Electronic Supplementary Information (ESI)

1. Experimental procedures

$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ (CZB) solid solution was prepared by mixing aqueous solutions of 1.0 mol dm^{-3} $Ce(NO_3)_3$, 0.1 mol dm^{-3} $ZrO(NO_3)_2$, and 0.5 mol dm^{-3} $Bi(NO_3)_3$ in a stoichiometric ratio. Polyvinylpyrrolidone K25 (PVP; mean molecular weight: 35,000; mean degree of polymerization: 315) was also dissolved into the mixture as a dispersant. After stirring using an agitator with a heater at 80 °C for 6 h, the solvent was removed at 180 °C. The resulting powder was dried at 80 °C for 6 h and then heated at 500 °C for 1 h in an ambient atmosphere. Supported platinum catalysts ($Pt/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$; Pt/CZB) were prepared by impregnating the CZB support with a platinum colloid stabilized with PVP. After impregnation, the catalysts were dried at 80 °C for 6 h and then calcined at 300–600 °C for 4 h. The amount of Pt in the catalyst was adjusted in the range 5–12 wt%.

The catalysts were characterized by X-ray fluorescence analysis, XRD, transmission electron microscopy (TEM), XPS, and BET specific surface area measurements. The CO oxidation activity was tested in a conventional fixed-bed flow reactor by feeding a gas mixture of CO (1 vol%) and air (balance) at a rate of 66.7 cm^3 min^{-1} over 0.2 g of catalyst; the space velocity (S.V.) over the catalyst was 20,000 cm^3 h^{-1} g^{-1}. Prior to the measurements, the catalysts were heated at 200 °C for 2 h in a flow of argon, hydrogen, or air. The in situ FT-IR spectroscopy experiments were performed in diffuse reflectance (DRIFT) mode with a PerkinElmer Spectrum One spectrometer in flowing CO(1 vol%)/air or CO(1 vol%)/H_2O(0.6 vol%)/air at 25 °C at a rate of 50 cm^3 min^{-1}. Prior to the measurement the sample was pre-heated at 200 °C for 2 h in N_2 and then cooled in N_2 to 25 °C where a background spectrum was collected. Temperature programmed reduction (TPR) and metal dispersion are measured with a BELCAT-B apparatus (BEL Japan). Reduction behavior was examined under a flow of 5%H_2–Ar (50 cm^3 min^{-1}) at a heating rate of 5 °C min^{-1}, and the metal dispersion analysis was carried out by a pulse method at –50 °C using 10%CO–He (0.03 cm^3).

2. X-ray diffraction patterns (XRD)

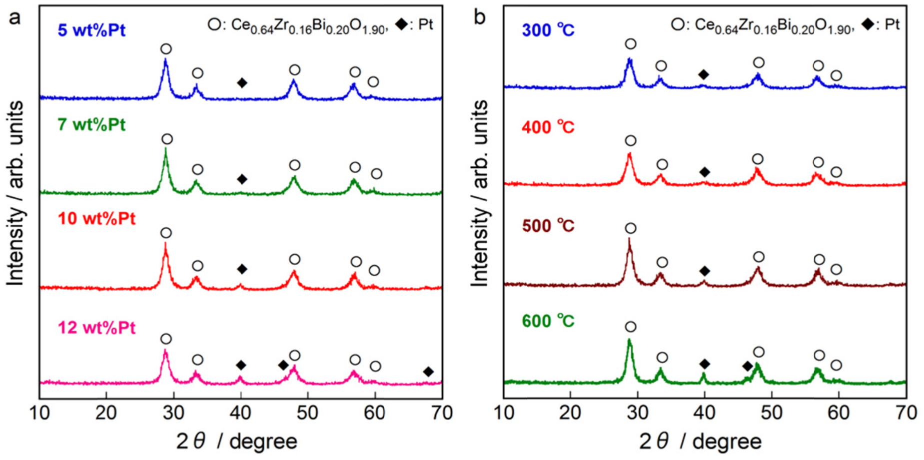

Fig. S1 a) XRD patterns of Pt(5–12 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ catalysts prepared at 500 °C; b) Those of Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ catalysts prepared at 300, 400, 500, and 600 °C.

