Supporting Information

Aqueous phase synthesis of benzyl ester over partially thiolated Au₂₅ nanocluster catalysts: improving selectivity with hydrophobic carbon support

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1. Methods

1.1 Chemicals

All chemicals were used as purchased without further purification. Hydrogen tetrachloroaurate (III) tetrahydrate (HAuCl₄ \cdot 4H₂O) was purchased from Tanaka Precious Metals. Sodium borohydride (NaBH₄), silica for column chromatography (SiO₂), sodium hydroxide (NaOH), benzyl alcohol, benzaldehyde, benzoic acid, hydrochloric acid (HCl), sodium chloride (NaCl), anhydrous magnesium sulfate (MgSO₄), magnesium nitrate hexahydrate (Mg(NO₃)₂· $6H_2O$), aluminum nitrate nonahydrate (Al(NO₃)₃· $9H_2O$), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·4H₂O), cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O), sodium carbonate (Na₂CO₃), tributylamine, ammonium acetate (NH₄OAc), hydrofluoric acid (HF) and all organic solvents except for tetrahydrofuran (THF) and acetonitrile (MeCN) were purchased from FUJIFILM Wako Pure Chemical Industries. THF (anhydrous, stabilizer-free) was purchased from Kanto Chemicals. MeCN, tetraoctylammonium bromide (TOAB), 2-(boc-amino)ethanethiol, Sephadex®, tert-butylamine and benzyl benzoate were purchased from Sigma-Aldrich. 2-Phenylethanethiol (PET-H), 1-phenylethanol, ptrans-2-[3-(4-tert-butylphenyl)-2-methyl-2mercaptobeonzoic acid (pMBA) and propenylidene]malononitrile (DCTB) were purchased from Tokyo Chemical Industry. Porous carbon support (CNovel, grade: P(3)010-00) was purchased from Toyo Tanso. Al₂O₃ nanoparticles (SBa-200) were purchased from Sasol. Milli-Q grade water (>18 M Ω cm) was used.

1.2 Characterization

Ultraviolet visible (UV-vis) absorption spectra were recorded by using a spectrophotometer (V-670 or V-630, Jasco) in the transmission mode. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) data were recorded using a SHIMADZU AXIMA-CFR mass spectrometer. Typically, MALDI-MS samples were prepared by dissolving $[Au_{25}(PET)_{18}]^0$ cluster (0.1 mg) and DCTB matrix (1.0 mg) in toluene (20 µL) and 1.0 µL of the mixed solution was spotted onto the MALDI plate. All the data were collected in negative ion mode. Thermogravimetric (TG) analysis was performed using an SII TG-DTA 7200 instrument (Hitachi High-Tech Science). Samples (~3.0 mg) were loaded on the aluminum pan and the data were collected under ambient air. The temperature was raised from ~20 °C to 500 °C at a rate of 5 °C/min and then held at 500 °C for 2 h. N₂ and H₂O-vapour adsorption/desorption isotherms of a variety of carbon

supports were obtained using a MicrotracBEL Corp., BELSORP-max system. The measurement temperature was fixed at -196 °C and 25 °C for N₂ and H₂O-vapour adsorption/desorption, respectively. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was calculated using the multipoint BET method from the adsorption data in the range of $P/P_0 = 0.05 \cdot 0.35$.^{S1} The total pore volume (V_{total}), which is the sum of micropore (V_{micro}) and mesopore (V_{meso}) volumes, was calculated from the adsorption amount at $P/P_0 = 0.96$. The value of V_{micro} was calculated using the Dubinin–Radushkevich (DR) equation. V_{meso} was obtained by subtracting V_{micro} from V_{total} . For the analysis of the mesopore size distribution, the Barrett–Joyner–Halenda (BJH) method was applied to the N₂ desorption isotherms. Temperature-programmed desorption mass spectrometry (TPD-MS) measurement was performed using an advanced TPD system developed by our group.^{S2-S4} CO, CO₂, H₂O, and H₂ were generated by the thermal decomposition of oxygen-containing functional groups and H-terminated edge sites. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) images were collected using a JEM-ARM200F microscope operated at an acceleration voltage of 200 kV, under 1×10^{-5} Pa at 298 K in the sample column. AC-HAADF-STEM specimens were prepared by dropping the ethanol dispersion of each specimen onto lacey carbon film-coated copper grids (Cu200LC, ALLIANCE Biosystems, Inc.). The resulting AC-HAADF-STEM images were analyzed using the Fiji ImageJ program.^{SS} Powder X-ray diffraction (PXRD) patterns were collected using a diffractometer and D/teX Ultra 250 detector (SmartLab 3, Rigaku) with Cu Kα characteristic radiation (λ = 1.5405 Å). X-ray absorption spectroscopy (XAS) was performed in a transmission mode using an ion chamber for the I_0 and I_1 at the BL01B1 beamline at SPring-8 of the Japan Synchrotron Radiation Research Institute (proposal numbers 2023A1635 and 2024A1734). The incident X-ray beam was monochromatized using a Si (111) double-crystal monochromator, and the X-ray energy was calibrated using an Au foil. XAFS data were analyzed using software (REX2000). The k^3 -weighted χ spectra in the k range of 3–14 Å⁻¹ were Fourier transformed into the r-space. Curve fitting analysis was performed over the *r* range of 1.6–3.1 Å.

