Supporting Information

Effects of phosphine ligand denticity on catalytic activity and durability of gold nanoparticles in the oxidation of benzyl alcohol

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1. Experimental

1.1. Chemicals

All chemicals were used as purchased without further purification. Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4·4H_2O$) was purchased from Tanaka Precious Metals. All organic solvents except for acetonitrile (MeCN), sodium borohydride ($NaBH_4$), benzyl alcohol (BnOH), *p*-methoxybenzyl alcohol, triphenylphosphine (TPP), 1, 2-dichloroethane (DCE), dichloromethane (DCM), potassium carbonate (K_2CO_3), and biphenyl were purchased from Fujifilm Wako Pure Chemical Industries. Bis(diphenylphosphino)ethane (DPPE) was purchased from Tokyo Chemical Industry. Acetonitrile (MeCN) and tris(2- (diphenylphosphino)ethyl)phosphine (TDEP) were purchased from Sigma-Aldrich. Cesium carbonate (Cs_2CO_3) was purchased from Kanto Chemicals. Al_2O_3 nanoparticles (SBa-200) were purchased from Sasol. Milli-Q grade water (>18 MΩcm) was used. TDEP$(AuCl)_4$ was synthesized using the same materials and procedures as described in previous reports.[1] DPPE$(AuCl)_2$ and Me_2SAuCl were synthesized according to the reported method.[2] TPPAuCl was synthesized according to the reported procedures.[3]

1.2. Synthesis

Au:Tetra

TDEP$(AuCl)_4$ (0.03 mmol, 47.6 mg) was dissolved in DCM (40 mL) in a 100 mL pressure tube. The suspension was stirred for 15 min until the solids had fully dissolved. Then Me_2SAuCl (0.1 mmol, 29.5 mg) was added to the pressure tube, and the solution was stirred for 2 min. A 3 mL ethanol solution of $NaBH_4$ (0.625 mmol, 23.8 mg) was then added dropwise to the reaction mixture over 100 seconds. The solution gradually turned wine red. The mixture was then stirred at room temperature for 16 h, after which the solvent was completely evaporated. The residue was washed with acetonitrile (2 × 5 mL) under sonication to remove the cluster species. The remaining solids were completely dried under vacuum. This residue was then washed with deionized water (10 mL) using sonication to remove residual borate, followed by centrifugation and drying under vacuum. The resulting solid was extracted with DCM (3 mL), and the supernatant was added dropwise to hexane (40 mL). The sample was centrifuged and dried under vacuum again. The solid was collected for further use.

Au:Bi

DPPE(AuCl)$_2$ (0.05 mmol, 43.1 mg) was dissolved in DCM (40 ml) in a 100 mL pressure tube. The suspension was stirred until the solids had fully dissolved. Then Me$_2$SAuCl (0.1 mmol, 29.5 mg) was added to the pressure tube, and the solution was stirred for 2 min. A 3 mL ethanol solution of NaBH$_4$ (0.625 mmol, 23.8 mg) was then added dropwise to the reaction mixture over a period of 100 seconds. The solution gradually turned wine red. The mixture was then stirred at room temperature for 16 h, after which the solvent was completely evaporated. The residue was washed with DCM (5 mL) using sonication. The remaining solids were completely dried under vacuum. This residue was then washed with deionized water (10 mL) using sonication to remove residual borate, followed by centrifugation and drying under vacuum. The resulting solid was extracted with methanol (3 mL), and the resulting solution was added dropwise to diethyl ether (40 mL), leading to slow precipitation. The sample was then centrifuged and dried under vacuum again. The solid was collected for further use.

Au:Mono

TPPAuCl (0.1 mmol, 49.5 mg) was dissolved in DCM (40 mL) in a 100 mL pressure tube. The suspension was stirred for 5 min until the solids had fully dissolved. Then Me$_2$SAuCl (0.05 mmol, 14.7 mg) was added to the pressure tube, and the solution was stirred for 2 min. A 3 mL ethanol solution of NaBH$_4$ (0.480 mmol, 18.1 mg) was added in one portion under vigorous stirring. The solution gradually turned pale purple. The mixture was then stirred at room temperature for 16 h, after which the solvent was then completely evaporated. The residue was washed with acetonitrile (2 × 5 mL) using sonication to remove the cluster species. The remaining solids were completely dried under vacuum. This residue was then washed with deionized water (10 mL) using sonication to remove residual borate, followed by centrifugation and drying under vacuum. The resulting solid was extracted with DCM (3 mL), and the resulting solution was added dropwise to hexane (40 mL), leading to slow precipitation. The sample was then centrifuged and dried under vacuum again. The solid was collected for further use.

1.3. Loading on Cs$_2$CO$_3$

Au:Tetra

Au:Tetra (1.0 mg) was dissolved in DCM (1 mL) and sonicated for 5 min. The resulting solution was stirred at room temperature for at least 5 min. Cs$_2$CO$_3$ (250 mg) was added directly to the solution to prevent the moisture adsorption. The suspension was then stirred vigorously overnight. The sample was centrifuged and dried under vacuum again. The solid was collected for further use.

Au:Bi, Au:Mono

Au:Bi or **Au:Mono** (1.0 mg) was dissolved in DCM (1 mL) and sonicated for 5 min. The resulting solution was stirred at room temperature for at least 5 min. Cs$_2$CO$_3$ (132 mg) was added directly to the solution to prevent the moisture adsorption. The suspension was then stirred vigorously overnight. The sample was centrifuged and dried under vacuum again. The solid was collected for further use.

1.4. Loading of Au:Tetra on Al$_2$O$_3$

A homogeneous suspension was prepared by adding 100 mg of Al$_2$O$_3$ into a 300 mL eggplant flask, followed by the addition of 100 mL of dichloromethane (DCM). The mixture was then sonicated for 30 min to ensure uniform dispersion. The eggplant flask was then transferred to a low-temperature reactor and equilibrated at 0 °C with stirring for 30 min. At the same time, a dichloromethane solution of 1 mg **Au:Tetra** was prepared in a 50 mL volumetric flask and subsequently added to the cooled suspension via the syringe pump at a controlled rate of 1 mL/min. After complete addition, the reaction mixture was maintained at 0 °C with continuous stirring for an additional 30 min. The solid product was isolated from the suspension by vacuum filtration using a 0.2 μm PTFE membrane and washed thoroughly with dichloromethane (3 × 10 mL). The collected material was then dried under vacuum overnight.

