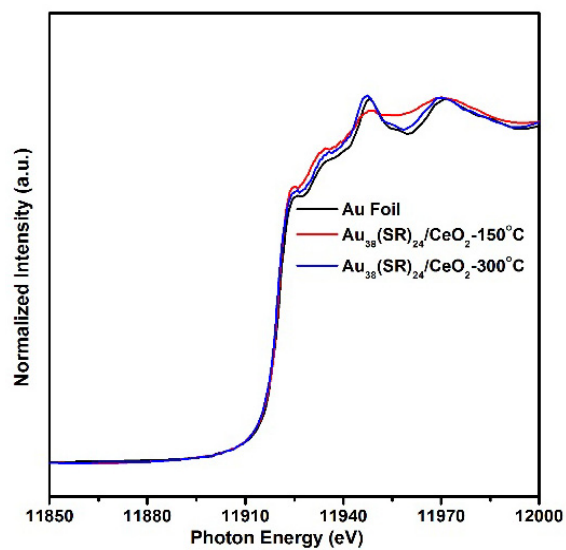


Figure S4. Normalized Au L3-edge XANES spectra of the $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ catalysts after the thermal treatment at 150 °C and 300 °C.

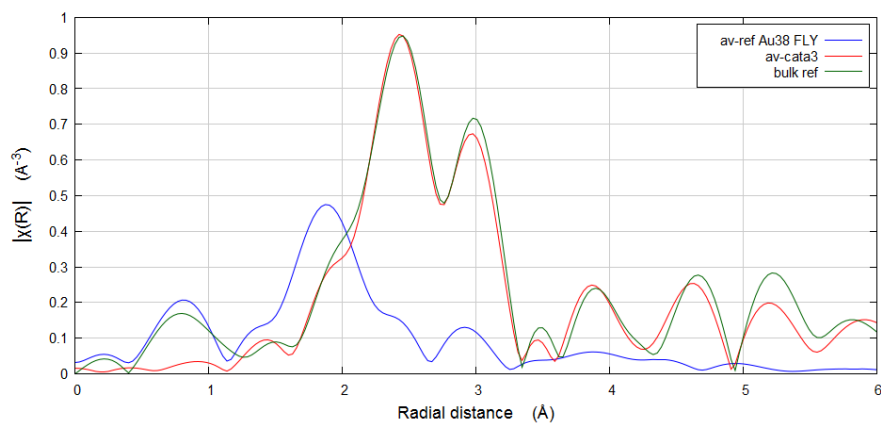


Figure S5. EXAFS spectra of bulk Au (in green), $\text{Au}_{38}(\text{SR})_{24}$ (in blue) and $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ (in red) catalysts after the thermal treatment at 300 °C.

