Supplementary Information

Skeletal Au prepared from Au-Zr amorphous alloy with controlled atomic compositions and arrangement for active oxidation of benzyl alcohol

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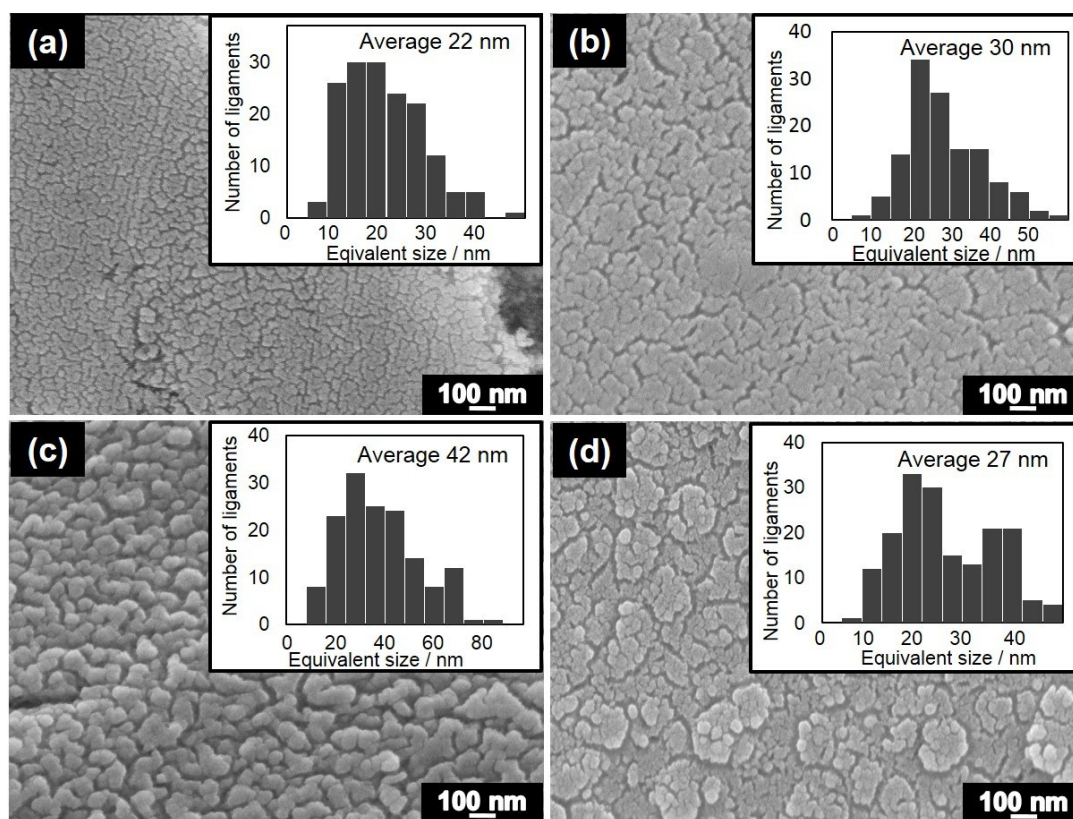
Paris, France