1.5. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded at room temperature using a SmartLab 3 diffractometer (Rigaku) with a D/teX Ultra 250 detector and Cu Kα characteristic radiation (λ = 1.5405 Å). Measurements were performed in the 2θ range of 20–90 degrees. SmartLab Studio II (Rigaku) was used for the measurements and their subsequent analysis. UV-vis absorption spectra were recorded by using a spectrophotometer (V-670 or V-630, Jasco) in the transmission mode. Diffusion reflectance UV-vis absorption spectra were recorded by using a spectrophotometer (V-670, Jasco) equipped with a 60 mm integration sphere (ISN-723 mode) over the range of 300–1000 nm. Thermogravimetric (TG) analysis was performed using an SII TG-DTA 7200 instrument (Hitachi High-Tech Science). Samples (~3.0 mg) were loaded onto an aluminum pan and data were collected under ambient air conditions or N_2 atmosphere. 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. Transmission electron microscope (TEM) images were collected using a JEM-ARM200F microscope operated at an acceleration voltage of 80 kV, under 1×10^{-5} Pa at 298 K in the specimen column. The TEM sample was prepared by drop-casting the EtOH dispersion of the catalysts onto copper grids (SHR-C075, Okenshoji). High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images were collected using a JEM-ARM200F Thermal FE STEM microscope, which was operated at an acceleration voltage of 200 kV, under 1×10^{-5} Pa at 298 K in the sample column. HAADF-STEM specimens were prepared by drop-casting the DCM dispersion of each sample onto lacey carbon film-coated copper grid (Cu200LC, ALLIANCE Biosystems, Inc.). The obtained TEM and HAADF-STEM images were analyzed using Fiji ImageJ program. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 VersaProbe instrument (ULVAC-PHI) with the Al Kα X-rays (1486.6 eV) at an energy resolution of 0.2 eV. The sample pellets were mounted on carbon tape for the measurement. Energy calibration was performed by combining the Au $4f_{7/2}$ of the Au foil and the C 1s of the carbon tape. First, the peak of Au $4f_{7/2}$ of the Au foil was adjusted to 84.0 eV, and the energy shift was also applied to C 1s peak. The C 1s peak of the samples was then adjusted to match the value of the Au foil, with the energy shift also applied to the Au 4f spectrum. X-ray absorption spectroscopy (XAS) was performed in the fluorescence and transmission modes using an ion chamber for the I_0 detector and 19 solid-state detectors (SSDs) for the I_1 detector in the BL01B1 or BL14B2 beamline at SPring-8 of the Japan Synchrotron Radiation Research Institute (proposal numbers 2024B1861 and 2025A1761). The incident X-ray beam was monochromatized using a Si (111) double-crystal monochromator at the Au L_3-edge, and the X-ray energy was calibrated using an Au foil. For the unsupported AuNPs, a pellet for the XAS measurement was prepared by grinding 4 mg of sample with 50 mg of boron nitride over 20 min, and the spectra was collected in transmission mode. In the case of the supported catalysts, 10 mg of the sample was hermetically sealed under an Ar atmosphere and analyzed in fluorescence mode. The XAFS data were analyzed by software (REX2000). The k^3-weighted χ spectra in the k range of 3–14 Å^{-1} were Fourier transformed into r–space. The curve-fitting analysis was performed over the r range of 1.4–3.1 Å.

1.6. Time-course study of the catalytic oxidation of benzyl alcohol using AuNP/Cs_2CO_3

Catalytic oxidation of benzyl alcohol (BnOH) was performed under temperature control using *Chemistation* equipment (PPS-15W and PPM-5512, EYELA). To estimate the rate constant under the condition shown in Fig. 4, a tube (~15 mL volume) was filled with a solution of BnOH and biphenyl in a molar ratio of 1:1 in dichloroethane (2.0 mL, 128 µM (metal 0.2 mol%)) and the gas phase was replaced with pure O_2 using a balloon. Biphenyl was used as an internal standard. **AuNP**/Cs_2CO_3 sample (**Au:Tetra**/Cs_2CO_3: 17.3 mg; **Au:Bi**/Cs_2CO_3: 14.4 mg; **Au:Mono**/Cs_2CO_3: 9.6 mg) was added to the solution and stirred at 60 °C with a pure O_2 balloon. An aliquot (150 µL) was taken at 2 h, 4 h, 8 h, 12 h, 16 h, 19 h, and 22 h. The aliquot was filtered by a syringe filter and collected. To compare the rate constant under O_2 and air atmosphere shown in Fig. S10, a tube (~15 mL volume) was filled with a solution of BnOH and biphenyl in a molar ratio of 1:1 in dichloroethane (2.0 mL, 128 µM (Au 0.2 mol%)). Biphenyl was used as an internal standard here. 17.3 mg **Au:Tetra**/Cs_2CO_3 was added to the solution and stirred at 60 °C under ambient atmosphere. An aliquot (150 µL) was taken at 2 h, 4 h, 16 h, 19 h, and 22 h. The aliquot was filtered by a syringe filter and collected. The obtained samples were analyzed by gas chromatography (GC-2025, Shimadzu) equipped with a flame ionization detector.

1.7. Time-course study of the catalytic oxidation of *p*-methoxybenzyl alcohol using AuNP/Cs_2CO_3

Catalytic oxidation of *p*-methoxybenzyl alcohol was performed under temperature control using *Chemistation* equipment (PPS-15W and PPM-5512, EYELA). To estimate the rate constant under the condition shown in Fig. S10, a tube (~15 mL volume) was filled with a solution of substrate and biphenyl in a molar ratio of 1:1 in dichloroethane (2.0 mL, 128 µM (metal 0.2 mol%)) and the gas phase was replaced with pure O_2 using a balloon. Biphenyl was used as an internal standard. **AuNP**/Cs_2CO_3 sample (**Au:Tetra**/Cs_2CO_3: 17.3 mg; **Au:Bi**/Cs_2CO_3: 14.4 mg; **Au:Mono**/Cs_2CO_3: 9.6 mg) was added to the solution and stirred at 60 °C with a pure O_2 balloon. An aliquot (150 µL) was taken at 2 h, 4 h, 22 h, and 24 h. The aliquot was filtered by a syringe filter and collected. The obtained samples were analyzed by gas chromatography (GC-2025, Shimadzu) equipped with a flame ionization detector.

1.8. Catalytic oxidation of benzyl alcohol using Au:Tetra/Al_2O_3

Catalytic oxidation of benzyl alcohol (BnOH) was performed under temperature control using *Chemistation* equipment (PPS-15W and PPM-5512, EYELA). A tube (~15 mL volume) was filled with a solution of BnOH in dichloroethane (1.0 mL, 64 µM (metal 1 mol%)) and the gas phase was replaced with pure O_2 using a balloon.
(1) With Cs_2CO_3:
40.6 mg **Au:Tetra**/Al_2O_3 sample and 30 mg Cs_2CO_3 were added to the solution and stirred at 60 °C with a pure O_2 balloon for 4 h.
(2) Without Cs_2CO_3 (control experiment):
40.6 mg **Au:Tetra**/Al_2O_3 sample was added without Cs_2CO_3, and the reaction was carried out under identical conditions (60 °C, O_2 balloon, 4 h)

The obtained solution was then filtered through a syringe filter and diluted to 10 mL in a volumetric flask. The obtained samples were analyzed by gas chromatography (GC-2025, Shimadzu) equipped with a flame ionization detector.