1.3 Synthesis of [Au₂₅(PET)₁₈]⁰

 $[Au_{25}(PET)_{18}]^{0}$ was prepared according to the reported procedures with slight modifications.^{S6} A 300 mL eggplant flask was charged with HAuCl₄ · 4H₂O (1068 mg), TOAB (1564 mg), THF (70 mL), and a magnetic stirring bar. After stirring the solution at room temperature for 15 min, PET (1.8 mL) was added dropwise, followed by further stirring for 2 h. Then, a freshly prepared ice-cold aqueous solution of NaBH₄ (980 mg in 24 mL H₂O) was added at once, and the resulting dark brown solution was stirred at room temperature for 4 days. The THF layer was collected and evaporated to obtain black oil covered with water. The oil was precipitated and washed by centrifugation in MeOH. This washing procedure was repeated for at least five times. The precipitate was extracted with MeCN and evaporated to dryness. The product was oxidized and further purified by SiO₂ column chromatography. The eluent was the mixture of DCM and *n*-hexane, in which the ratio of DCM to *n*-hexane was gradually increased from 1:1 to 10:1 (v/v). The greenish-yellow band was collected and dried by evaporation. The products were recrystallized in toluene by layering EtOH (toluene/EtOH = 1:14 (v/v)). The formed crystal was collected by filtration, washed with MeOH, and dried *in vacuo* to give the title compound. The yield was 74 mg (9.6 % based on Au).

1.4 Synthesis of carbon mesosponge (CMS) and graphene mesosponge (GMS)

CMS and GMS were prepared according to previous works by using Al₂O₃ nanoparticles (SBa-200, Sasol) as a template.^{S7-S9}

1.5 Catalyst preparation by depositing [Au₂₅(PET)₁₈]⁰ on CMS, GMS, and CNovel

The carbon supported Au cluster catalysts were synthesized according to the reported procedures with slight modifications.^{S10} For the catalyst with the loading amount of 0.2 or 1 wt% Au, a 300 mL Erlenmeyer flask was charged with carbon (CMS, GMS, or CNovel) (300 mg), toluene (100 mL) and a magnetic stirring bar. The solution was sonicated at room temperature for 30 min to disperse the carbon in the toluene, followed by vigorous stirring at 0 °C for 30 min. Toluene solution (100 mL) containing a

calculated amount of $[Au_{25}(PET)_{18}]^0$ was added dropwise at a rate of 1 mL/min. After mixing the solution at 0 °C for ~2 h, the composites were filtered, washed with acetone, and dried *in vacuo* to obtain Au₂₅(PET)₁₈/C. The filtrate was also collected and concentrated for measurement of UV-vis absorption spectra.

The Au₂₅(PET)₁₈/C composites (~100 mg) were placed on the quartz boat and calcined in the furnace under vacuum to partially remove the protecting ligands. The temperature was raised to the target temperature at a rate of 5 °C/min and held at that temperature for the calcination time. The optimized calcination conditions were at 375 °C for 12 h for Au₂₅(PET)/CMS, 400 °C for 12 h for Au₂₅(PET)/GMS and 425 °C for 18 h for Au₂₅(PET)/CNovel, respectively.

For the synthesis of $Au_{25}(PET)/GMS$ with 2 wt% loading, the procedure is almost the same except that the amount of GMS was reduced from 300 to 150 mg during deposition.