3. BET specific surface area

Table S1 BET specific surface area of Pt(5-12 wt%)$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ catalysts

Catalyst	Preparation temperature (°C)	BET surface area (m^2 g^{-1})
5 wt%Pt/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$	500	69
7 wt%Pt/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$	500	68
10 wt%Pt/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$	500	64
12 wt%Pt/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$	500	62
10 wt%Pt/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$	300	80
10 wt%Pt/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$	400	79
10 wt%Pt/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$	600	43

4. Transmission electron microscopic image

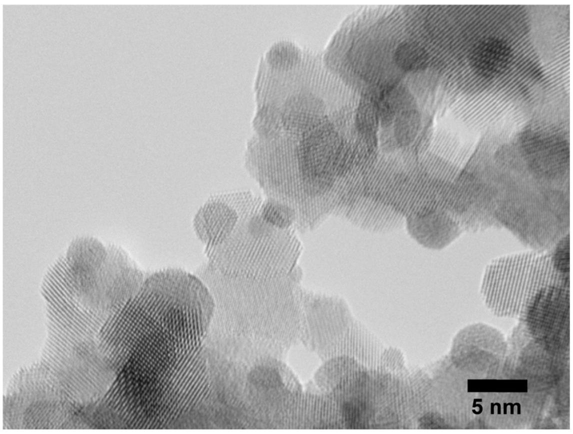

Fig. S2 Transmission electron micrograph of the Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ catalyst prepared at 400 °C.

5. X-ray photoelectron spectroscopy (XPS)

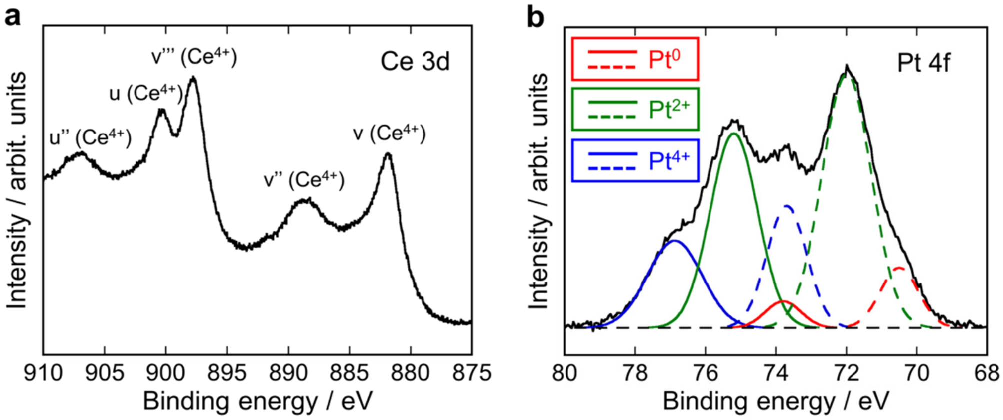

Fig. S3 XPS of a) Ce 3d core level and b) Pt 4f core level of Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ catalyst prepared at 400 °C. Solid and broken lines in b) correspond to the Pt($4f_{5/2}$) and Pt($4f_{7/2}$) peaks, respectively.

