Electronic Supporting Information

NHC-Ligated gold nanoparticles derived from cluster

precursors for carbon monoxide oxidation reactions

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Experimental

Materials and reagents

NHC-1 (1,3-dimesityl-4,5-dihydro-1H-imidazol-3-ium chloride), NHC-2 (1,3-dimesityl-1H-imidazol-3-ium chloride) and NHC-3 (1,3-diisopropyl-1H-imidazol-3-ium chloride) were procured from Bidepharm. Chloroauric acid and ceria nanospheres (CeO₂) were obtained from Macklin. The [(AuNHC-n)₃O]BF₄ (n = 1, 2 and 3) clusters were synthesized according to the reported work.^[1] All other reagents and experimental equipment were sourced from commercial suppliers.

Measurements

High-resolution electrospray ionization mass spectra (ESI-MS) were obtained using an AB Sciex X500R Q-TOF spectrometer, with simulations conducted using the opensource Isotope Pattern software for Mass Spectrometry. Powder X-ray diffraction (PXRD) patterns were acquired using a Rigaku MiniFlex diffractometer equipped with Cu-K α radiation ($\lambda = 1.54178$ Å). Bruker 400 Avance NMR spectrometer was used to collect the nuclear magnetic resonance (NMR) data. Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) absorption spectra were recorded on a Bio-Logic MOS-500 multifunctional circular dichroism spectrometer. Thermogravimetric analysis (TGA) of the synthesized clusters was performed from ambient temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere using a TA Instruments SDT 2960 thermal analyzer. Transmission electron microscopy (TEM) images were captured using a FEI Talos F200X microscope. In situ Fourier transform infrared (FT-IR) spectra were recorded on a Bruker INVENIO-S spectrometer. The Fourier transforms infrared (FT-IR) spectrum was recorded on a Bruker ALPHA II FT-IR spectrometer in the range of 400-4000 cm⁻¹ with KBr pellets. The detection of CO and CO_2 was achieved via gas chromatography (GC).

Loading gold NCs on CeO₂ supports

The preparation of CeO₂-supported Au catalysts involved the following steps: 15.0 mg of $[(AuNHC-n)_3O]BF_4$ clusters (n = 1, 2, 3) were weighed and dissolved in 0.5 mL of a mixed solvent with a volume ratio of methanol (CH₃OH) to N,N-dimethylformamide (DMF) of 2:3. Subsequently, 1.0 g of CeO₂ was added to the solution, followed by ultrasonication to ensure uniform dispersion of the clusters on the support. The resulting mixtures were allowed to stand for 12 hours and then dried at 50 °C for 12 hours to remove residual solvents and moisture.

Preparation of CeO₂-supported Au NPs catalysts

100 mg samples of the CeO₂-supported gold catalysts were loaded into a straight quartz tube with a narrowed middle section and secured with quartz wool. The catalysts were pretreated in an atmosphere of 5% O₂ and 95% Ar. They were heated from room temperature to 250 °C, 300 °C, and 350 °C at a rate of 10 °C/min, with each target temperature maintained for 30 minutes at a gas flow rate of 40 mL/min. Finally, the pre-treated catalysts were cooled to room temperature at a flow rate of 100 mL/min,

yielding the catalysts designated as AuNHC-1/CeO₂, AuNHC-2/CeO₂, and AuNHC-3/CeO₂, respectively.

Catalytic performance testing

The gas stream was then switched to a mixture of 1% CO, 4% O₂, and 95% Ar (flow rate of 37 mL/min) for the actual test. During the test, the temperature was increased from 25 °C at a rate of 2 °C/min. After stabilizing the temperature for 20 minutes, gas chromatography (GC) analysis was performed. Throughout the experiment, the space velocity was maintained at 14800 mL·h⁻¹·g⁻¹.

In situ FT-IR measurements

In situ FT-IR measurements were carried out as follows: 100 mg of CeO₂-supported gold catalyst was placed under a 5% O₂ and 95% Ar atmosphere (flow rate of 40 mL/min). The sample was heated at a rate of 10 °C/min to 300 °C and held at this temperature for 30 minutes, with spectra collected at 5-minute intervals during this period. The sample was then cooled to room temperature under a 5% O₂ and 95% Ar atmosphere (flow rate of 100 mL/min). Upon reaching room temperature, the gas stream was switched to pure Ar at a flow rate of 50 mL/min for 30 minutes, followed by collection of the background spectrum. Subsequently, the gas stream was changed to 1% CO and 99% Ar at a flow rate of 40 mL/min for 30 minutes, with spectra collected at 2-minute intervals. Finally, the system was purged with argon for 30 minutes.