1.6 Synthesis of Au₂₅ nanocluster catalysts on hydrotalcite (Mg₃Al) and double metal hydroxide (Co₃Ce) supports

Hydrotalcite (Mg₃Al) and double metal hydroxide composed of Co and Ce (Co₃Ce)-supported Au₂₅ nanocluster catalysts were synthesized according to the previous reports.^{S6, S11}

1.7 Catalytic oxidation of alcohols

Catalytic reactions were performed using ChemiStation equipment (PPS-1510, EYELA). The error bars were determined by repeating the same experiment at least three times.

For benzyl alcohol (**1**) oxidation, a test tube was filled with a magnetic stirring bar, 5.0 mg of samples and aqueous solutions of benzyl alcohol (Au 0.33 mol%) and NaOH (300 mol%). The total volume of H₂O was fixed at 2 mL. The tube was immediately stirred at 30 °C, and the gas phase was replaced with pure O₂ through a balloon. After the reaction time, an excess of HCl (35%, 150 μ L) was added to quench the reaction. The substrates and products were extracted with toluene at least three times. To improve the extraction efficiency, an excess amount of NaCl was added during the extraction. The organic phase was collected and dehydrated with anhydrous MgSO₄. The solids were removed through a syringe filter and the extract was diluted to 10 mL using a volumetric flask. The extract obtained was subjected to analysis by gas chromatography (GC).

The oxidation of 1-phenylethanol was carried out with a similar procedure, except that 1-phenylethanol was added instead of benzyl alcohol (**1**). The reaction time was set at 3 h.

The hydrolysis of benzyl benzoate (2) was conducted with a similar procedure, except that benzyl benzoate (Au 0.66 mol%) was added instead of **1**. The amount of **2** was halved compared to **1**, since two molecules of **1** would be coupled in the reaction to form **2**; the maximum moles of **2** formed in the reaction are half the moles of **1**. The reaction time was set at 1 h.

The optimization of the reaction conditions was also done in a similar way by changing the amounts of NaOH and H_2O . In the optimized reaction condition, all conditions were the same as above except for the amounts of NaOH (30 mol%) and H_2O (0.2 mL).

For the mechanistic studies, the amount of solvent was set at 2 mL to completely dissolve benzaldehyde (**3**) in the reaction medium. The reaction time was set to 12 h.

All results were analyzed by GC (GC-2025, Shimadzu) with a flame ionization detector (FID) equipped with an SH-Wax column (60 m, P/N: 221-75893-60). The concentrations of the reactants and the products were quantitatively analyzed by the external standard method. Calibration curves for benzyl alcohol (1), benzyl benzoate (2), benzaldehyde (3), and benzoic acid (4) were constructed using each authentic compound. The conversion and the yield of the reaction were obtained using the following equations:

Conversion (%) =
$$\left(\frac{[\mathbf{1}]_0 - [\mathbf{1}]}{[\mathbf{1}]_0}\right) \times 100$$

Yield
$$\boldsymbol{n}$$
 (%) = $\left(\frac{[\boldsymbol{n}]}{[\mathbf{1}]_0}\right) \times 100 \; (\boldsymbol{n} = \mathbf{1}, \mathbf{3}, \mathbf{4})$

Yield **2** (%) =
$$\left(\frac{[2]}{0.5 \times [1]_0}\right) \times 100$$

where $[1]_0$ is the initial concentration of 1 and [n] (n = 1, 2, 3 and 4) is the concentration of 1, 2, 3 and 4 after the reaction.

1.8 Adsorption of substrate and products onto the carbon supports

Adsorption of each substrate was performed using ChemiStation equipment (PPS-1510, EYELA). For benzyl alcohol adsorption, the test tube was filled with a magnetic stirring bar, 5.0 mg of pristine carbon supports, and aqueous solutions of benzyl alcohol (1) and NaOH (300 mol%). The amount of benzyl alcohol was fixed at the condition of Au 0.33 mol%. The volume of H₂O was fixed at a total of 2 mL. The tube was immediately stirred at 30 °C and the gas phase was replaced with pure O₂ through a balloon. After 1 h of the reaction, the reaction solution and the sample powder were immediately separated by centrifugation and poured into separate test tubes. Each was quenched with an excess amount of HCl (35%, 150 μ L) and extracted similarly as above for GC analysis.