1.9. Hot filtration test of benzyl alcohol oxidation using AuNP/Cs_2CO_3

Catalytic oxidation of benzyl alcohol (BnOH) was performed under temperature control using

Chemistation equipment (PPS-15W and PPM-5512, EYELA). To estimate the rate constant under the condition shown in Fig. S11, a tube (~15 mL volume) was filled with a solution of BnOH and biphenyl in a molar ratio of 1:1 in dichloroethane (2.0 mL, 128 μM (metal 0.2 mol%)) and the gas phase was replaced with pure O_2 using a balloon. Biphenyl was used as an internal standard. **AuNP**/Cs_2CO_3 sample (**Au:Tetra**/Cs_2CO_3: 17.3 mg; **Au:Bi**/Cs_2CO_3: 14.4 mg; **Au:Mono**/Cs_2CO_3: 9.6 mg) was added to the solution and stirred at 60 °C with a pure O_2 balloon. An aliquot (150 μL) was taken at 2 h, 4 h, and 8 h. Then the reaction mixture was immediately passed through a syringe filter to remove the solid catalyst. The filtrate was then transferred to a clean tube and subjected to the same reaction conditions without any additional catalyst. An aliquot (150 μL) was taken at 20 h and 22 h from the beginning of the original reaction. The aliquot was filtered by a syringe filter and collected. The obtained samples were analyzed by gas chromatography (GC-2025, Shimadzu) equipped with a flame ionization detector.

1.10. Estimation of key structure parameters of AuNP

In the following estimation of key structure parameters of AuNPs, we made several approximations and assumptions: (i) the NPs are spheres with an identical diameter of d_{TEM}; (ii) all the phosphine ligands bind to the AuNP at all the P sites.

First, we estimated the number of the total Au atoms in a single AuNP (N_{Tot}) by dividing the mass of one AuNP by the mass of a single Au atom. The number of moles of Au (n_{Au}) in the sample is given as:

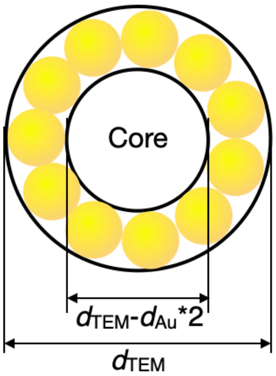
$$n_{Au} = \frac{m_{Au}}{M_{Au}} = \frac{(1-W_{Loss})m_{Sample}}{M_{Au}} \tag{S1}$$

where m_{Au} and M_{Au} represent the mass of gold contained in the sample and atomic weight of gold, respectively. For a single AuNP with an FCC stacking pattern, the N_{Tot} was estimated as follows:

$$N_{Tot} = \frac{m_{Tot}}{m_{Single\ Atom}} = \frac{V_{Tot}d_{Au}}{\frac{M_{Au}}{N_A}} = \frac{\frac{4}{3}\pi r^3 d_{Au}}{\frac{M_{Au}}{N_A}} = \frac{\frac{4}{3}\pi\left(\frac{1}{2}d_{TEM}\right)^3 d_{Au}}{\frac{M_{Au}}{N_A}} \tag{S2}$$

where m_{Tot}, V_{Tot}, d_{Au} and $m_{Single\ Atom}$ represent mass of a single AuNP, volume of a single AuNP, density of bulk gold, and mass of a single Au atom, respectively. The N_{Tot} values were 330 and 680 for d_{TEM} = 2.2 nm and 2.8 nm, respectively.

Second, we estimated the number of the surface Au atoms in a single AuNP (N_{S}) according to the model shown below:



Since d_{Au} can be approximated by the Au(111) interplanar spacing of 0.24 nm,[4] the N_{s} is given as follows:

$$N_S = N_{Tot} - N_{core} = N_{Tot} - \frac{m_{core}}{m_{Single\ Atom}} = N_{Tot} - \frac{\frac{4}{3}\pi(\frac{d_{TEM}-2\times 0.24}{2})^3 d_{Au}}{\frac{M_{Au}}{N_A}} \tag{S3}$$

where m_{core} represents mass of Au core. The N_S values were 173, 173, and 294 for **Au:Tetra**, **Au:Bi**, and **Au:Mono**, respectively.

The number of phosphine ligands contained in an AuNP sample with a mass of m_{sample} ($N_{\mathrm{phosphine}}$) is given as follows:

$$N_{Phosphine} = \frac{m_{Phosphine} \times N_A}{M_{Phosphine}} = \frac{W_{Loss} m_{Sample} N_A}{M_{Phosphine}} \tag{S4}$$

where $m_{Phosphine}$, N_A, and W_{Loss} represent mass of phosphine ligands in the sample, Avogadro constant, and weight percentage of the ligand determined by TGA, respectively. The number of the ligands on a single NP (n_L) is expressed as:

$$n_L = \frac{N_{Phosphine}}{N_{AuNP}} = \frac{W_{loss} d_{Au} N_A \frac{4}{3}\pi\left(\frac{1}{2}d_{TEM}\right)^3}{(1-W_{loss}) M_{Phosphine}} \tag{S5}$$

where N_{AuNP} represents the total number of AuNPs in the sample given by:

$$N_{AuNP} = \frac{n_{Au}}{N_{Tot}} N_A = \frac{(1-W_{loss}) m_{sample}}{\frac{4}{3}\pi\left(\frac{1}{2}d_{TEM}\right)^3 d_{Au}} \tag{S6}$$

The n_L values were 16, 30, and 69 for **Au:Tetra**, **Au:Bi**, and **Au:Mono**, respectively.

Therefore, the number of the unligated surface Au atoms in a single AuNP (N_{ULS}) is given by:

$$N_{ULS} = N_S - n_L \times D \tag{S7}$$

where D is a denticity of the ligand. Thus, the N_{ULS} values were 109, 113, and 225 for **Au:Tetra**, **Au:Bi**, and **Au:Mono**, respectively.

The ratio of the ligated surface Au atoms with respect to the total surface Au atoms in a single AuNP (R_{LS}) is given as follows:

$$R_{LS} = \frac{n_L \times D}{N_S} \tag{S8}$$

Thus, the R_{LS} values were 0.37, 0.35, and 0.23 for **Au:Tetra**, **Au:Bi**, and **Au:Mono**, respectively.

The ratio of the unligated surface Au atoms with respect to the total Au atoms in a single AuNP (R_{ULS}) is given as:

$$R_{ULS} = \frac{N_{ULS}}{N_{Tot}} \tag{S9}$$

The R_{ULS} values were 0.33, 0.34, and 0.33 for **Au:Tetra**, **Au:Bi,** and **Au:Mono**, respectively.

