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Tailoring nano-catalysts: turn gold-nano-particles on bulk-metal-oxides to inverse nano-metal-oxides on large-gold-particles

Guofeng Zhao,[a] Xin-Ping Wu,[b] Ruijuan Chai,[a] Qiaofei Zhang,[a] Xue-Qing Gong,[b] Jun Huang*[c] and Yong Lu*[a]

[a] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China

[b] Key Laboratory for Advanced Materials, Centre for Computational Chemistry and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, China

[c] School of Chemical and Biomolecular Engineering, University of Sydney, NSW 2006, Australia

*Corresponding author. E-mail: *ylu@chem.ecnu.edu.cn* (Y.L.); *jun.huang@sydney.edu.au* (J.H.)

Experimental

Catalysts preparation

The catalyst Au/Ti-fiber was prepared by impregnating paper-like 40-μm Ti-fiber substrate with $HAuCl_4$ solution, which was then dried at 80 ^oC overnight, and subsequently calcined at 400 ^oC for 4 h in ultra-purified Ar atmosphere. The Au/Ti-fiber catalyst was then re-impregnated with aqueous $M(NO_3)_2$ (M = Ni, Mn, and Co) solutions followed by drying at 80 ^oC overnight, impregnating by concentrated ammonia solution, and calcining at 400 ^oC for 2 h in ultra-purified Ar atmosphere, and the nitrate salts were transformed into the corresponding oxide nanoparticles (ONPs). The ONPs phase and co-existed Au particles produce a ONPs-decorated Au/Ti-fiber catalyst (denoted as ONPs/Au/Ti-fiber). The catalysts with different Au and ONPs loadings were prepared by the same procedures except tuning the amount of $HAuCl_4$ and corresponding nitrates in their solutions. In addition, Au/Ti-fiber catalyst was also re-impregnated with aqueous $Mn(Ac)_2$, $Co(Ac)_2$ and $NiCl_2$ solutions, followed by the same procedures, and the obtained catalysts were denoted as ONPs/Au-5/Ti-fiber-Ac and ONPs/Au-5/Ti-fiber-Cl, respectively. Moreover, the ONPs/Au/Ti-fiber catalysts were conveniently prepared by co-impregnating Ti-fiber with both $HAuCl_4$ and transition metal salts solutions, drying at 80 ^oC to remove water, and then calcining at 400 ^oC in ultra-purified Ar atmosphere.

For reference, several contrastive ONPs/Ti-fiber catalysts were prepared by impregnating Ti-fiber with the aqueous solutions containing needed amount of corresponding nitrate salts, followed by drying at 80 ^oC overnight, impregnating by concentrated ammonia solution, and calcining at 400 ^oC for 2 h in ultra-purified Ar atmosphere. Then, the ONPs/Ti-fiber catalysts were re-impregnated with the aqueous solution containing needed amount of $HAuCl_4$, followed by drying at 80 ^{o}C overnight and calcining at 400 ^{o}C for 4 h in ultra-purified Ar atmosphere, and the Au/ONPs/Ti-fiber catalysts were obtained. Additionally, the Au-2/γ-Al_2O_3 catalyst (Au NPs highly dispersed on γ-Al_2O_3 with gold loading of 2 wt%) was prepared according to the reported method.[S1]

The electrolytic silver catalyst (20-40 mesh with bulk density of 5-6 g/cm^3) was purchased from the HePing noble metal catalyst company. Electrolytic silver was impregnated with aqueous $M(NO_3)_2$ (M = Ni, Mn, and Co) solutions followed by drying at 80 ^{o}C overnight, impregnating by ammonia solution (0.5 mol/L), washing with distilled water, and calcining at 400 ^{o}C for 2 h in ultra-purified Ar atmosphere.

Catalysts characterization

The catalysts were characterized by X-ray diffraction (XRD, Rigaku Uitima IV diffractometer (Cu Kα)), scanning electron microscope (SEM, Hitachi S-4800), and transmission electron microscope (TEM, JEOL-JEM-2010 instrument at 200 kV). UV-vis DRS spectra were recorded in the range 200–800 nm at room temperature using a Shimadzu UV-2400PC spectrophotometer. Gold and ONPs loadings of all the samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Thermo Scientific iCAP 6300 ICP spectrometer.

Reactivity tests

The gas-phase selective oxidation of alcohols on these catalysts was performed on a fixed-bed quartz tube reactor (600 mm length by 16 mm inner diameter) under atmospheric pressure as described previously.[S2] The catalyst used in testing experiments was 0.3 g if not specifically noted. Alcohols were continuously fed using a high-performance liquid pump in parallel with O_2

(oxidant) and N_2 (diluted gas of 50 mL/min) feeding using calibrated mass flow controllers into the reactor. Weight hourly space velocity (WHSV) was calculated by dividing the mass flow rate of alcohol feedstock by the catalyst mass. The effluent was cooled using an ice-salt bath (-15 ^{o}C) to liquefy the condensable vapours for analysis using an Shimadzu-2014 GC gas chromatography-flame ionization detector (GC-FID) with a 60 m HP-5ms capillary column. The gas-phase products, such as H_2, CO_x, and C1-C3 hydrocarbons, were analyzed using an HP-5890 GC with a TCD and a 30 m AT-plot 300 capillary column.

Details for DFT calculations

PBE functional was used to do the spin-polarized DFT+U calculations by using the Vienna ab initio Simulation Package (VASP).[S3,S4] The project-augmented wave method (PAW) was used to describe the electron-core interaction with Au (5d, 6s), Ni (3d, 4s), O (2s, 2p) and H (1s) electrons being treated as valence electrons.[S5] The on-site Coulomb interaction correction was introduced to proper describe the *3d* electrons and related electronic and geometric properties of Ni. As suggested by Ebensperger et al.[S6] the Hubbard U value was set to 5.5 eV. Energy cutoff of 400 eV and 2×2×1 Monkhorst-Pack grid were used for all calculations. The structure optimizations were converged until the Hellman-Feynman forces on each ion were less than 0.02 eV/Å. The calculated lattice parameters of bulk Au (4.173 Å) and NiO (4.170 Å) which has a antiferromagnetic ground state are in good agreement with the experimental values of 4.078 Å for bulk Au[S7] and 4.177 Å for bulk NiO[S8].