1.9 Recycling test of Au₂₅(PET)/GMS

A test tube was filled with a magnetic stirring bar, 25.0 mg of samples and aqueous solutions of benzyl alcohol (Au 0.33 mol%) and NaOH (300 mol%). The total volume of H₂O was fixed at 1 mL. The tube was immediately stirred at 30 $^{\circ}$ C, and the gas phase was replaced with pure O₂ through a balloon. After 30 min, the catalyst was separated from the suspension by centrifugation (14,000 rpm, 1 min). The supernatant was quenched with an excess amount of HCl. The recovered catalyst was washed once with H₂O, three times with acetone, twice with H₂O and the supernatant was also collected for extraction. Finally, the catalyst was immediately dispersed in the new reaction solution and the next reaction was started. After the second cycle, the same procedure was used to wash the catalyst and collect the reaction solution. The substrates and products were extracted with toluene at least three times. To improve the extraction efficiency, an excess amount of NaCl was added during the extraction. The organic phase was collected and dehydrated with anhydrous MgSO₄. The solids were removed through a syringe filter and the extract was diluted to 50 mL using a volumetric flask. The extract obtained was subjected to GC analysis.

2. Results



Fig. S1 (A) Negative mode MALDI mass spectrum, (B) UV-vis absorption spectrum in DCM and (C) TG analysis curve of $[Au_{25}(PET)_{18}]^0$. The percentage in panel (C) indicates the experimental weight loss, while that in parenthesis is the theoretical weight loss.



Fig. S2 (A) N₂ adsorption/desorption isotherm and (B) pore size distribution by BJH method of pristine CNovel, CMS and GMS. Closed and open circles in (A) correspond to adsorption and desorption, respectively.



Fig. S3 TPD profiles of CNovel, CMS and GMS for H₂, CO, CO₂ and H₂O evolution.



Fig. S4 UV-vis absorption spectra of (a) a toluene solution of $[Au_{25}(PET)_{18}]^0$ and (b) a toluene filtrate after adsorption of $[Au_{25}(PET)_{18}]^0$ on CNovel, CMS and GMS.



Fig. S5 Catalytic activity of (a) $Au_{25}(PET)_{18}/C$ and $Au_{25}(PET)/C$ prepared by calcination (T_{cal}) at (b) 325, (c) 350, (d) 375, (e) 400 and (f) 425 °C for 12 h in the oxidation of 1-phenylethanol. Reaction conditions: 1-phenylethanol (Au 0.33 mol%), catalyst (5.0 mg), NaOH (300 mol%), H₂O (2 mL), O₂ (1 atm, balloon), 30 °C, 3 h.



Fig. S6 PXRD patterns of (a) $Au_{25}(PET)_{18}/C$ and $Au_{25}(PET)/C$ prepared by calcination (T_{cal}) at (b) 350, (c) 375, (d) 400 and (e) 425 °C for 12 h.



Fig. S7 Au L₃-edge (A) XANES, (B) and (C) EXAFS oscillations, and (D) FT-EXAFS of (a) Au₂₅(PET)₁₈/C and Au₂₅(PET)/C prepared by calcination at optimized T_{cal} for each carbon for t_{cal} of (b) 6, (c) 12, (d) 18 and (e) 24 h. The solid and dotted lines in panels (C) and (D) represent the raw data and the fitted results, respectively. The intensity of the FT-EXAFS of the Au foil is halved for clarity.



Fig. S8 Catalytic activity of Au₂₅(PET)₁₈/C ($t_{cal} = 0$) and Au₂₅(PET)/C prepared by calcination at optimized T_{cal} for each carbon for t_{cal} of 6, 12, 18 and 24 h. Reaction conditions: 1-Phenylethanol (Au 0.33 mol%), catalyst (5.0 mg), NaOH (300 mol%), H₂O (2 mL), O₂ (1 atm, balloon), 30 °C, 3 h.



Fig. S9 Typical AC-HAADF-STEM images and size distributions of Au₂₅(PET)₁₈/C with C = CNovel, CMS and GMS.



Fig. S10 Catalytic activity of Au₂₅ NC catalysts for the oxidation of PhCH₂OH (**1**). Reaction conditions: **1** (Au 0.33 mol%), catalyst (5.0 mg), NaOH (300 mol%), H₂O (2 mL), O₂ (1 atm, balloon), 30 °C, 30 min.