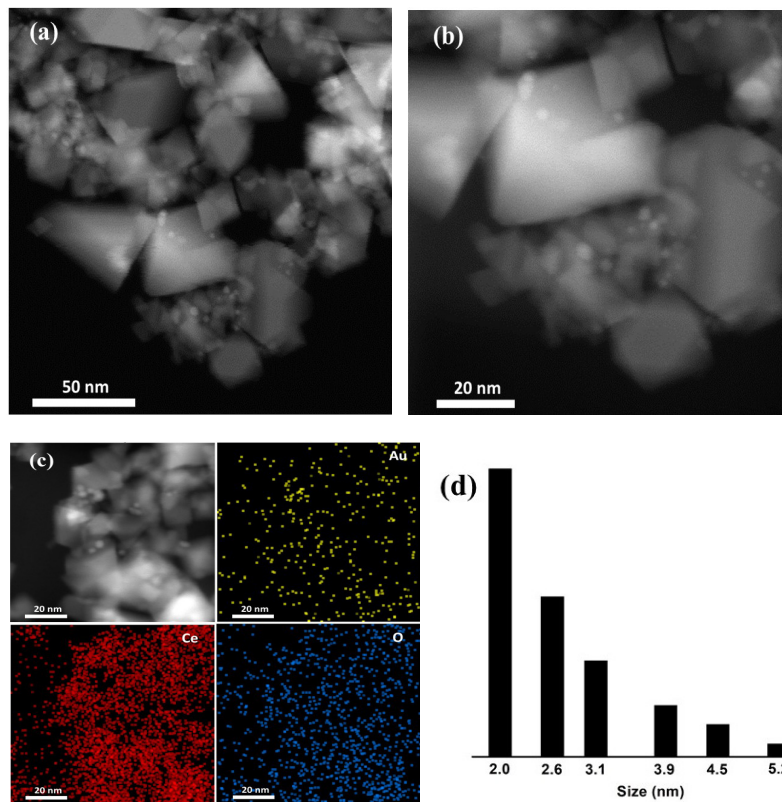


Figure S6. (a), (b) Representative HAADF-STEM images of $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ after ligand removal; (c) HAADF-STEM image and the corresponding element maps showing Au (yellow), Ce (red), and O (blue); (d) The size distribution of ligand-off gold nanoclusters.

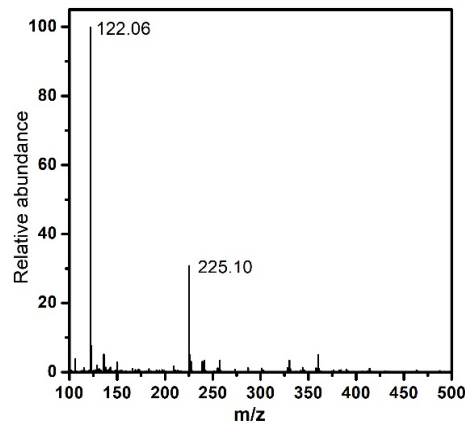


Figure S7. ESI-MS spectrum of the reaction solution.

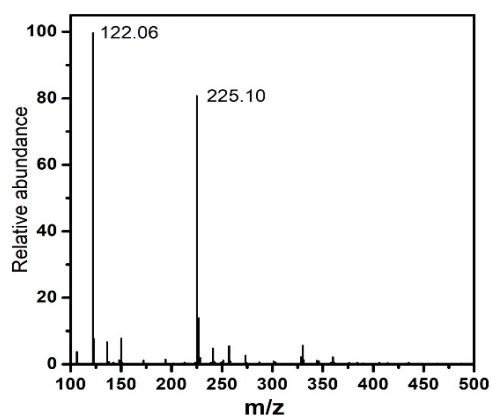


Figure S8. ESI-MS spectrum of the reaction solution after it is allowed to stand for about 8 h at r.t.

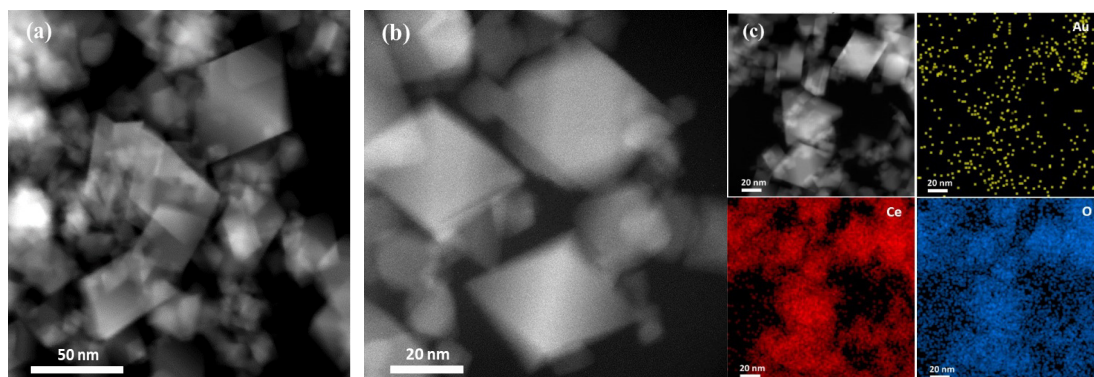


Figure S9. (a), (b) Representative HAADF-STEM images of $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ after reaction; (c) HAADF-TEM image and the corresponding element maps showing Au (yellow), Ce (red), and O (blue).