Fig. S1 FE-SEM images of (a) s-aAu(1 h) (b) s-aAu(3 h), (c) s-aAu(12 h) and (d) s-cAu(0.5 h) : (Inset) Distribution of Au ligament sizes.
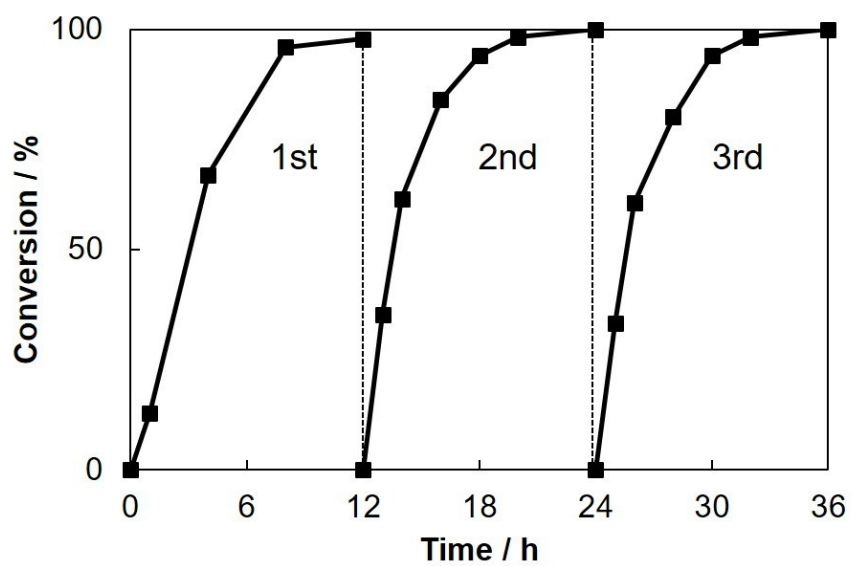
Fig. S2 Recycling experiment using s-aAu(1 h) in the oxidation of benzyl alcohol.
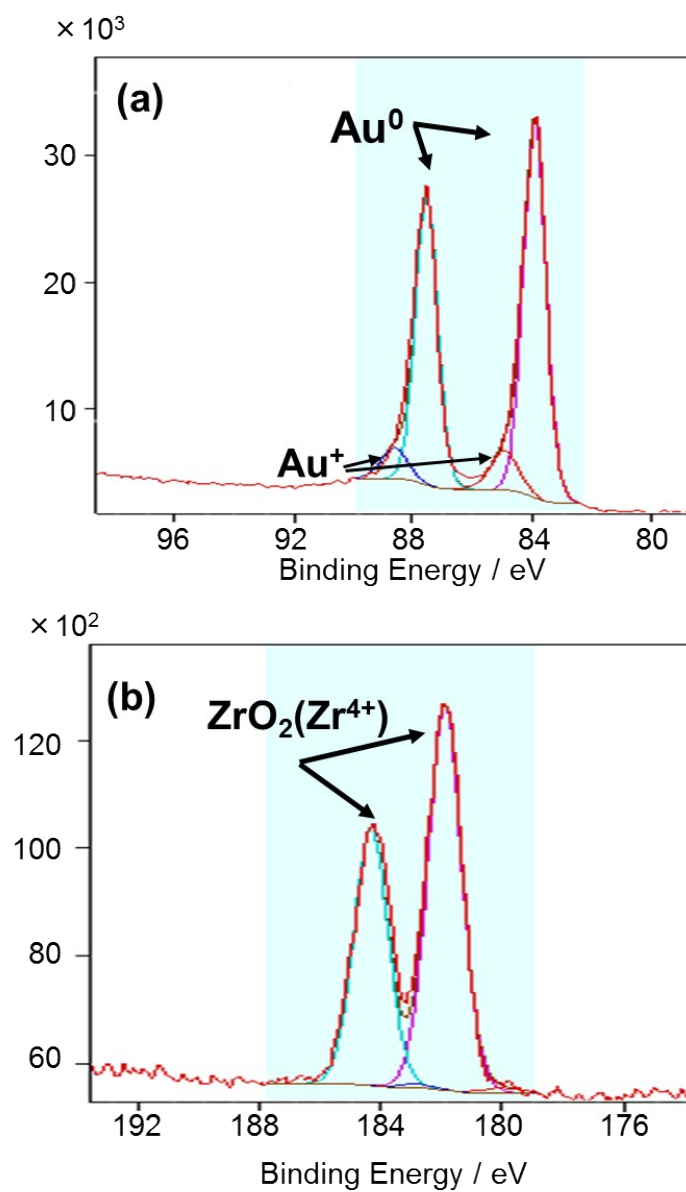
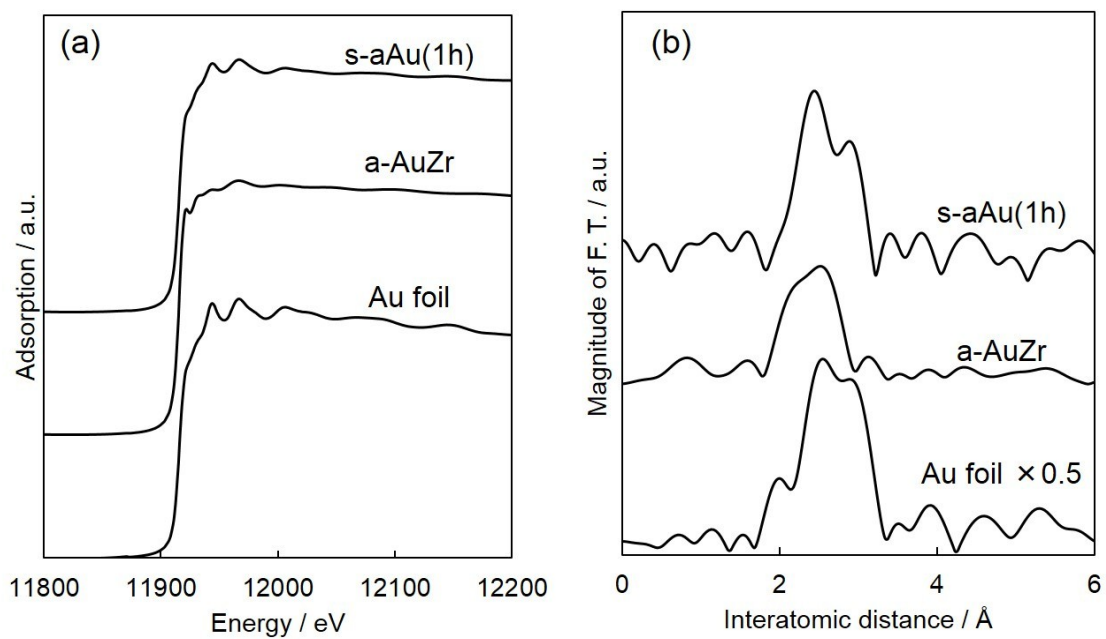**Fig. S3** XPS spectra of s-aAu(1 h) (a) Au 4f, (b) Zr3d.