Fig. S11 Hydrolysis of PhCOOCH₂Ph (**2**) with or without **Au**₂₅(**PET**)/**C** catalysts. Reaction conditions: **2** (Au 0.66 mol%), catalyst (5.0 mg), NaOH (600 mol%), H₂O (2 mL), O₂ (1 atm, balloon), 30 °C, 1 h.



Fig. S12 Adsorption of 1⁻ and product 2–4 onto the three pristine carbon supports. Reaction conditions: substrate (Au 0.33 mol% for 1, 3, 4, or Au 0.66 mol% for 2), carbon support (5.0 mg), NaOH (300 mol% for 1, 3, 4, or 600 mol% for 2), H₂O (2 mL), O₂ (1 atm, balloon), 30 °C, 1 h. The amount of substrate for 2 was halved compared to 1, 3 and 4, because 2 can be formed by coupling of two 1 during the reaction. After the reaction, the reaction solution and the carbon support were separated by centrifugation and extracted separately.



Fig. S13 (A) Overview and (B) magnified view of water-vapour adsorption isotherms of CNovel (purple), CMS (orange) and GMS (pink). Closed and open circles correspond to adsorption and desorption, respectively.



Fig. S14 Effect of the amount of base (NaOH) on the activity and selectivity of **Au**₂₅(**PET**)/**GMS** for benzyl alcohol (**1**) oxidation for (A) short (0.5 or 2 h) and (B) long (12 h) reaction times. Reaction conditions: **1** (Au 0.33 mol%), **Au**₂₅(**PET**)/**GMS** (5.0 mg), NaOH (*x* mol%), H₂O (2 mL), O₂ (1 atm, balloon), 30 °C. The amount of NaOH was changed from 10 to 500 mol%.



Fig. S15 Effect of the amount of solvent (H₂O) on the activity and selectivity of **Au**₂₅(**PET**)/**GMS** for benzyl alcohol (**1**) oxidation. Reaction conditions: **1** (Au 0.33 mol%), **Au**₂₅(**PET**)/**GMS** (5.0 mg), NaOH (30 mol%), H₂O (*x* mL), O₂ (1 atm, balloon), 30 °C. Reaction time was 0.5, 2 or 12 h. The amount of H₂O was changed from 2 to 0.2 mL.



Fig. S16 UV-vis absorption spectra of (a) a toluene solution of $[Au_{25}(PET)_{18}]^0$ and (b) a toluene filtrate after adsorption of $[Au_{25}(PET)_{18}]^0$ on GMS. The loading amount of Au was 0.2 and 2 wt% based on the amount of Au.



Fig. S17 Au L₃-edge (A) XANES, (B) and (C) EXAFS oscillations, and (D) FT-EXAFS of **Au**₂₅(**PET**)/**GMS** (2 wt%) calcined at 400 °C for (a) 0 and (b) 12 h, respectively. The solid and dotted lines in panels (C) and (D) represent the raw data and the fit, respectively. The intensity of the FT-EXAFS of the Au foil is halved for clarity.



Fig. S18 PXRD patterns of **Au**₂₅**(PET)/GMS** (2 wt%) (a) without and (b) with calcination at 400 °C for 12 h.



Fig. S19 Typical AC-HAADF-STEM image and size distribution of **Au**₂₅(**PET**)/**GMS** (2 wt%) with calcination at 400 °C for 12 h.



Fig. S20 Catalytic activity and selectivity of **Au**₂₅(**PET**)/**GMS** at 0.2, 1, and 2 wt% for the oxidation of benzyl alcohol (1). Reaction conditions: 1 (Au 0.33 mol%), **Au**₂₅(**PET**)/**GMS**, NaOH (30 mol%), H₂O (0.2 mL), O₂ (1 atm, balloon), 30 °C. The amount of sample used for catalysis was 25, 5.0, and 2.5 mg for 0.2, 1, and 2 wt% catalysts, respectively, to keep the amount of Au constant in all systems. The data for 1 wt% are identical to those shown in **Fig. 5**.



Fig. S21 Conversion and yield in the recycling test of **Au**₂₅(**PET**)/**GMS** (1 wt%). Reaction conditions: **1** (Au 0.33 mol%), **Au**₂₅(**PET**)/**GMS** (25.0 mg), NaOH (30 mol%), H₂O (1 mL), O₂ (1 atm, balloon), 30 °C, 30 min.