The Au(111) surface was modelled by a 4-layer slab repeated in a 4×4 surface unit cell with the bottom one layer being fixed to the bulk parameters, while other layers were allowed to fully relax. For NiO, the *p*(3×3) 6-atomic layer slab and *p*(4×4) 9-atomic layer slab were used for

(100) and (111) surfaces, respectively. The bottom two/four layers of the (100)/(111) surface of NiO were fixed during structure optimizations. In the surface calculations of NiO, a ferromagnetic/antiferromagnetic alignment was set for Ni in same/neighboring planes as suggested by Ref. S6. To compensate the polarity of the NiO(111) surfaces, we used a most stable $p(2\times2)$ O-terminated octopolar NiO(111) model with the lowest surface energy.[S6] In this model (see Fig. S7), 3/4 atoms and 1/4 atoms are missing in the first and second layers with remaining atoms forming pyramids (a pyramid consists three second surface Ni atoms and one first surface O atom). For the inverse model of gold, Ni_7O_9/Au(111) and Ni_7O_6/Au(111) were constructed (see Fig. S8). To avoid interactions between slabs, all slabs were separated by a vacuum gap greater than 10 Å.

We studied some specific surface sites, i.e. fcc site of Au(111) and green O of other surfaces, for H adsorption as shown in Fig. S9. In the O vacancy formation process, the green colored O atoms were removed to calculate the reduced surfaces.

The adsorption energies of H ($E_{ad}[H]$) and O_2 ($E_{ad}[O_2]$), and the O vacacy formation energy (E_{ov}) were calculated as follows:

$$E_{ad}[H] = E_{surface} + 1/2\, E_{H2} - E_{H/surface},$$

$$E_{ad}[O_2] = E_{surface} + E_{O2} - E_{O2/surface},$$

$$E_{ov} = E_{ov/surface} + 1/2\, E_{O2} - E_{surface},$$

where $E_{surface}$, $E_{H/surface}$, $E_{O2/surface}$, $E_{ov/surface}$, E_{H2} and E_{O2} represent the DFT total energies of clean surfaces, H adsorbed surfaces, O_2 adsorbed surfaces, reduced surfaces with one O vacancy, gas-phase H_2 and O_2 molecules, respectively.

Transition states were searched with use of a constrained optimization scheme.[S9]

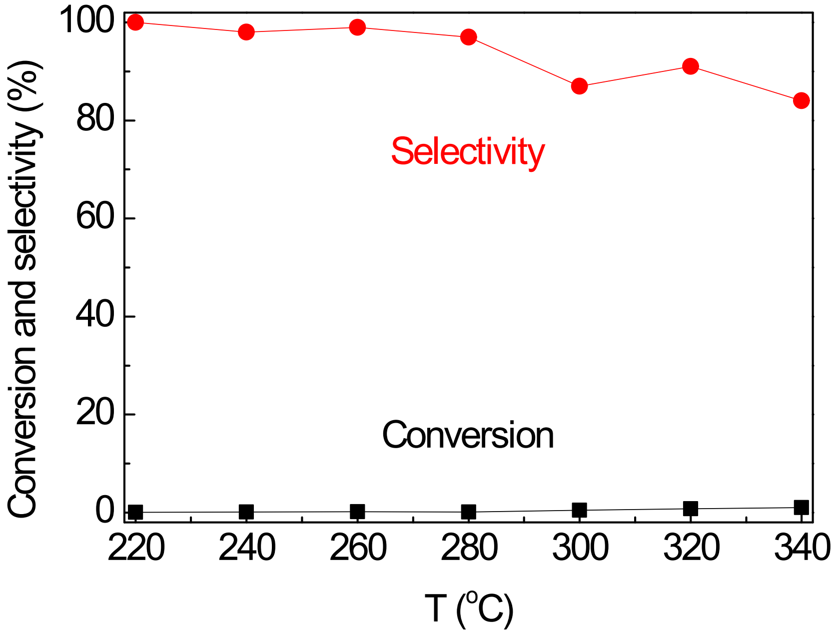


Fig. S1. The benzyl alcohol conversion and benzaldehyde selectivity over the pure Ti-fiber (~40 μm). Reaction conditions: Ti-fiber of 0.3 g, O_2/ol (molar ratio of O_2 to hydroxyl group in alcohol) of 0.6, WHSV of 20 h^{-1}, N_2 of 50 mL/min.