Fig. S4 Au L^3-edge (a) XANES and (b) fourier transformed EXAFS spectra of Au foil, a-AuZr and s-aAu(1h). The EXAFS spectrum of Au foil reduced the scale of 1/2.
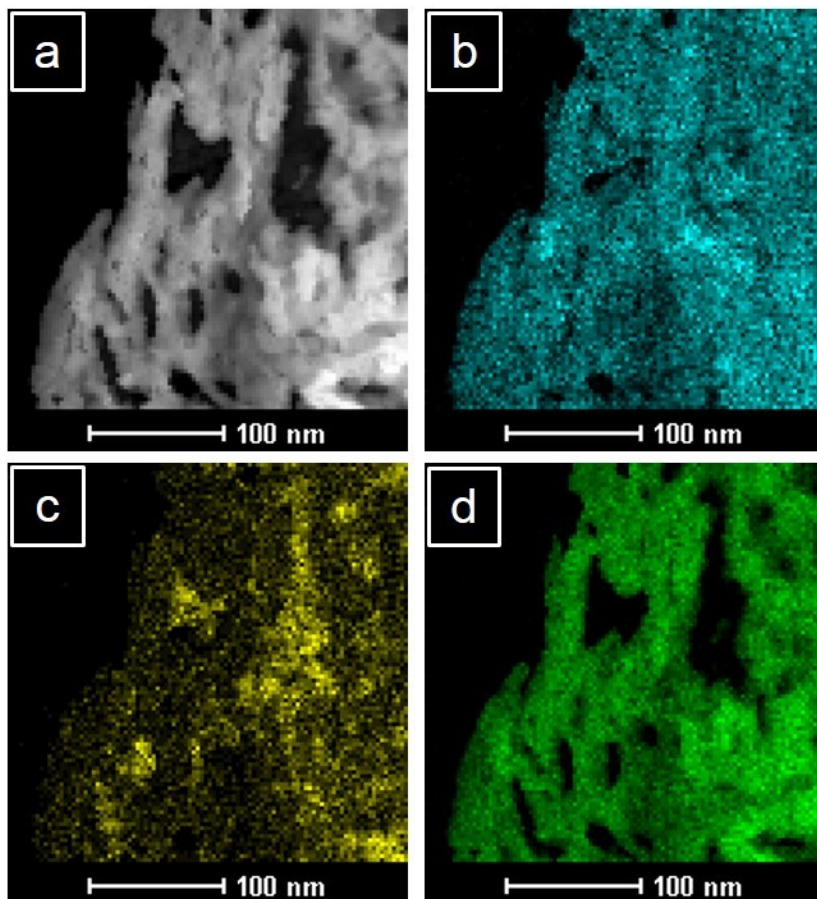
Fig. S5 TEM images of s-aAu(1h) ; **a**, dark-field TEM image. **b**, O-Kα chemical map of the selected area. **c**, Zr-Kα chemical map of the selected area. **d**, Au-Mα chemical map of the selected area.
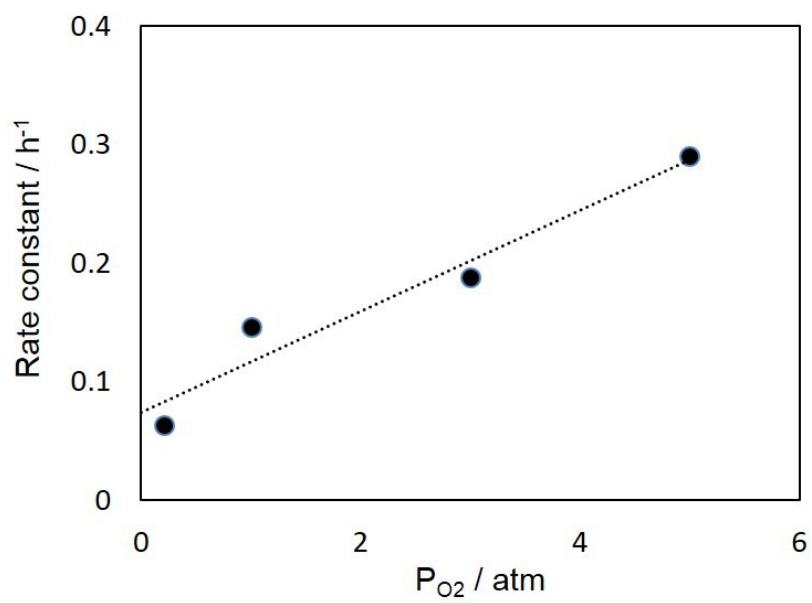
Fig. S6 The effect of oxygen pressure during the oxidation reaction on the rate constants of s-aAu(1 h).