6. Pretreatment dependencies of CO oxidation on Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ calcined at 400°C

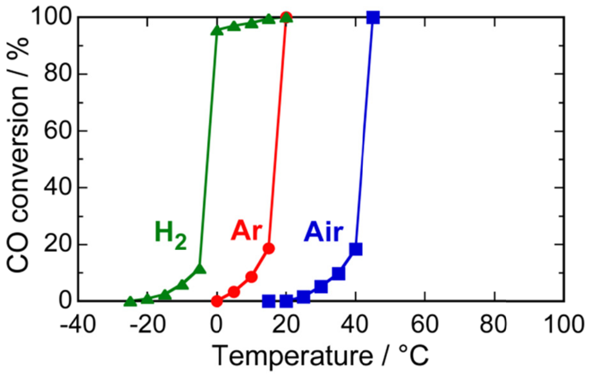

Fig. S4 Pretreatment dependencies of CO oxidation on Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ calcined at 400°C.

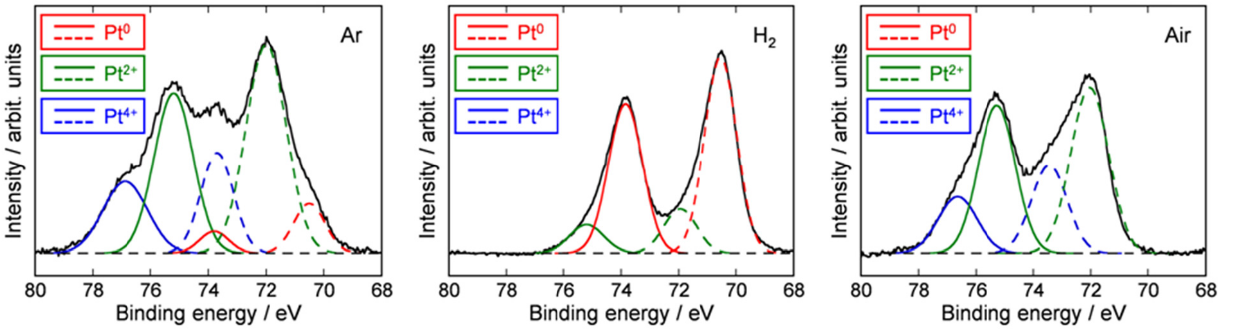

Fig. S5 Pretreatment dependencies of XPS of Pt4f core level on Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ catalyst prepared at 400 °C. Solid and broken lines correspond to the Pt($4f_{5/2}$) and Pt($4f_{7/2}$) peaks, respectively.

Table S2 Relative peak intensities of platinum species in Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ prepared at 400°C.

Pretreatment condition	Relative peak intensity		
	Pt^0	Pt^{2+}	Pt^{4+}
Ar 200°C 2h	9%	63%	28%
H_2 200°C 2h	82%	18%	0%
Air 200°C 2h	0%	69%	31%

7. Support effect on CO oxidation

Table S3 Characterization of Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ (Pt/CZB), Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Y_{0.20}O_{1.90}$ (Pt/CZY), and Pt(10 wt%)/$Ce_{0.80}Zr_{0.20}O_{2.0}$ (Pt/CZ) prepared at 400°C.

Catalyst	BET surface area (m^2 g^{-1})	Pt dispersion (%)	Reduction peak temperature (°C)	Activation energy (eV)	TOF (s^{-1})
Pt/CZB	79	2.6	–34	42	0.52 (15 °C)
Pt/CZY	107	13.3	0	117	0.19 (50 °C)
Pt/CZ	99	10.5	–11	120	0.16 (50 °C)