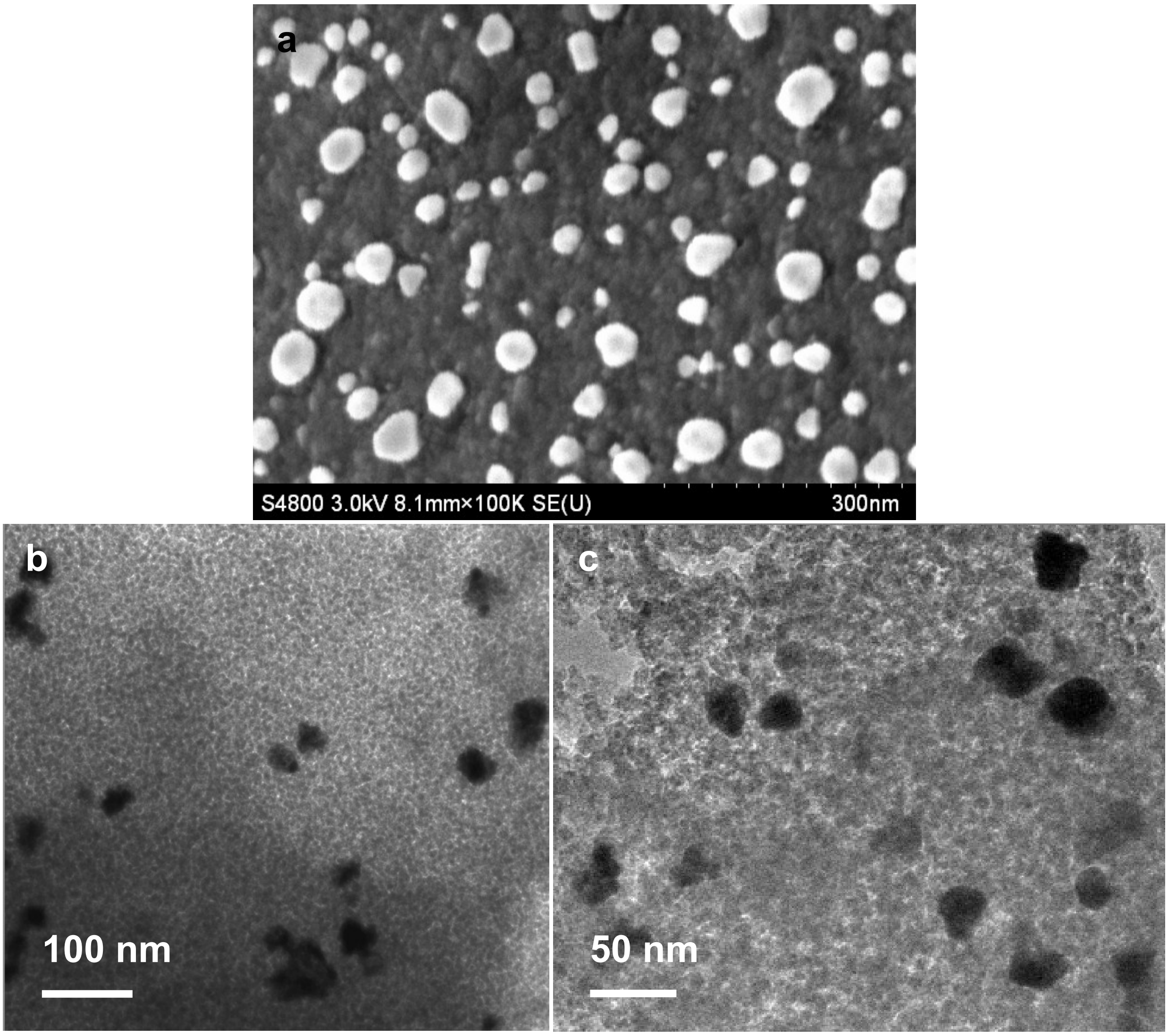


Fig. S2. (a) SEM image of the used NiO-1/Au-5/Ti catalyst as an example indicates average Au size of 40 nm is well preserved without obvious agglomeration.[S10] (b,c) TEM images of different zones of the used NiO-4/Au-5/Ti-fiber catalyst as an example to indicate that few gold particles smaller than 10 nm are observed.

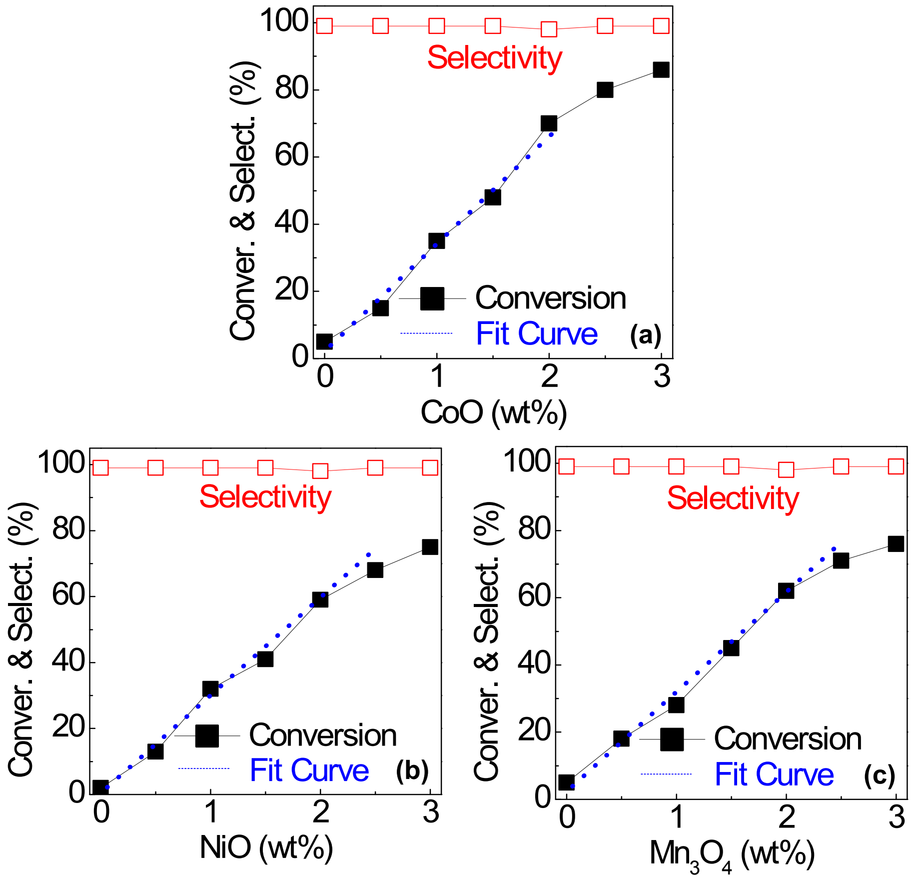


Fig. S3. The evolution of benzyl alcohol conversion along with ONPs loadings of the ONPs/Au-5/Ti-fiber. (a) CoO loading. (b) NiO loading. (c) Mn_3O_4 loading. Reaction conditions: 280 ^{o}C, WHSV of 30 h^{-1}, O_2/ol of 0.6, N_2 of 50 mL/min.

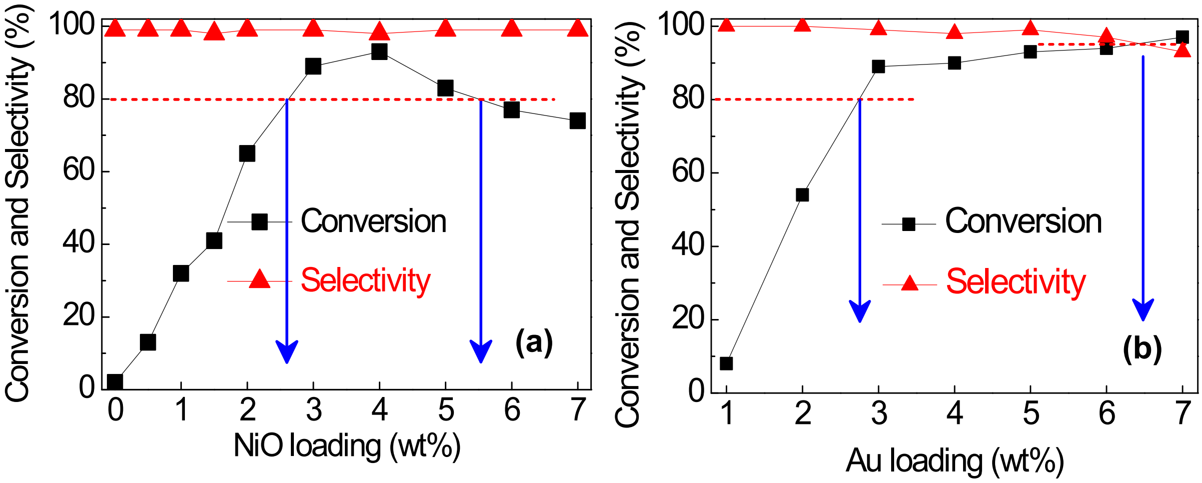


Fig. S4. The influence of Au and NiO loadings on the catalytic activity and selectivity of the catalysts NiO/Au/Ti-fiber for the gas-phase selective oxidation of benzyl alcohol at 280 ^{o}C using O_2/ol of 0.6 and WHSV of 20 h^{-1}. (a) The influence of NiO loading with Au loading of 5 wt%. (b) The influence of Au loading with NiO/Au weight ratio of 0.8.