Fig. S22 Typical AC-HAADF-STEM image and size distribution of Au₂₅(PET)/GMS after the sixth cycle of the recycling test (Fig. S21).

Sample	$S_{BET} (m^2 g^{-1})^{a}$	V_{total} (cm ³ g ⁻¹) ^b	<i>V</i> _{micro} (cm ³ g ^{−1}) ^c	V _{meso} (cm ³ g ⁻¹) ^d	Φ (nm) ^e	V _{gas} (mmol g ⁻¹) ^f
CNovel	2,041	3.97	0.78	3.19	10.9	3.8
CMS	2,023	3.45	0.71	2.74	7.1	1.3
GMS	1,738	3.08	0.62	2.46	8.3	0.1

Table S1. Structures of carbon supports.

^a Specific surface area estimated from **Fig. S2**A. ^b Total pore volume estimated from **Fig. S2**A. ^c Micropore volume estimated from **Fig. S2**A. ^d Mesopore volume estimated from **Fig. S2**A. ^e Average pore size estimated by the BJH method from **Fig. S2**B. ^f Total amount of gas evolved in the TPD-MS measurement in **Fig. S3**.

Table S2. Structural parameters obtained by curve-fitting analysis of EXAFS (Fig. S7).

Sample ^a	Calcination time t_{cal} (h)	Bond	CN ^b	<i>r</i> (Å) °	DW (Ų) ^d	R (%) ^e	
	0	Au–Au	0.8(5)	2.73(4)	0.0083(69)	4.6	
	0	Au–S	1.7(2)	2.32(1)	0.0071(18)	4.0	
	6	Au–Au	1.5(7)	2.74(2)	0.0071(45)	12.9	
	0 -	Au–S	1.3(1)	2.33(1)	0.0056(29)		
	10	Au–Au	4.2(8)	2.77(1)	0.0106(23)	10.0	
Au ₂₅ (FET)/CNOVE	12	Au–S	1.1(2)	2.33(1)	0.0059(23)	12.5	
	19 -	Au–Au	4.4(8)	2.79(1)	0.0106(21)	8.8	
	10	Au–S	0.9(1)	2.33(1)	0.0050(21)	0.0	
	24 -	Au–Au	4.8(8)	2.80(1)	0.0108(19)	7.0	
	27	Au–S	0.8(1)	2.33(1)	0.0064(29)	7.0	
	0 -	Au–Au	0.5(3)	2.77(2)	0.0041(15)	1 9	
	0	Au–S	1.8(2)	2.32(1)	0.0067(40)	4.5	
	6	Au–Au	3.7(2)	2.80(1)	0.0110(25)	8.8	
		Au–S	1.0(1)	2.33(1)	0.0074(22)	0.0	
	12 -	Au–Au	3.7(2)	2.79(1)	0.0104(22)	14 5	
		Au–S	0.9(1)	2.31(1)	0.0061(33)		
	18 -	Au–Au	4.7(9)	2.77(1)	0.0110(21)	14.7	
		Au–S	0.9(2)	2.30(2)	0.0072(29)		
	24	Au–Au	5.7(3)	2.82(2)	0.0098(16)	14.0	
		Au–S	0.7(1)	2.30(1)	0.0066(40)	14.0	
	0 -	Au–Au	0.6(3)	2.78(2)	0.0050(44)	4.8	
		Au–S	1.6(2)	2.32(1)	0.0062(16)	4.0	
	6 -	Au–Au	5.6(3)	2.75(1)	0.0119(19)	14.8	
		Au–S	0.5(1)	2.31(2)	0.0061(34)	14.0	
Augr(PET)/GMS	12 -	Au–Au	5.7(3)	2.76(1)	0.0112(19)	17 2	
/1025(1 2 1)/ CIVIC		Au–S	0.6(1)	2.30(2)	0.0076(50)	17.2	
	18 -	Au–Au	5.5(8)	2.79(1)	0.0106(16)	79	
		Au–S	0.4(1)	2.30(3)	0.0066(61)	1.0	
	24 -	Au–Au	6.7(3)	2.77(1)	0.0106(21)	14 1	
	۲	Au–S	0.4(1)	2.35(1)	0.0023(8)		
Au foil		Au–Au	11.8(1.3)	2.85(1)	0.0088(11)	8.8	

^a Entry in **Fig. S7**. Samples with calcination time $t_{cal} = 0$ correspond to $Au_{25}(PET)_{18}/C$. ^b Coordination number. ^c Bond length. ^d Debye-Waller factor. ^eR = $(\sum (k^3 \chi^{data}(k) - k^3 \chi^{fit}(k))^2)^{1/2} / (\sum (k^3 \chi^{data}(k))^2)^{1/2}$. Standard deviation values are given in parentheses.