2. Results

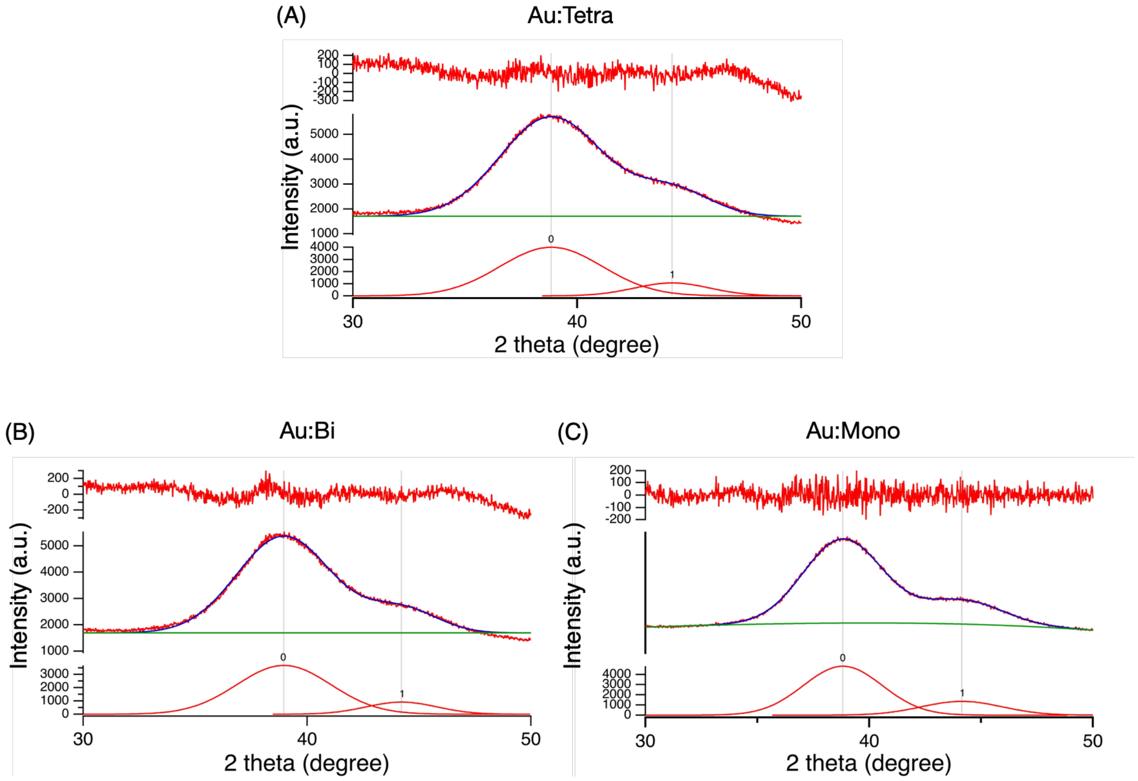


Fig. S1 PXRD patterns showing the (111) and (200) diffraction peaks and their fitted curves for (A) **Au:Tetra**, (B) **Au:Bi**, and (C) **Au:Mono**. The top trace of each pattern represents the difference between the experimental and fitted patterns.

Table S1. Parameters Used in Scherrer's Equation in Figure S1.

Sample	K	λ (nm)	FWHM (°)	2θ (°)	Crystallite size (nm)
Au:Tetra	0.9	0.154	5.36	38.8	1.9
Au:Bi			4.95	39.0	2.1
Au:Mono			4.16	38.8	2.5

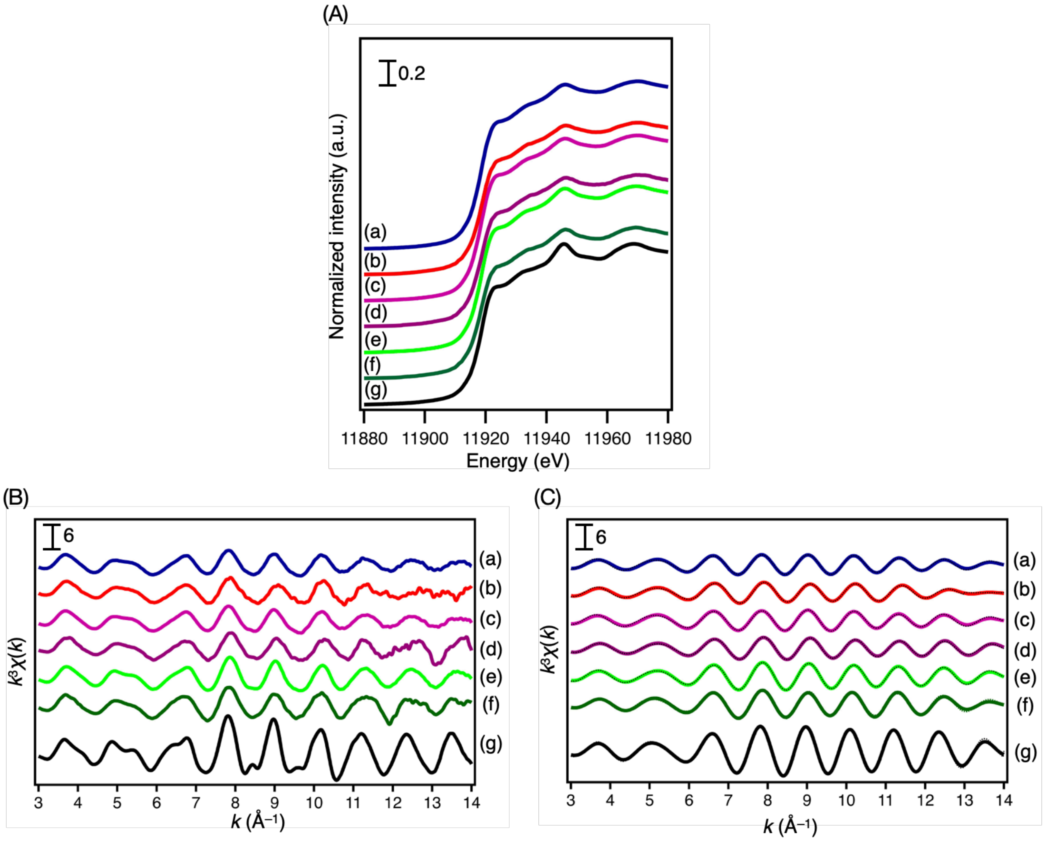


Fig. S2 Au L$_3$-edge (A) XANES spectra, (B) EXAFS oscillations and (C) fitted curves of EXAFS in *k*-space over the *r* range of 1.6–3.1 Å of (a) **Au:Tetra**, (b) **Au:Tetra**/Cs$_2$CO$_3$, (c) **Au:Bi**, (d) **Au:Bi**/Cs$_2$CO$_3$, (e) **Au:Mono**, (f) **Au:Mono**/Cs$_2$CO$_3$ and (g) Au foil. In panel (c), the dotted and solid lines represent the raw and fitted data, respectively.