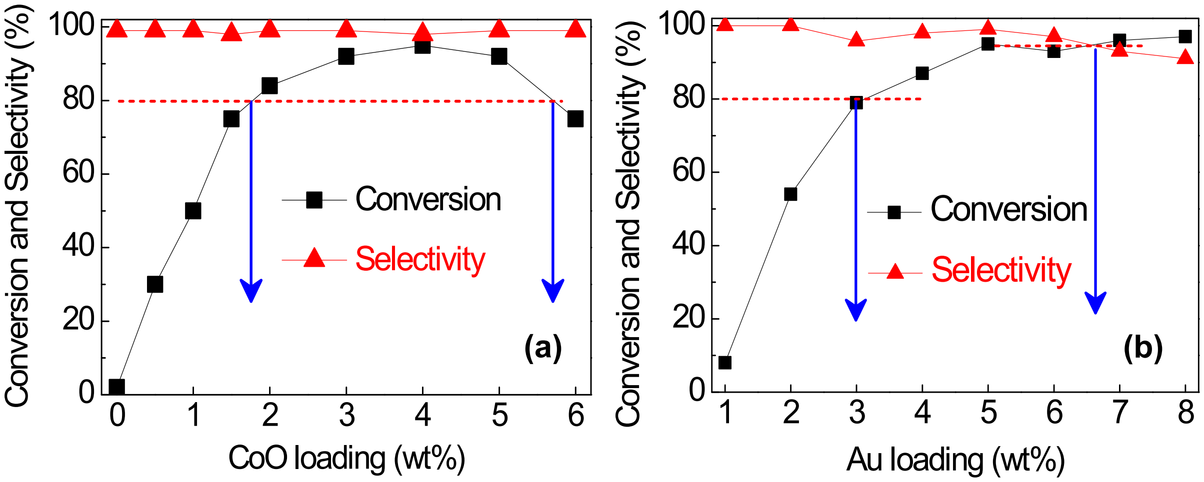


Fig. S5. The influence of Au and CoO loadings on the catalytic activity and selectivity of the catalysts CoO/Au/Ti-fiber for the gas-phase selective oxidation of benzyl alcohol at 280 ^{o}C using O_2/ol of 0.6 and WHSV of 20 h^{-1}. (a) The influence of CoO loading with Au loading of 5 wt%. (b) The influence of Au loading with CoO/Au weight ratio of 0.8.

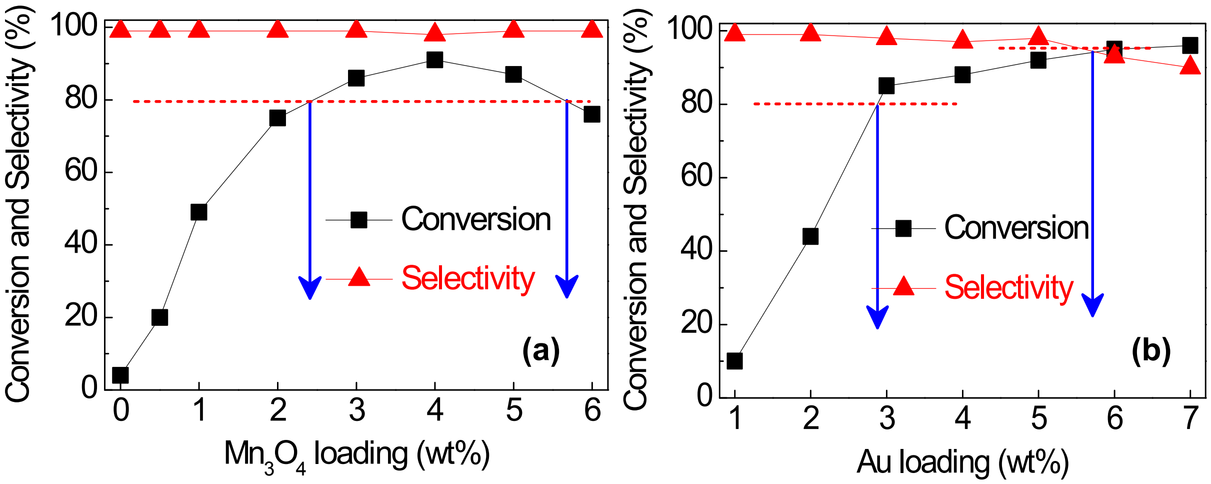


Fig. S6. The influence of Au and Mn_3O_4 loadings on the catalytic activity and selectivity of the catalysts Mn_3O_4/Au/Ti-fiber for the gas-phase selective oxidation of benzyl alcohol at 280 ^oC using O_2/ol of 0.6 and WHSV of 20 h^{-1}. (a) The influence of Mn_3O_4 loading with Au loading of 5 wt%. (b) The influence of Au loading with Mn_3O_4/Au weight ratio of 0.8.