	5	1		5 1		
	Sample	Calcination temperature (°C)	Calcination time (h)	CNAU-AU	$CN_{Au=S}$	Diameter (nm)
_	Au ₂₅ (PET)/CNovel	425	18	4.4 ± 0.8	0.9 ± 0.1	1.0 ± 0.2
_	Au ₂₅ (PET)/CMS	375	12	3.7 ± 0.2	0.9 ± 0.1	1.1 ± 0.2
-	Au ₂₅ (PET)/GMS	400	12	5.7 ± 0.3	0.6 ± 0.1	1.0 ± 0.3

Table S3. Summary of structural parameters of Au₂₅(PET)/C obtained by optimized calcination conditions.

Table S4. Conversion and yield of benzyl alcohol oxidation in aqueous phase by Au₂₅(PET)/C (Fig. 4).

ОН	Au ₂₅ (PET)/O NaOH H ₂ O (2 mL),	(Au 0.33 mol ⁶ (300 mol%) O ₂ (1 atm), 30					
,	and the second second		2	Jield (%)	4		
Sample	Reaction time (min)	Conversion (%)			ОН	Total	
-	10	37(8)	14(2)	3(1)	18(5)	35(7)	
-	20	57(7)	21(2)	2(1)	31(4)	54(6)	
-	30	62(6)	23(1)	2(1)	36(4)	60(5)	
Au ₂₅ (PET)/CNovel	40	76(9)	25(1)	2(1)	46(7)	73(6)	
	50	87(7)	27(1)	1(1)	55(6)	84(7)	
-	60	92(5)	28(1)	1(1)	59(3)	88(4)	
	120	96(4)	27(1)	<1(1)	64(4)	92(4)	
	180	>99(1)	26(1)	<1(1)	71(3)	96(3)	
_	10	32(5)	12(2)	3(1)	15(3)	30(5)	
_	20	52(8)	19(3)	3(1)	28(5)	50(8)	
_	30	64(8)	22(3)	2(1)	37(6)	61(9)	
A. (DET)(CMS	40	64(2)	22(1)	2(1)	37(1)	62(2)	
	50	78(2)	25(1)	2(1)	47(1)	74(2)	
	60	85(4)	26(1)	1(1)	53(5)	81(6)	
-	120	98(1)	26(1)	<1(1)	68(2)	94(1)	
-	180	>99(1)	24(1)	<1(1)	69(2)	93(1)	
	10	38(4)	22(2)	3(1)	12(3)	36(5)	
-	20	57(1)	32(1)	3(1)	21(3)	56(4)	
-	30	64(3)	34(2)	3(1)	25(1)	62(2)	
-	40	73(2)	36(3)	2(1)	30(1)	68(3)	
Au ₂₅ (PET)/GMS	50	84(7)	38(3)	2(1)	39(9)	79(7)	
-	60	86(1)	39(1)	1(1)	41(3)	82(1)	
-	120	95(2)	36(1)	1(1)	52(1)	89(1)	
-	180	97(3)	34(1)	<1(1)	58(5)	93(4)	

Reaction conditions: **1** (Au 0.33 mol%), **Au₂₅(PET)/C** (5.0 mg), NaOH (300 mol%), H₂O (2 mL), O₂ (1 atm, balloon), 30 °C. Each value is the average of three data points. Standard deviation values are given in parentheses.

Table S5. Hydrolysis of benzyl benzoate in aqueous phase by Au₂₅(PET)/C (Fig. S11).