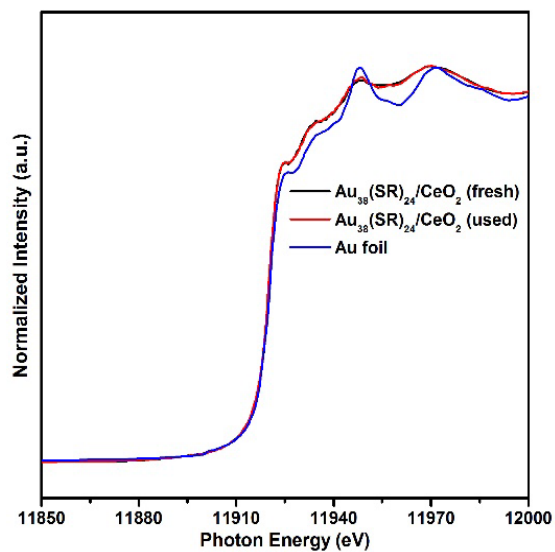


Figure S10. Normalized Au L_3 -edge XANES spectra of the fresh and the used $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$.

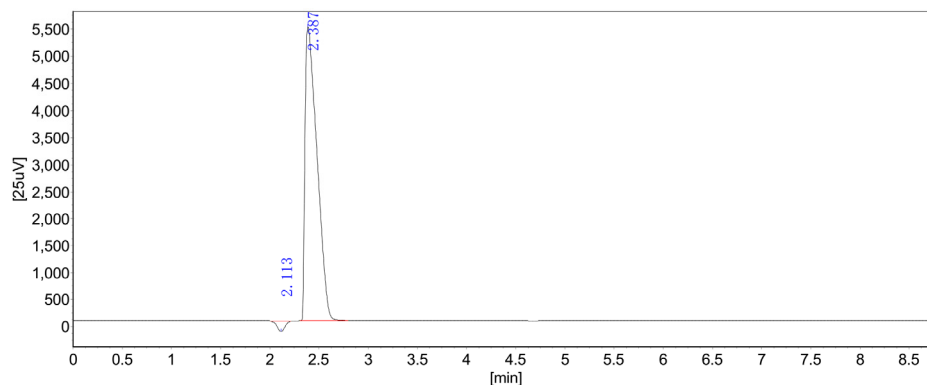


Figure S11. The gas chromatogram of the gas mixture after the hydrogenation.

Table S1. Comparison of the activity based on the turnover frequency ^a

Nanoclusters ^b	MW	Mol (nmol)	Exposed Au atoms (based on X-ray structure, surface & sub-surf.)	Molar amount of exposed Au atoms (surface & sub-surf., nmol)	Conv.(%) ^c	TOF, h ⁻¹
Au ₂₅ (SR) ₁₈	7842	127	24	3048	41.7	0.57
Au ₃₈ (SR) ₂₄	10754	93	36	3348	86.7	1.08
Au ₅₂ (SR) ₃₂	14601	68	46	3128	53.2	0.71

[a] Reaction conditions: 100 mg Au_n(SR)_m/oxide (1 wt % loading), 1 mL H₂O, 0.05 mmol 4-nitrobenzaldehyde, 0.25 mmol HCOOK, 80 °C, 12h.

[b] SR=SCH₂CH₂Ph, counter ion=N(C₈H₁₇)₄⁺.

[c] The conversion of 4-nitrobenzaldehyde was determined by ¹H-NMR analysis.

Supporting References

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