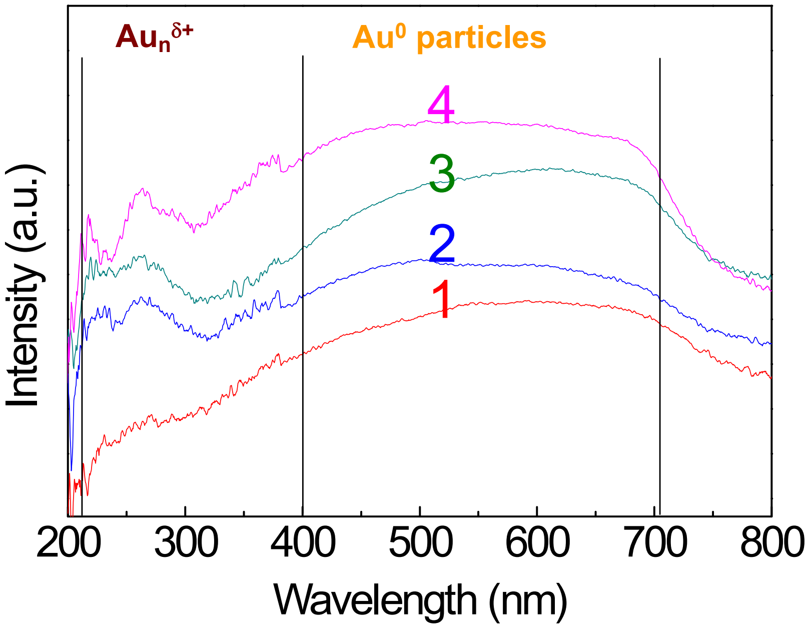


Fig. S7. Diffuse reflectance spectra of the Au-containing samples in UV-vis range. 1: Au-5/Ti-fiber; 2: NiO-4/Au-5/Ti-fiber; 3: CoO-4/Au-5/Ti-fiber; 4: Mn_3O_4-4/Au-5/Ti-fiber.

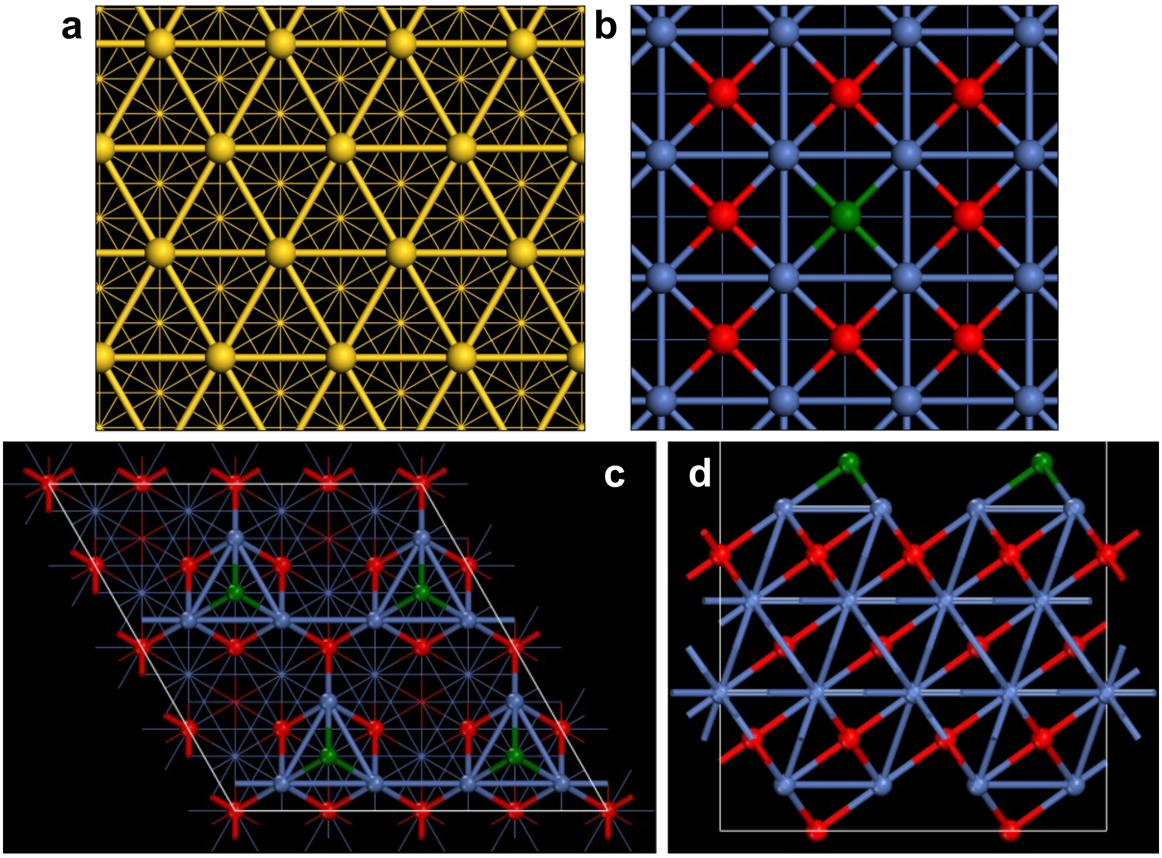
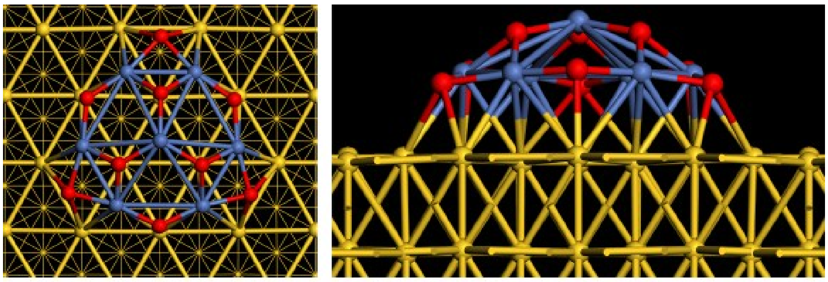
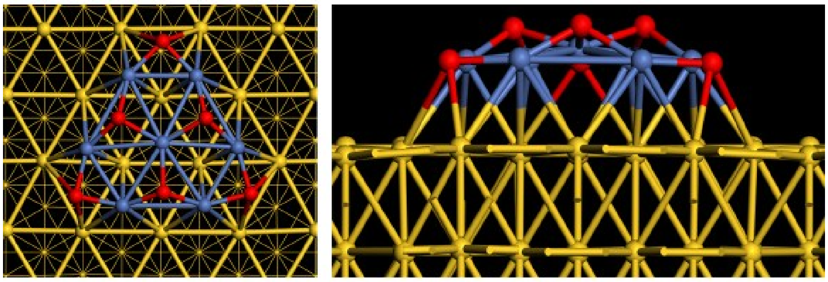


Fig. S8. (a) Top view of Au(111). (b) Top view of NiO(100). (c) Top and (d) side views of NiO(111). The first layer O atoms are green colored.