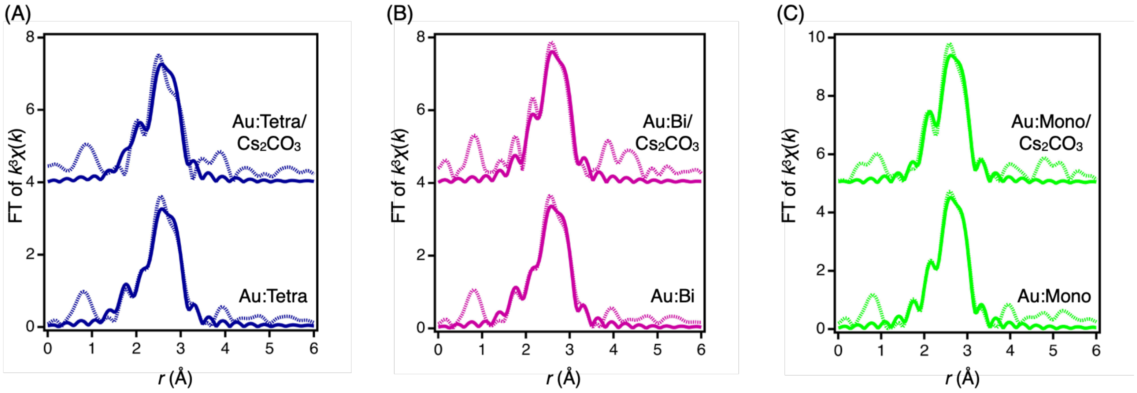


Fig. S3 Au L$_3$-edge FT-EXAFS of unsupported AuNPs and deposited samples protected by (A) TDEP, (B) DPPE, and (C) TPP. Dotted and solid lines represent the raw and fitted data, respectively.

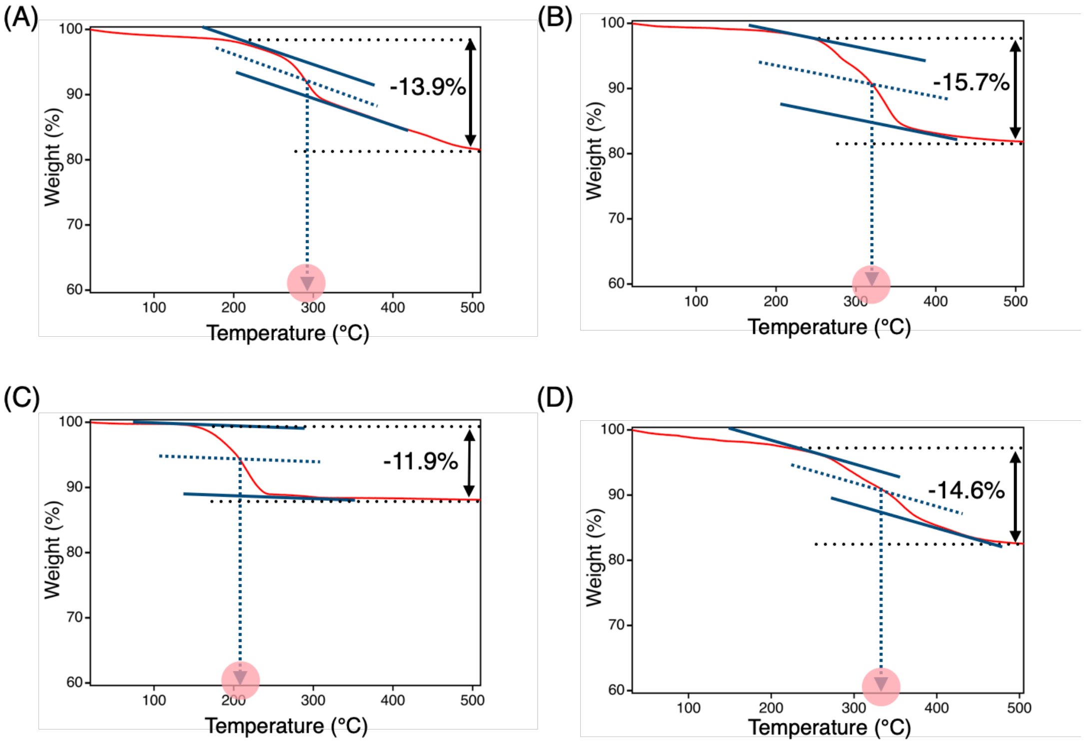


Fig. S4 TG analysis curve of (A) **Au:Tetra**, (B) **Au:Bi** , (C) **Au:Mono** measured in air, and (D) **Au:Tetra** measured under an N_2 atmosphere. The percentage indicates the experimental weight loss.

Table S2. Estimation of the Relative Amount of Surface-Exposed Sites in Au:Tetra (N_2)

Sample	d_{TEM}	N_{Tot}[a]	N_S[b]	n_L[c]	N_{ULS}[d]	R_{LS}[e]	R_{ULS}[f]
Au:Tetra (N_2)	2.2	330	173	17	105	0.39	0.32

[a]Number of the total Au atoms in a single AuNP. [b]Number of the surface Au atoms in a single AuNP. [c]Number of the ligands on a single AuNP. [d]Number of the unligated surface Au atoms in a single AuNP calculated by $N_{ULS} = N_S - D \cdot n_L$ (D = denticity). [e]Ratio of the ligated surface Au atoms with respect to the total surface Au atoms in a single AuNP, calculated by $R_{LS} = D \cdot n_L / N_S$. [f]Ratio of the unligated surface Au atoms with respect to the total Au atoms in a single AuNP, calculated by $R_{ULS} = N_{ULS} / N_{Tot}$.

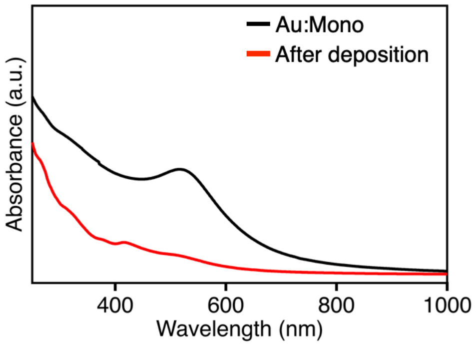
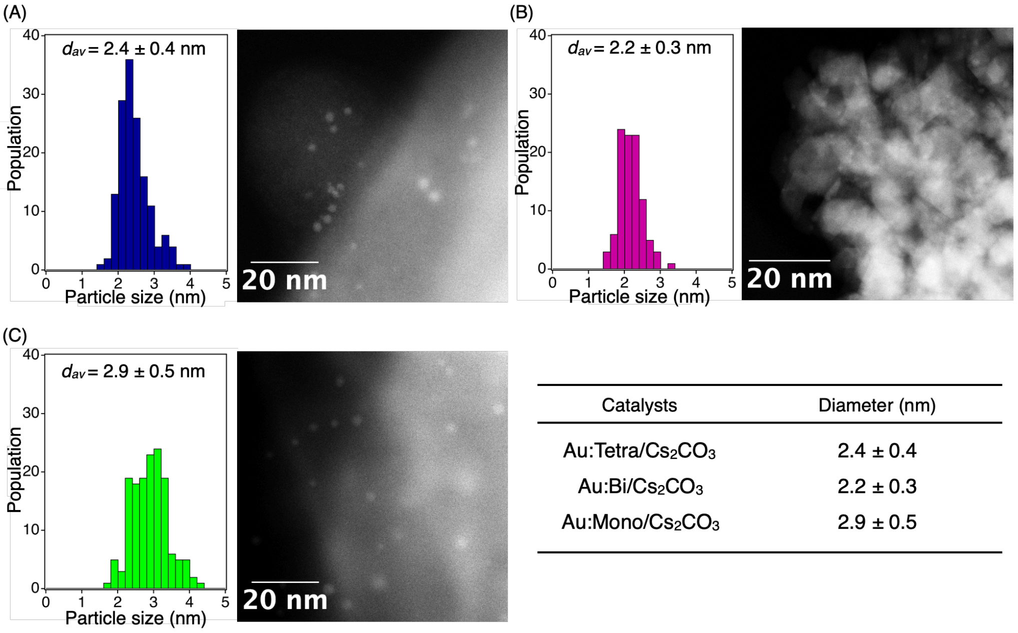