A plausible mechanism is shown in Scheme S1.[1] In the first step of the reaction, oxygen was dissociated and adsorbed at the perimeter of the Au-ZrO$_2$ interface and deprotonation of the alcohol is promoted by the adsorbed atomic oxygen on Au. In the second step, the base in the reaction assists to cut O–H bond. In the third step, Au–OH catalyses the C-H elimination yielding benzaldehyde and H$_2$O. The perimeter between Au and ZrO$_2$ acts as active sites and base acts as a promoter.
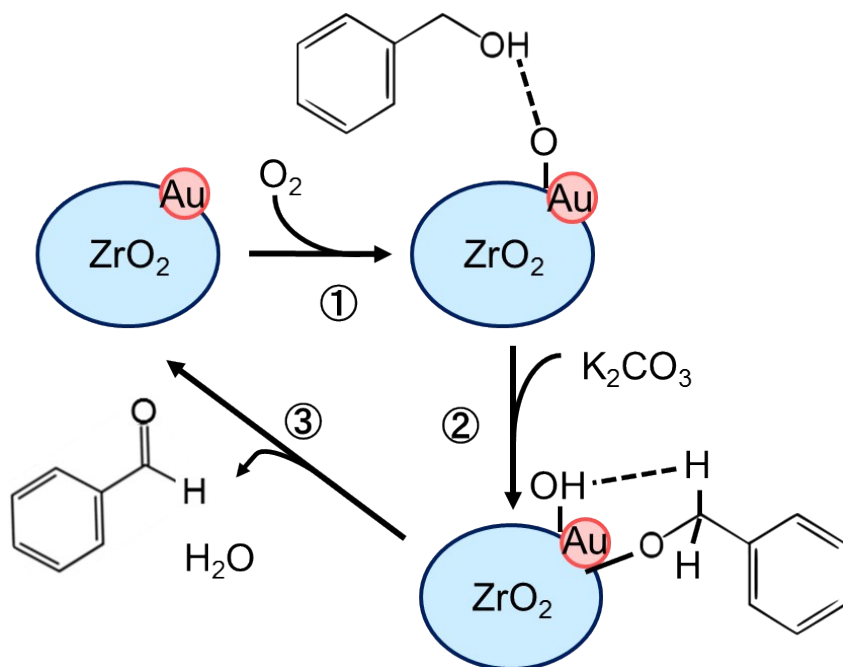
Scheme S1 Plausible mechanism for oxidation of benzyl alcohol over skeletal Au.[1]