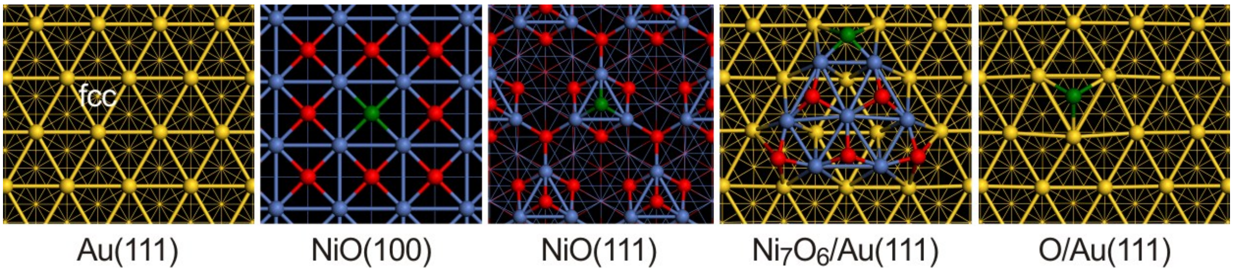


Ni_7O_9/Au(111)



Ni_7O_6/Au(111)

Fig. S9. Calculated structures of Ni_7O_9/Au(111) and Ni_7O_6/Au(111).



Au(111) NiO(100) NiO(111) Ni_7O_6/Au(111) O/Au(111)

Fig. S10. Surface sites (fcc site of Au(111) and green colored O of other surfaces) for H adsorption, and O atoms (green colored O) for removal in the O vacancy formation process.

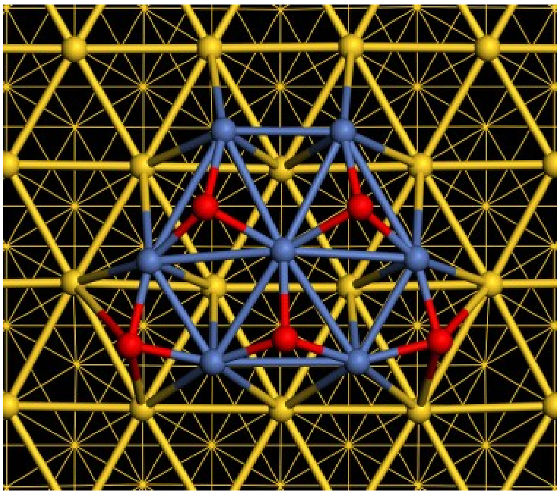


Fig. S11. The calculated structure of Ni_7O_5/Au(111).

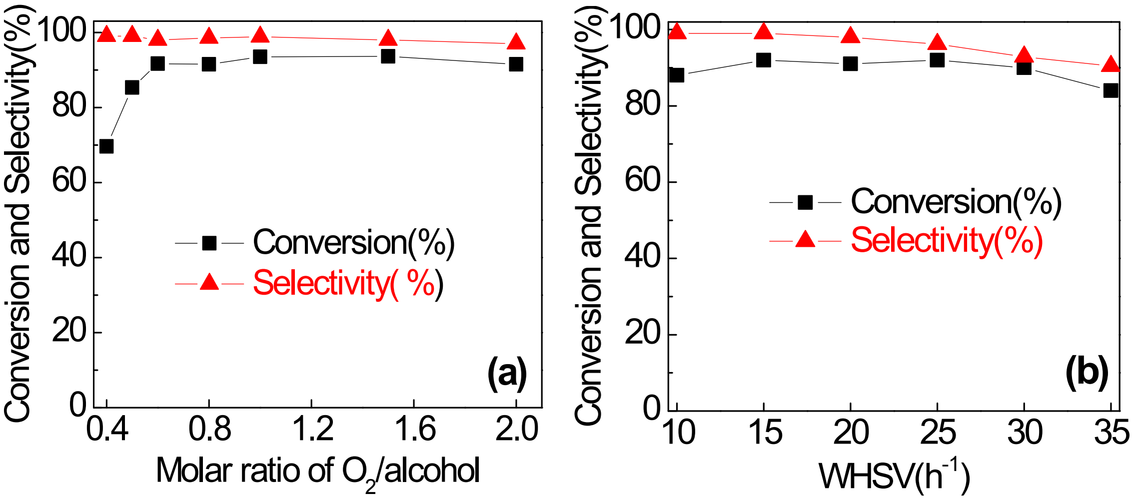


Fig. S12. Influence of reaction condition ((a) molar ratio of O_2/ol and (b) WHSV) on gas-phase selective oxidation of benzyl alcohol over the catalyst CoO-4/Au-5/Ti-fiber.

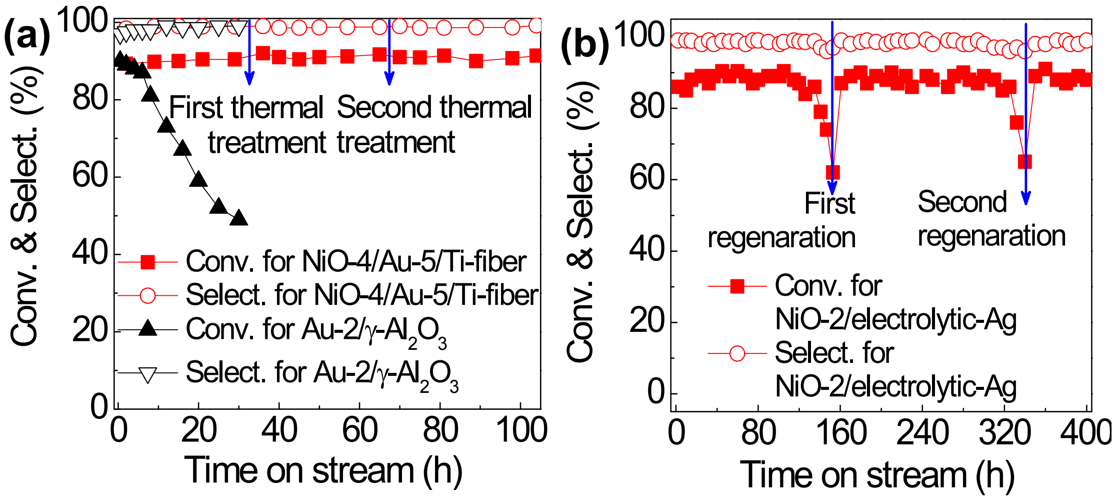


Fig. S13. Long-term stability tests for the gas-phase selective oxidation of benzyl alcohol. (a) Au/γ-Al_2O_3 and NiO-4/Au-5/Ti-fiber (catalyst of 0.3 g, 280 ^oC, WHSV of 20 h^{-1}, O_2/ol of 0.6, N_2 of 50 mL/min). (b) NiO-2/electrolytic-Ag (catalyst of 2 g, 280 ^oC, WHSV of 3 h^{-1}, O_2/ol of 0.6, N_2 of 50 mL/min).