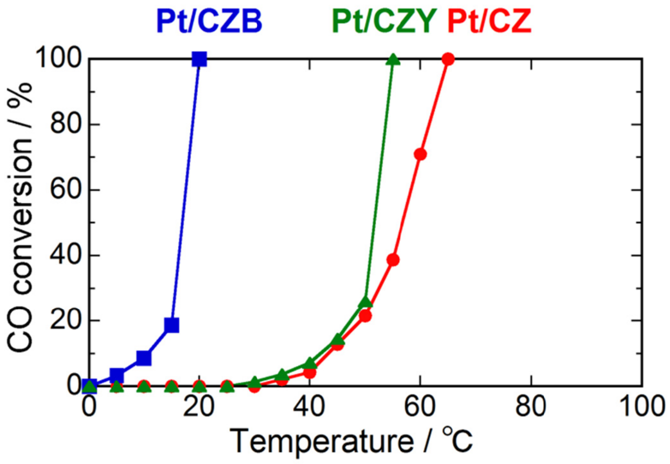

Fig. S6 Temperature dependencies of CO oxidation on Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ (Pt/CZB, 79 m^2 g^{-1}), Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Y_{0.20}O_{1.90}$ (Pt/CZY, 107 m^2 g^{-1}), and Pt(10 wt%)/$Ce_{0.80}Zr_{0.20}O_{2.0}$ (Pt/CZ, 99 m^2 g^{-1}) prepared at 400°C. It was confirmed by thermogravimetric analysis that polyvinylpyrrolidone K25 (PVP) is thermally decomposed completely by calcination at 400 °C.

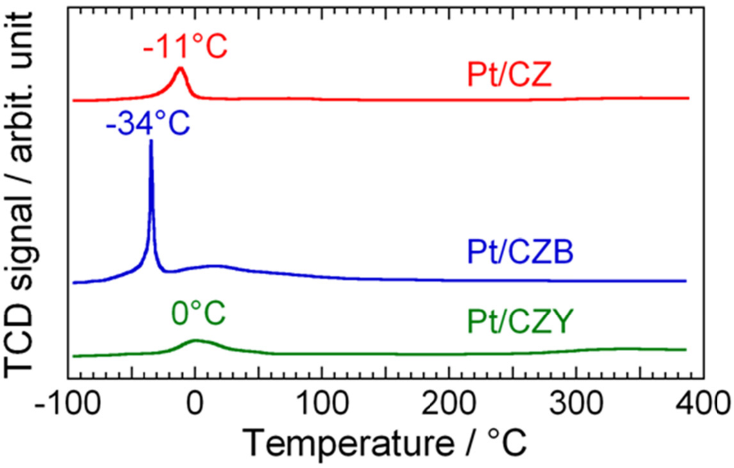

Fig. S7 Temperature programmed reduction profiles for Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ (Pt/CZB), Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Y_{0.20}O_{1.90}$ (Pt/CZY), and Pt(10 wt%)/$Ce_{0.80}Zr_{0.20}O_{2.0}$ (Pt/CZ) prepared at 400°C.

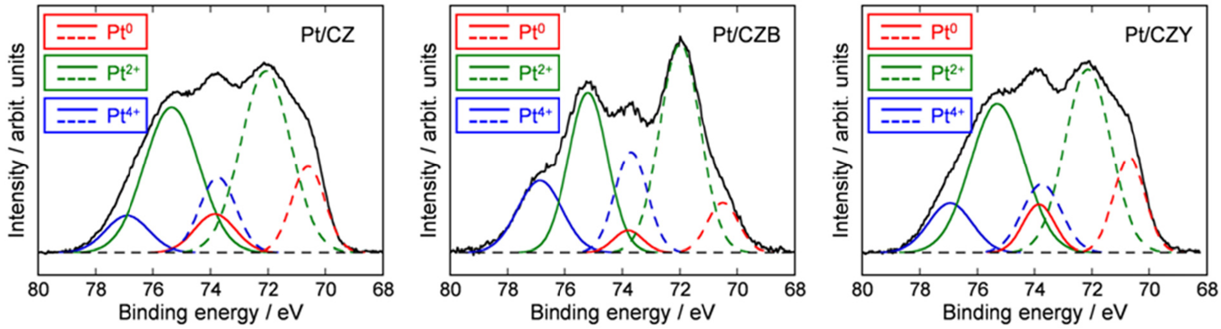

Fig. S8 XPS of Pt4f core level of Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ (Pt/CZB), Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Y_{0.20}O_{1.90}$ (Pt/CZY), and Pt(10 wt%)/$Ce_{0.80}Zr_{0.20}O_{2.0}$ (Pt/CZ) prepared at 400°C. Solid and broken lines correspond to the Pt($4f_{5/2}$) and Pt($4f_{7/2}$) peaks, respectively.