Fig. S5 UV-vis absorption spectra of the solution of AuNPs before and after deposition for **Au:Mono** dissolved in DCM.



Catalysts	Diameter (nm)
Au:Tetra/Cs_2CO_3	2.4 ± 0.4
Au:Bi/Cs_2CO_3	2.2 ± 0.3
Au:Mono/Cs_2CO_3	2.9 ± 0.5

Fig. S6 HAADF-STEM images and size distributions of (a) **Au:Tetra**/Cs_2CO_3, (b) **Au:Bi**/Cs_2CO_3, and (c) **Au:Mono**/Cs_2CO_3.

Table S3. Structural Parameters Obtained by Curve-Fitting Analysis of Au L_3-edge EXAFS

Sample	Bond	CN[a]	r (Å)[b]	σ ($Å^2$)[c]	R (%)[d]
Au foil	Au–Au	11.5(1.2)	2.85 (1)	0.0085(11)	8.5
Au:Tetra/Cs_2CO_3	Au–Au	6.8(1.3)	2.80 (1)	0.0108(15)	14
	Au–P	0.3(1)	2.36 (0)	0.0059(11)	
Au:Bi/Cs_2CO_3	Au–Au	6.9(8)	2.82 (1)	0.0102(14)	7.7
	Au–P	0.1(1)	2.30 (0)	0.0056(11)	
Au:Mono/Cs_2CO_3	Au–Au	7.4(8)	2.82 (1)	0.0096(12)	18
	Au–P	–	–	–	

[a]Coordination number. [b]Bond length. [c]Debye-Waller factor. [d]R factor, defined as follows: [e]R = $(\Sigma(k^3\chi^{data}(k) - k^3\chi^{fit}(k))^2)^{1/2}/(\Sigma(k^3\chi^{data}(k))^2)^{1/2}$. Standard deviation values are given in parathesis.

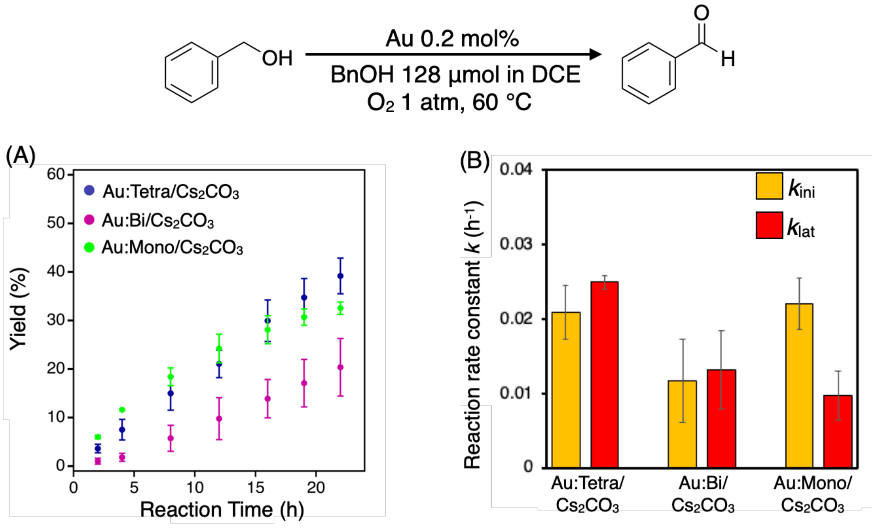
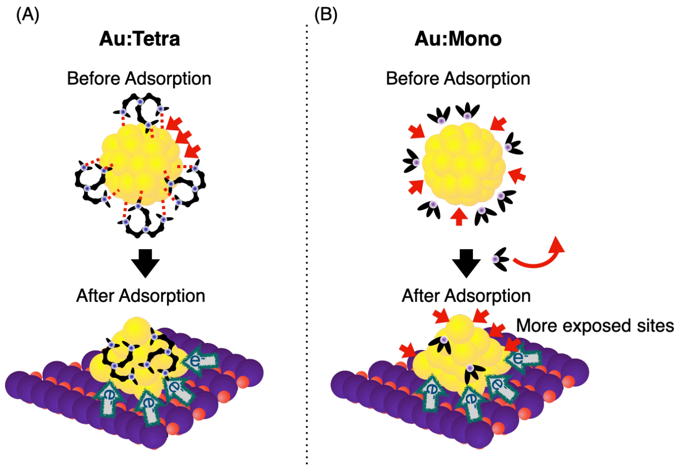


Fig. S7 (A) Time-dependent yields of benzaldehyde and (B) rate constants k_{ini} and k_{lat} for **Au:Tetra**/Cs_2CO_3, **Au:Bi**/Cs_2CO_3 and **Au:Mono**/Cs_2CO_3. The error bars on each data point correspond to the standard deviation determined by three independent measurements. Reaction conditions: BnOH 128 µmol (Au 0.2 mol%), DCE 2 mL, 60 °C, O_2 balloon.

Table S4. Summary of ICP-AES Data for All Deposited Catalysts

Sample	Weight (%)[a]	Averaged weight (%)
Au:Tetra/Cs_2CO_3	0.27	0.29
	0.31	
Au:Bi/Cs_2CO_3	0.36	0.35
	0.34	
Au:Mono/Cs_2CO_3	0.54	0.52
	0.51	
Au:Tetra/Al_2O_3	0.31	0.31

[a] Obtained by independent measurements.



Scheme S1. Illustration of the adsorption process of (A) **Au:Tetra** and (B) **Au:Mono** on Cs_2CO_3.