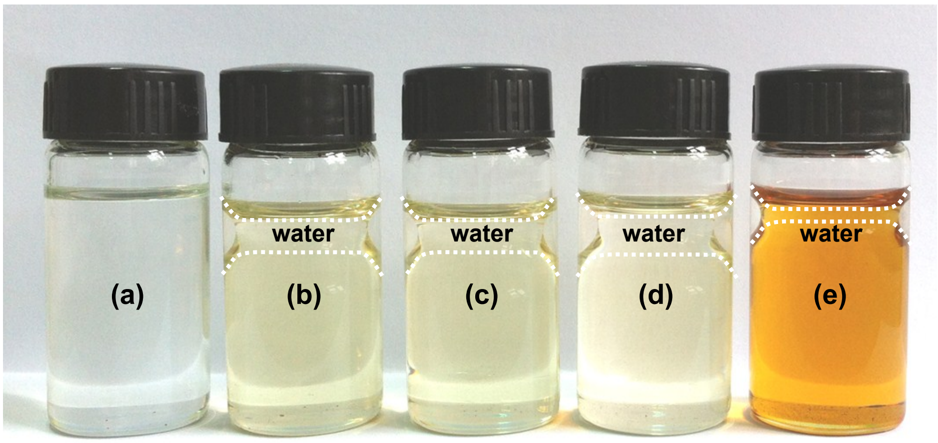


Fig. S14. (a) Pure product purchased from Alfa Aesar (CAS: 100-52-7, Benzaldehyde, 99+%). (b) Obtained from NiO-4/Au-5/Ti-fiber. (c) Obtained from Mn_3O_4-4/Au-5/Ti-fiber. (d) Obtained from CoO-4/Au-5/Ti-fiber. (e) Obtained from Au-2/γ-Al_2O_3. Reaction conditions of ONPs-4/Au-5/Ti-fiber: catalyst of 0.3 g, 280 ^oC, WHSV of 20 h^{-1}, O_2/ol of 0.6, N_2 of 50 mL/min. Reaction conditions of Au-2/γ-Al_2O_3: catalyst of 0.3 g, 280 ^oC, O_2/ol of 0.6, WHSV of 20 h^{-1}, N_2 of 50 mL/min. Substrate: Benzyl alcohol.

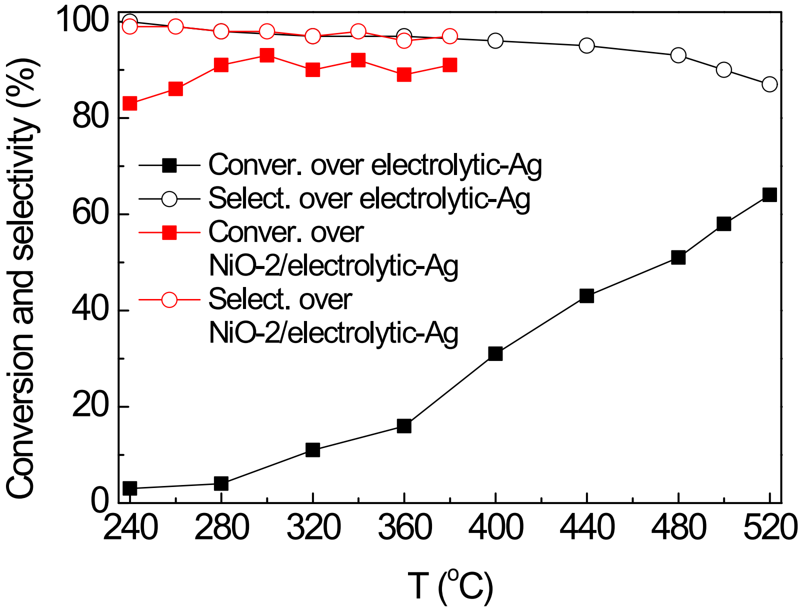


Fig. S15. The gas-phase selective oxidation of benzyl alcohol over electrolytic-Ag and NiO-2/electrolytic-Ag. Reaction conditions: catalyst of 2 g, O_2/ol of 0.6, WHSV of 3 h^{-1}, N_2 of 50 mL/min.

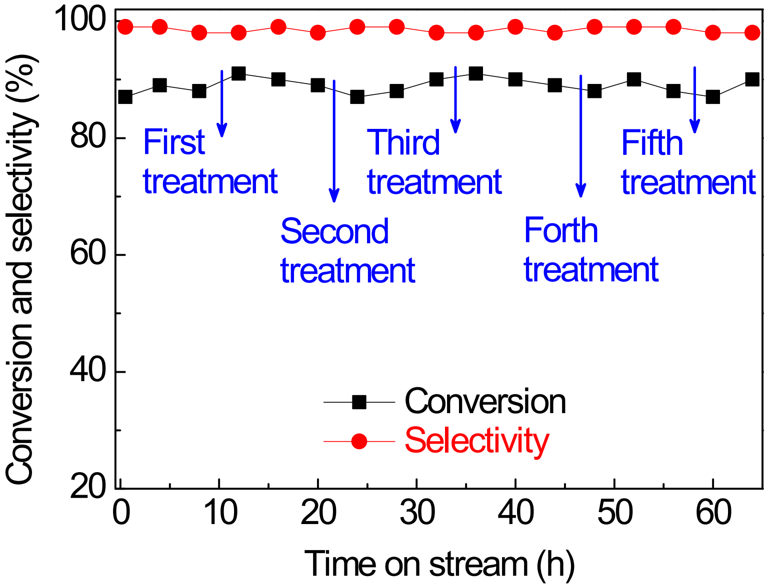


Fig. S16. The stability and regenerability testing of the NiO-2/electrolytic-Ag for gas-phase selective oxidation of benzyl alcohol. Reaction conditions: catalyst of 2 g, O_2/ol molar ratio of 0.6, WHSV of 3 h^{-1}, N_2 of 50 mL/min. Thermal treatment conditions: 500 ^{o}C, in air, 2-4 hours.