Table S1 Rate constant and OSC of skeletal Au prepared from amorphous alloy and crystalline alloy.

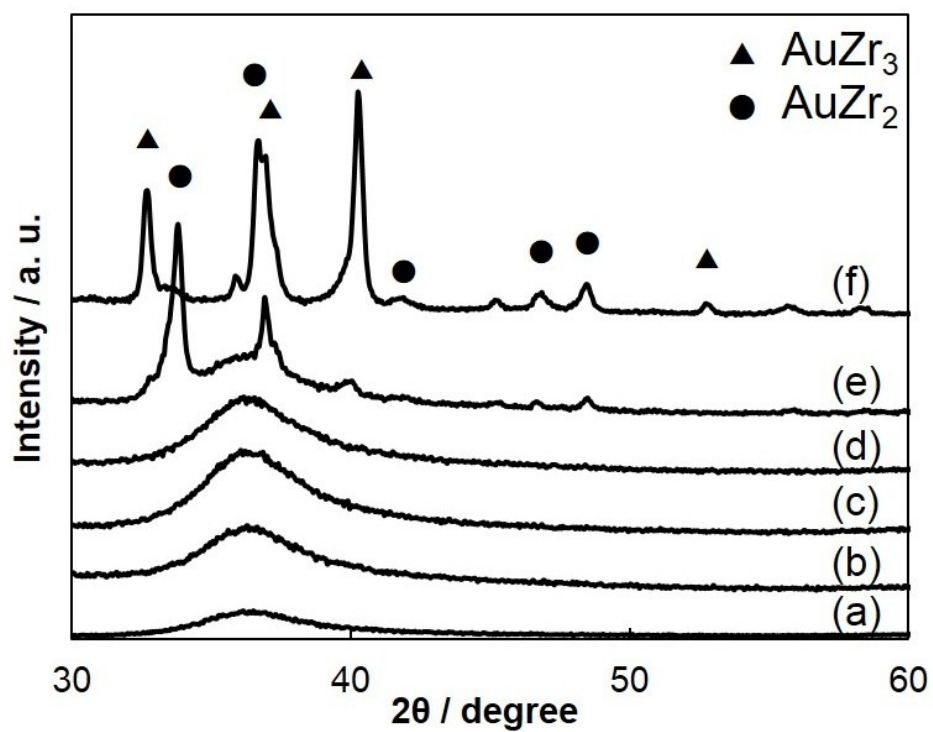|	a-AuZr	s-aAu (0.5 h)	s-aAu (1 h)	s-aAu (3 h)	s-cAu (0.5 h)
Rate constant $(10^{-3} h^{-1})$	4	7	138	42	102
OSC $(10^{-6} cm^3 mg_{Au}^{-1})$	12	62	462	164	468

Fig. S7 XRD patterns of Au-Zr alloy heated at various temperatures (a) a-AuZr, and (b) AuZr(473), (c) AuZr(573), (d) AuZr(673), (e) AuZr(773), and (f) AuZr(873).

Table S2 Apparent activation energies over the various Au catalysts.