			Yiel	d (%)		
Sample	Conversion (%)	ОН	O H	ОЦОН	Total	
Blank	22	13	0.3	9	22	
Au ₂₅ (PET)/CNovel	8	2	0.4	4	7	
Au ₂₅ (PET)/CMS	14	4	1	8	13	
Au ₂₅ (PET)/GMS	10	3	1	5	9	

Reaction conditions: 2 (Au 0.66 mol%), Au₂₅(PET)/C (5.0 mg), NaOH (600 mol%), H₂O (2 mL), O₂ (1 atm, balloon), 30 °C, 1 h.

		0 ⁻	С З Н	ОН 4	
CNovel	On Carbon	28	37	6	77
	In Solution	73	55	85	1
CMS	On Carbon	39	53	8	76
	In Solution	59	40	84	2
GMS	On Carbon	34	48	13	74
	In Solution	62	46	75	6

Table S6. Adsorption of each substrate and product on the carbon supports (Fig. S12).

Values represent the yield of each substrate and product. Reaction conditions: Substrate, carbon support (5.0 mg), NaOH (300 or 600 mol%), H_2O (2 mL), O_2 (1 atm), 30 °C, 1 h.

Table S7. Structural	parameters	obtained by	v curve-fitting	analysis	of EXAFS	(Fig.	. S17)

Sample ^a	Calcination time t _{cal}	Bond	CN ^b	<i>r</i> (Å) ^c	DW (Ų) ^d	R (%) ^e
Au ₂₅ (PET)/GMS (2 wt%)	0	Au–Au	0.8(6)	2.76(1)	0.0061(73)	5.2
	0 -	Au–S	1.5(3)	2.33(5)	0.0058(27)	
	10	Au–Au	7.4(6)	2.81(4)	0.0108(21)	11.7
	12 -	Au–S	0.3(1)	2.36(1)	0.0048(15)	
Au foil		Au–Au	11.8(1.3)	2.85(1)	0.0088(11)	8.8

^a Entry in **Fig. S17**. Sample with calcination time $t_{cal} = 0$ corresponds to $Au_{25}(PET)_{18}/C$. ^b Coordination number. ^c Bond length. ^d Debye-Waller factor. ^a R = $(\sum (k^3 \chi^{data}(k) - k^3 \chi^{fit}(k))^2)^{1/2} / (\sum (k^3 \chi^{data}(k))^2)^{1/2}$. The standard deviation values are given in parentheses.

Table S8. Conversion and yield of benzyl alcohol oxidation in aqueous phase by Au₂₅(PET)/C (Fig. 5).

$ \begin{array}{c} & \begin{array}{c} & Au_{25}(\text{PET})/\text{GMS} (Au \ 0.33 \ \text{mol}\%) \\ & \begin{array}{c} & \text{NaOH} (30 \ \text{mol}\%) \\ & \begin{array}{c} & H_{2}O \ (0.2 \ \text{mL}), \ O_{2} \ (1 \ \text{atm}), \ 30 \ ^{\circ}\text{C}. \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & O \\ & \end{array} \end{array} \begin{array}{c} & O \\ & \end{array} \end{array} \begin{array}{c} & O \\ & \end{array} \begin{array}{c} & O \\ & \end{array} \begin{array}{c} & O \\ & \end{array} \end{array} \begin{array}{c} & O \\ & \end{array} \begin{array}{c} & O \\ & \end{array} \begin{array}{c} & O \\ & \end{array} \end{array} \begin{array}{c} & O \\ & \end{array} \begin{array}{c} & O \\ & \end{array} \end{array} \begin{array}{c} & O \\ & \end{array} \begin{array}{c} & O \\ & \end{array} \end{array} \begin{array}{c} & O \\ & \end{array} \end{array}$								
				Yield (%))			
Sample	Reaction time (h)	Conversion (%)		O H	ОН	Total		
	0.5	61(3)	47(3)	5(1)	8(1)	60(3)		
	2	84(5)	61(5)	5(1)	16(3)	83(5)		
Au ₂₅ (PET)/GMS	4	91(3)	66(5)	5(2)	20(3)	90(6)		
_	6	95(1)	66(5)	3(1)	25(1)	95(4)		
	12	97(2)	67(2)	3(2)	26(2)	96(2)		

Reaction conditions: **1** (Au 0.33 mol%), **Au₂₅(PET)/GMS** (5.0 mg), NaOH (30 mol%), H₂O (0.2 mL), O₂ (1 atm, balloon), 30 °C. Each value is the average of three data points. Standard deviation values are given in parentheses.

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