Table S4 Relative peak intensities of platinum species in Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ (Pt/CZB), Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Y_{0.20}O_{1.90}$ (Pt/CZY), and Pt(10 wt%)/$Ce_{0.80}Zr_{0.20}O_{2.0}$ (Pt/CZ) prepared at 400°C.

Catalyst	Relative peak intensity		
	Pt^0	Pt^{2+}	Pt^{4+}
Pt/CZ	17%	66%	17%
Pt/CZB	9%	63%	28%
Pt/CZY	18%	67%	18%

8. DRIFT-IR spectra

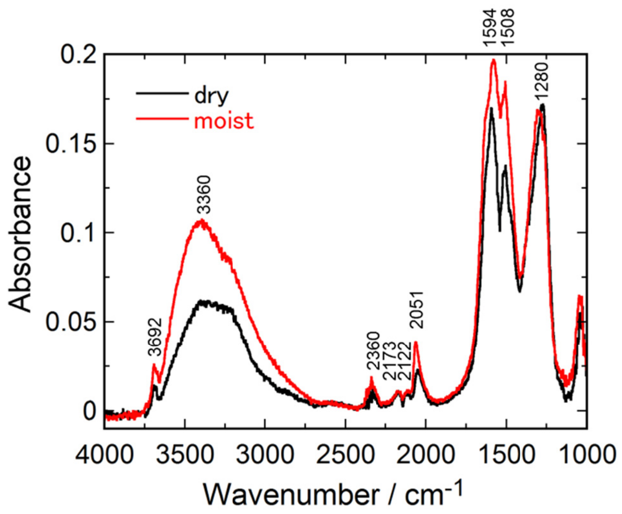

Fig. S9 DRIFT-IR spectra of the Pt(10 wt%)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ catalyst in a flow of CO(1 vol%)/air (black) and CO(1 vol%)/H_2O(0.6 vol%)/air (red) at 25 °C.

9. Brief comparison with Au/CeO_2-ZrO_2

Table S5 Comparison of CO oxidation activity over Pt/CeO_2-ZrO_2-Bi_2O_3 and Au/CeO_2-ZrO_2 catalysts.

Catalyst	S_{BET} (m^2 g^{-1})	Metal loading (wt%)	Metal particle size (nm)	Complete CO oxidation temperature (°C)*	Reaction conditions; catalyst weight	Ref.
Pt/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$	79	10	2– 5	20	1% CO, air balance, 66.7 cm^3 min^{-1}; 200 mg	–
Au/$Ce_{0.8}Zr_{0.2}O_2$	n.r.	2.0	n.r.	140	0.5 cm^3 min^{-1} CO 33.3 cm^3 min^{-1} air; 50 mg	S1
Au/$Ce_{0.75}Zr_{0.25}O_2$	48	3.31	4.4	45	1.6% CO, 3.3%O_2, He balance, 50 cm^3 min^{-1}; 200 mg	S2
Au/$Ce_{0.5}Zr_{0.5}O_2$	65	0.86	n.r.	17	0.49% CO, air balance, 55 cm^3 min^{-1}; 50 mg	S3

n.r. Not reported; *, data obtained in dry condition.

S1. S.-P. Wang, T.-Y. Zhang, X.-Y. Wang, S.-M. Zhang, S.-R. Wang, W.-P. Huang and S.-H.Wu, *J. Mol. Catal. A*, 2007, **272**, 45.

S2. I. Dobrosz-Gómez, I. Kocemba and J. M. Rynkowski, *Appl. Catal. B: Environ.*, 2008, **83**, 240.

S3. F. Moreau, G. C. Bond, B. van der Linden, B. A. A. Silberova and M. Makkee, *Appl. Catal. A: General*, 2008, **347**, 208.