Theoretical calculations

All ligands and their frontier molecular orbitals (HOMO-LUMO) were optimized using density functional theory (DFT) calculations performed with the Gaussian 16 program.^[2] Geometry optimizations were conducted at the PBE0/def2-SVP level of theory, employing the hybrid PBE0 functional to balance exchange-correlation effects and the def2-SVP basis set to ensure computational efficiency while maintaining accuracy for main-group element.^[2] For molecular orbital analysis, the optimized structures were subjected to single-point energy calculations at the same level of theory. The Multiwfn program was utilized to extract HOMO-LUMO energies, visualize orbital isosurfaces, and quantify orbital contributions via Löwdin population analysis. Orbital diagrams were rendered using VMD, with isosurface colors mapped to wavefunction phases and lighting parameters adjusted for clarity.^[3,4]



Fig. S1 ¹H NMR and ¹³C NMR spectra of [(AuNHC-1)₃O]BF₄ for (a-b), [(AuNHC-2)₃O]BF₄ for (c-d), and [(AuNHC-3)₃O]BF₄ for (e-f) in DMSO-*d*₆, with corresponding cluster structures. Color code: Au (yellow), O (red), N (blue), C (light grey). Other ligands are dimmed for clarity. ¹H NMR (600 MHz, DMSO-*d*₆) of [(AuNHC-1)₃O]BF₄, $\delta = 7.03$ -6.92 (m, 12H), 4.06-3.87 (m, 12H), 2.28-2.10 (m, 54H) ppm. ¹³C NMR (151 MHz, DMSO-*d*₆) of [(AuNHC-1)₃O]BF₄, $\delta = 186.31$, 137.43, 135.24, 135.06, 129.02, 50.21, 20.66, 17.34 ppm. ¹H NMR (600 MHz, DMSO-*d*₆) of [(AuNHC-2)₃O]BF₄, $\delta = 7.83$ -7.63 (m, 6H), 7.13-7.02 (m, 12H), 2.33-2.32 (d, 18H), 2.07-1.90 (m, 36H) ppm. ¹³C NMR (151 MHz, DMSO- *d*₆) of [(AuNHC-2)₃O]BF₄, $\delta = 163.30$, 138.43, 134.80, 134.18, 128.78, 123.09, 20.66, 17.18 ppm. ¹H NMR (600 MHz, DMSO-*d*₆) of [(AuNHC-3)₃O]BF₄, $\delta = 7.57$ (s, 6H), 4.93-4.88 (p, 6H), 1.44-1.45 (d, 36H) ppm. ¹³C NMR (151 MHz, DMSO-*d*₆) of [(AuNHC-3)₃O]BF₄, $\delta = 158.58$, 118.15, 52.98, 22.69. ppm.



Fig. S2 ¹⁹F NMR spectra of [(AuNHC-1)₃O]BF₄ for (a), [(AuNHC-2)₃O]BF₄ for (b), and [(AuNHC-3)₃O]BF₄ for (c) in DMSO-*d*₆. ¹⁹F NMR (565 MHz, DMSO-*d*₆) of [(AuNHC-1)₃O]BF₄, δ = 148.32 ppm. ¹⁹F NMR (565 MHz, DMSO-*d*₆) of [(AuNHC-2)₃O]BF₄, δ =148.33 ppm. ¹⁹F NMR (565 MHz, DMSO-*d*₆) of [(AuNHC-2)₃O]BF₄, δ = 148.33 ppm. ¹⁹F NMR (565 MHz, DMSO-*d*₆) of [(AuNHC-3)₃O]BF₄, δ = 148.27 ppm.



Fig. S3 PXRD patterns of newly loaded catalysts AuNHC-1/CeO₂, AuNHC-2/CeO₂, AuNHC-3/CeO₂ and CeO₂.



Fig. S4 Solid-state UV-Vis spectra of the newly loaded catalyst samples



Fig. S5 TGA of Au clusters: (a) $[(AuNHC-1)_3O]BF_4$, (b) $[(AuNHC-2)_3O]BF_4$ and (c) $[(AuNHC-3)_3O]BF_4$.



Fig. S6 In-situ time-resolved Fourier transform infrared spectroscopy (FT-IR) of (a) **AuNHC-1/CeO₂**, (b) **AuNHC-2/CeO₂** and (c) **AuNHC-3/CeO₂** conducted at 300°C in an oxygen atmosphere (5% O₂/95% Ar).



Fig. S7 PXRD patterns of catalysts AuNHC-1/CeO₂, AuNHC-2/CeO₂ and AuNHC-3/CeO₂ before reaction (pretreatment at 300 °C) and after reaction.



Fig. S8 Solid-state UV-vis absorption spectra of the three catalysts (a) before reaction (pretreatment at 300 °C) and (b) after reaction.



Fig. S9 Lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for the NHC-1-3 ligands and their corresponding energy level distribution.



Fig. S10 TEM images before reaction (after pretreatment at 300 °C in 5% O₂ and 95% Ar atmosphere): (a) **AuNHC-1/CeO₂**, (b) **AuNHC-2/CeO₂** and (c) **AuNHC-3/CeO₂**.



Fig. S11 TEM and mapping images after reaction: (a) AuNHC-1/CeO₂, (b) AuNHC-2/CeO₂ and (c) AuNHC-3/CeO₂. The far left is the size distribution diagram of the corresponding gold NPs catalyst.



Fig. S12 TG-MS of (a) AuNHC-1/CeO₂, (b) AuNHC-2/CeO₂ and (c) AuNHC-3/CeO₂.

References

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