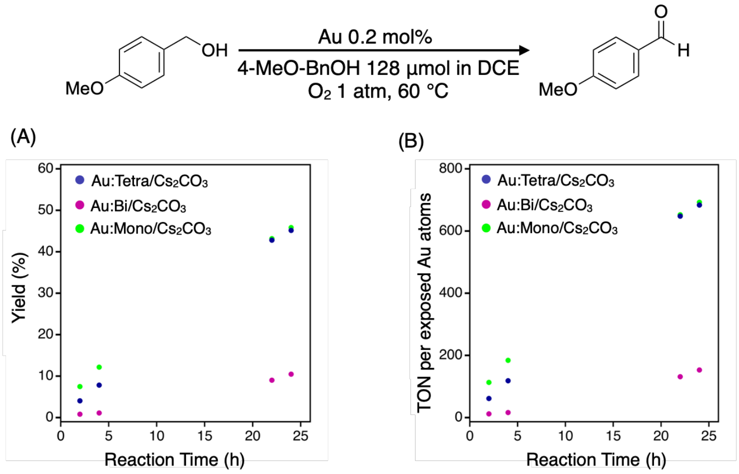


Fig. S8 Time-course (A) yield of the benzaldehyde and (B) TON for the *p*-methoxybenzyl alcohol (4-MeO-BnOH) oxidation over **Au:Tetra**/Cs_2CO_3, **Au:Bi**/Cs_2CO_3 and **Au:Mono**/Cs_2CO_3. TON was normalized by the number of unligated surface Au atoms. Reaction conditions: BnOH 128 μmol (Au 0.2 mol%), DCE 2 mL, 60 °C, O_2 balloon.

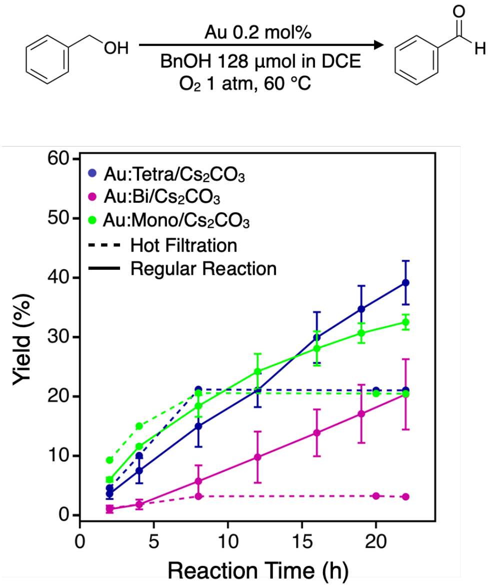


Fig. S9 The results of the hot filtration tests for **Au:Tetra**/Cs_2CO_3, **Au:Bi**/Cs_2CO_3 and **Au:Mono**/Cs_2CO_3 in benzyl alcohol oxidation. The dashed lines correspond to the yields after the removing the solid catalysts at 8 h, while the solid lines represent the yields with the solid catalysts present. Reaction conditions: BnOH 128 μmol (Au 0.2 mol%), DCE 2 mL, 60 °C, O_2 balloon.

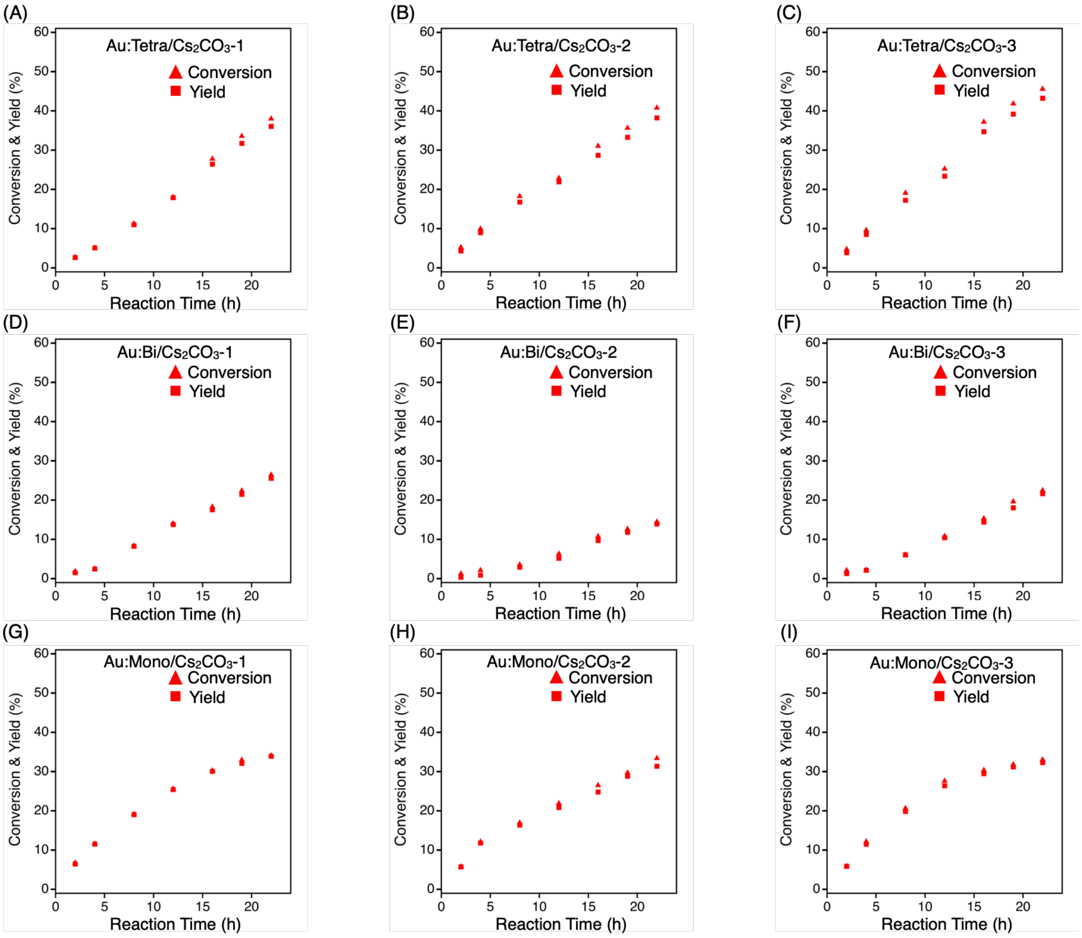


Fig. S10 The plots of conversion and yield as a fraction of time of (a) **Au:Tetra**/Cs_2CO_3-1, (b) **Au:Tetra**/Cs_2CO_3-2, (c) **Au:Tetra**/Cs_2CO_3-3, (d) **Au:Bi**/Cs_2CO_3-1, (e) **Au:Bi** /Cs_2CO_3-2, (f) **Au:Bi** /Cs_2CO_3-3, (g) **Au:Mono**/Cs_2CO_3-1, (h) **Au:Mono**/Cs_2CO_3-2 and (i) **Au:Mono** /Cs_2CO_3-3. Reaction conditions: BnOH 128 μmol (Au 0.2 mol%), DCE 2 mL, 60 °C, O_2 balloon. Each catalyst was evaluated by three independent experimental runs.