Table S1. The catalytic performance of the various catalysts for benzyl alcohol oxidation.

Entry	Catalyst	Au Size (nm)	Temp. (^{o}C)	Con. (%)	Rate$_{Reaction}$[a] ($g_{BzH}/(g_{cat.}\cdot h)$)	Select. (%)[b]				
						A	B	C	D	E
1[c]	Au-5/Ti-fiber	~ 40	300	2.1	0.6	97.3	0.7	0.6	1.2	0.2
2[d]	NiO-4/Au-5/Ti-fiber	~ 40	280	25.0	24.2	98.7	0.2	0.2	0.7	0.2
3[d]	NiO-4/Au-5/Ti-fiber	~ 40	250	21.4	20.8	99.0	0.2	0.3	0.3	0.2
4[d]	Mn_3O_4-4/Au-5/Ti-fiber	~ 40	280	21.9	21.3	99.2	0.1	0.2	0.4	0.1
5[d]	Mn_3O_4-4/Au-5/Ti-fiber	~ 40	250	19.7	19.1	98.7	0.1	0.5	0.6	0.1
6[d]	CoO-4/Au-5/Ti-fiber	~ 40	280	27.2	26.3	98.5	0.2	0.3	0.8	0.2
7[d]	CoO-4/Au-5/Ti-fiber	~ 40	260	25.2	24.4	98.8	0.2	0.1	0.7	0.2
8[d]	CoO-4/Au-5/Ti-fiber	~ 40	250	21.2	20.6	99.0	0.2	0.2	0.5	0.1
9[c]	NiO-4/Ti-fiber	---	300	4.8	1.4	98.6	0.3	0.4	0.6	0.1
10[c]	Mn_3O_4-4/Ti-fiber	---	300	3.4	1.0	99.1	0.3	0.1	0.4	0.1
11[c]	CoO-4/Ti-fiber	---	300	6.2	1.8	98.5	0.3	0.4	0.6	0.2
12[c,e]	Au-5/Ti-fiber & CoO-4/Ti-fiber	~ 40	280	12.4	3.6	98.4	0.3	0.5	0.6	0.2
13[c,e]	Au-5/Ti-fiber & NiO-4/Ti-fiber	~ 40	280	10.3	3.0	98.6	0.2	0.4	0.5	0.3
14[c,e]	Au-5/Ti-fiber & Mn_3O_4-4/Ti-fiber	~ 40	280	11.7	3.4	98.5	0.3	0.5	0.6	0.1
15[c]	Au-5/NiO-4/Ti-fiber	~ 30	280	21.2	6.2	99.3	0.1	0.1	0.4	0.1
16[c]	Au-5/CoO-4/Ti-fiber	~ 30	280	19.9	5.8	98.8	0.2	0.3	0.5	0.2
17[c]	Au-5/Mn_3O_4-4/Ti-fiber	~ 25	280	23.4	6.8	98.6	0.3	0.4	0.4	0.3
18[d,f]	Mn_3O_4-4/Au-5/Ti-fiber	~ 20	270	30.4	29.4	98.5	0.1	0.4	0.7	0.3
19[d,f]	NiO-4/Au-5/Ti-fiber	~ 20	270	33.4	32.5	99.0	0.1	0.2	0.5	0.2
20[d,g]	NiO-4/Au-5/Ti-fiber-Cl	~ 25	280	25.9	25.2	99.3	0.1	0.1	0.3	0.2
21[d,g]	CoO-4/Au-5/Ti-fiber-Ac	~ 25	280	25.1	24.4	98.9	0.2	0.2	0.6	0.1

22[d,g]	Mn_3O_4-4/Au-5/ Ti-fiber-Ac	~ 25	280	21.9	21.3	99.3	0.1	0.1	0.4	0.1

[a] The rate represents the mass of obtained benzaldehyde (BzH) per gram catalyst per hour. [b] The main product is benzaldehyde (A), and the by-products are benzene (B), toluene (C), benzoic acid (D) and trace CO_x (E: CO and CO_2). [c] Reaction conditions: catalyst of 0.3 g with gold loading of 4.6-4.8 wt% and oxide loading of 3.5-3.8 wt% determined by ICP-AES, O_2/ol of 0.6, WHSV of 30 h^{-1}, N_2 of 50 mL/min. [d] Reaction conditions: catalyst of 0.1 g with gold loading of 4.6-4.8 wt% and oxide loading of 3.5-3.8 wt% determined by ICP-AES, O_2/ol of 0.6, WHSV of 100 h^{-1}, N_2 of 50 mL/min. [e] The catalysts Au-5/Ti-fiber and ONPs-4/Ti-fiber are physically mixed. [f] The two catalysts are prepared by impregnating Ti-fiber with both $HAuCl_4$ and transition metal salts solutions, drying at 80 °C to remove water, and then calcining at 400 °C. [g] These catalysts are fabricated by using chloride and acetate salts as precursors, drying at 80 °C to remove water, and then calcining at 400 °C (the catalysts are denoted as ONPs/Au/Ti-fiber-Ac and ONPs/Au/Ti-fiber-Cl).

Table S2. Activation energy (Ea) of gas-phase selective oxidation of benzyl alcohol over various catalysts.[a]

Catalyst	Ea (kJ/mol)	Catalyst	Ea (kJ/mol)
CoO-0.4wt%/Ti-fiber	69	CoO-0.4wt%/Au-0.5wt%/Ti-fiber	43
NiO-0.4wt%/Ti-fiber	72	Mn_3O_4-0.4wt%/Au-0.5wt%/Ti-fiber	50
Mn_3O_4-0.4wt%/Ti-fiber	75	NiO-0.4wt%/Au-0.5wt%/Ti-fiber	46
Au-0.5wt%/Ti-fiber	87		

[a] Catalyst of 0.3 g, O_2/ol of 0.6, WHSV of 30 h^{-1}, N_2 of 50 mL/min.

Table S3. Oxidation of various alcohols catalyzed by CoO-4/Au-5/Ti-fiber.[a]

Substrate	O_2/ol (mol/mol)	Temp. (°C)	Conversion (%)	Selectivity (%)
1-phenylethanol	0.6	280	94	98
2-phenylethanol	0.7	320	54	98
1-octanol	0.6	280	58	92
2-octanol	0.6	280	25	67
Cyclohexanol	0.6	280	72	93
1,2-propanediol	1.2	300	84	74

[a] Catalyst of 0.3 g, WHSV of 20 h^{-1}.

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