Catalysts	Ea (kJ/mol)
s-aAu(1 h)	19.0
s-cAu(0.5 h)	25.7
Au(1)/ZrO_2	50.2
Au NP (PVP)[a]	45
Au/TS-1[b]	38.2

[a]Ref. [2], [b]Ref.[3]

The apparent activation energies were estimated from Arrhenius plots for oxidation of benzyl alcohol over different Au catalysts (Fig. S7, Table S2). The value of activation energy over the s-aAu(1 h) was estimated to be 19.0 kJ/mol, which was slightly lower than that over s-cAu(0.5 h) (25.7 kJ/mol). It is assumed that the unsaturated Au atoms in s-aAu(1 h) strongly stabilize the terminal O of O_2 on ZrO_2 and led to lower activation energy, as described above. However, the value of activation energy over Au nanoparticles supported on ZrO_2 (Au/ZrO_2) was higher (50.2 kJ/mol) than that over skeletal Au catalysts. There are some studies on activation energy for oxidation of benzyl alcohol over Au catalysts. Huang et al. reported the oxidation of benzyl alcohol using Au nanoparticles as catalysts.[2] The activation energy was calculated to be 45 kJ/mol. Recently, Guowu et al. showed that the value of activation energy over Au/TS-1 was 38.2 kJ/mol.[3] In our case, the prepared skeletal Au showed quite low activation energy compared to other reported Au catalysts. The low activation energy might indicate that the oxidation of benzyl alcohol was determined by the dispersibility of catalysts.[4] The prepared skeletal Au have a ribbon shape and poor dispersibility. Kameoka et al. studied the CO oxidation over the nanoporous Au prepared from ordered $AuCu_3$ alloy by extracted Cu moieties.[5] The nanoporous Au showed lower activation energy than Au nanoparticles supported on TiO_2 (Au/TiO_2). This result corresponds well with our result, suggesting that the poor dispersibility of skeletal Au might lead to the low activation energy.
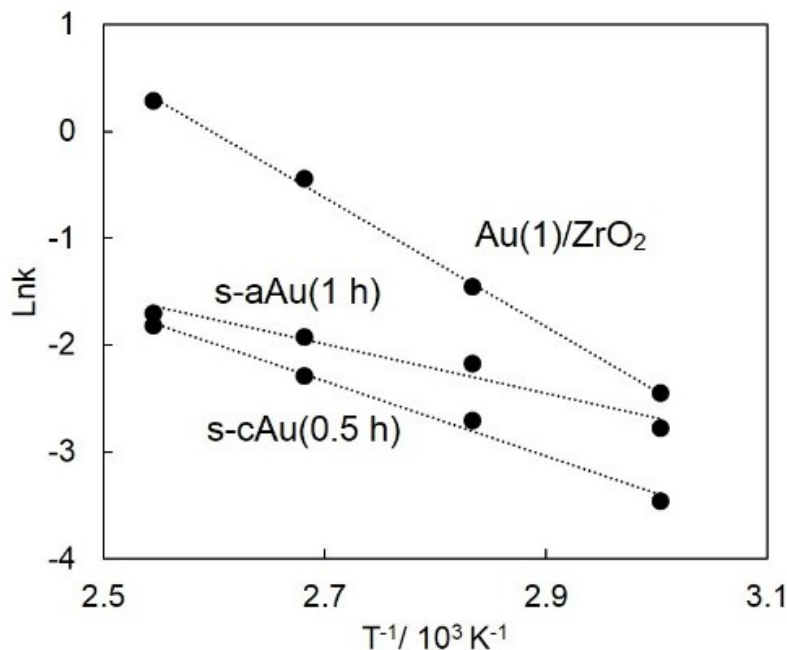

Fig. S8 Arrhenius plots of the skeletal Au and Au nanoparticles supported on ZrO_2 (Au/ZrO_2)

References

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4. A. Mehri, H. Kochkar, G. Berhault, D. F. C. Merchán and T. Blasco, Mater. Chem. Phys. 2015, 149, 59.
5. S. Kameoka and A. P. Tsai, Catal. Lett. 2010, 121, 337.