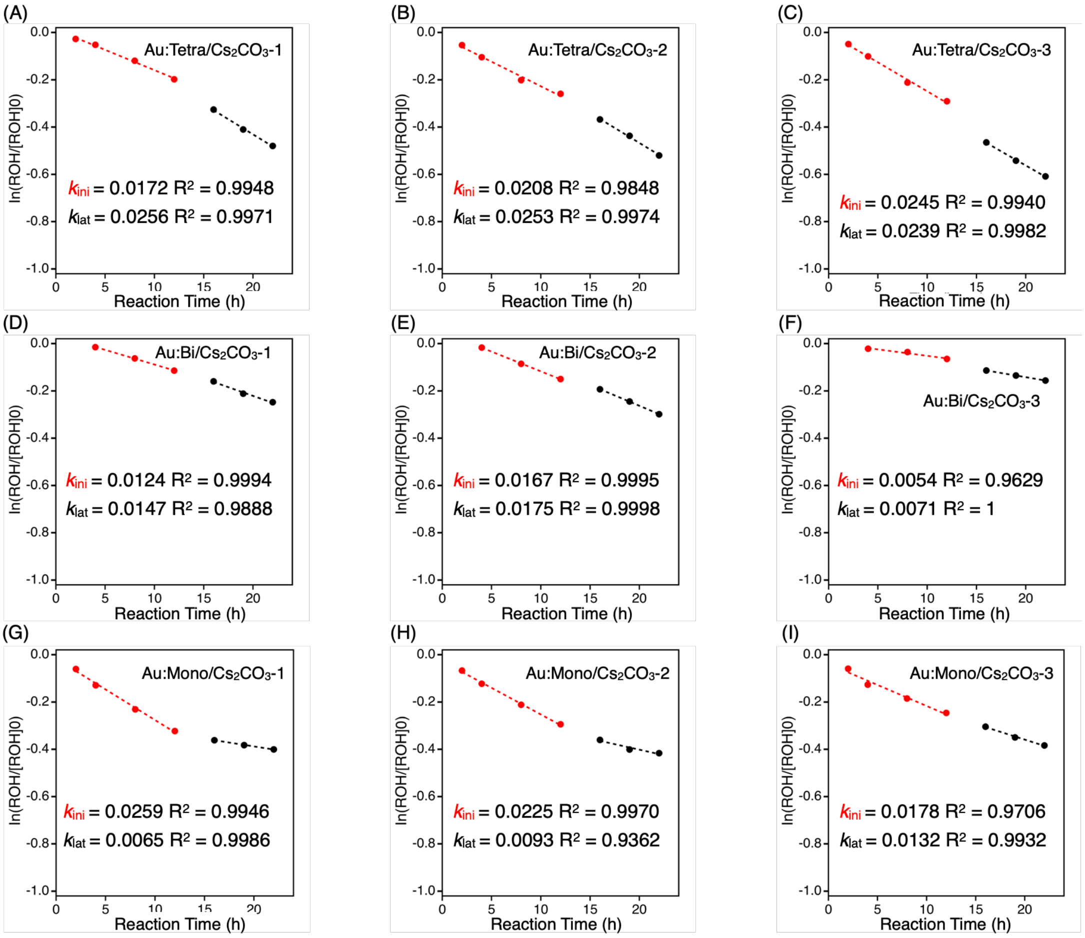


Fig. S11 Time course of the BnOH concentration during the catalytic oxidation over (a) **Au:Tetra**/Cs_2CO_3-1, (b) **Au:Tetra**/Cs_2CO_3-2, (c) **Au:Tetra**/Cs_2CO_3-3, (d) **Au:Bi**/Cs_2CO_3-1, (e) **Au:Bi** /Cs_2CO_3-2, (f) **Au:Bi** /Cs_2CO_3-3, (g) **Au:Mono**/Cs_2CO_3-1, (h) **Au:Mono**/Cs_2CO_3-2 and (i) **Au:Mono** /Cs_2CO_3-3. Reaction conditions: BnOH 128 μmol (Au 0.2 mol%), DCE 2 mL, 60 °C, O_2 balloon. Each catalyst was evaluated by three independent experimental runs.

Table S5. Normalized rate constants at the initial and later stage of BnOH oxidation

Sample	k_{ini}^* (h^{-1})	k_{lat}^* (h^{-1})
Au:Tetra/Cs_2CO_3	0.021±0.004	0.025±0.001
Au:Bi/Cs_2CO_3	0.011±0.005	0.013±0.005
Au:Mono/Cs_2CO_3	0.022±0.003	0.0097±0.0033

Reaction conditions: BnOH 128 μmol (Au 0.2 mol%), DCE 2 mL, 60 °C, O_2 balloon.

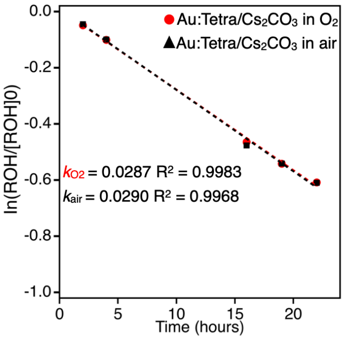


Fig. S12 Time course of the BnOH concentration during the catalytic oxidation over **Au:Tetra**/Cs_2CO_3 in O_2 and air atmosphere. Reaction conditions: BnOH 128 μmol (Au 0.2 mol%), DCE 2 mL, 60 °C, O_2 balloon.

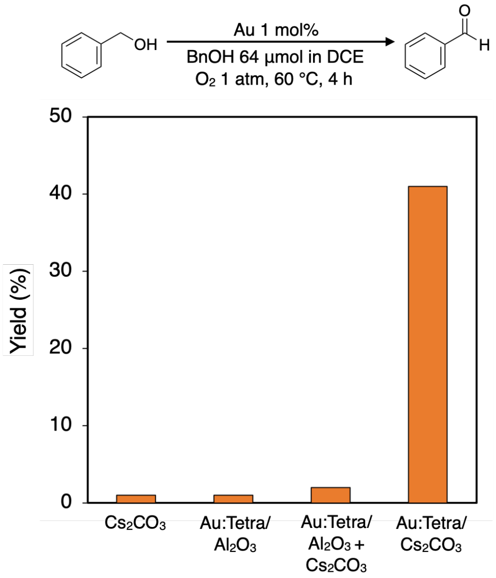


Fig. S13 Comparison of the catalytic performance of Cs_2CO_3, **Au:Tetra**/Al_2O_3, **Au:Tetra**/Al_2O_3 + Cs_2CO_3 and **Au:Tetra**/Cs_2CO_3. Reaction conditions: BnOH 64 μmol (Au 1 mol%), DCE 1 mL, 60 °C, O_2 balloon, 4 h.

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