Supplementary Information (SI) for Catalysis Science & Technology.

Electronic supplementary information

Effect of Zirconia Support Crystal Structure on the Alloying of Rhodium and Iridium for the Improvement of Three-way Catalysts

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1. Characterization details

1.1 X-ray Diffraction. X-ray diffraction patterns were recorded using a MiniFlexII diffractometer (Rigaku, Japan) with Cu Kα radiation at 30 kV and 15 mA.

1.2 CO Chemisorption Experiments. Metal dispersion was calculated from the CO chemisorption measured using the pulse method at room temperature. First, the catalysts were pretreated with 5% H_2 diluted with He at 400 °C for 60 min, and the residual H_2 was then purged with He at the same temperature. After cooling to room temperature, several pulses of 5% CO diluted with He were introduced to the catalysts until no further adsorption was observed.

1.3 CO_2-temperature Programmed Desorption (CO_2-TPD). CO_2-temperature programmed desorption was performed using a fixed-bed flow reactor system. First, the samples were pretreated with 5% O_2 diluted with Ar at 600 °C for 10 min, and then the residual O_2 was purged with Ar at the same temperature. After cooling to 50 °C, 5% CO_2 diluted with Ar was introduced into the reactor, followed by purging residual CO_2 with Ar for 60 min. The samples were then heated in increments of 10 °C/min to 600 °C, and the effluent gases were continuously monitored using quadrupole mass spectrometer (Omnistar GSD320, Pfeiffer Vacuum, Germany). To normalize the TPD signals, a 1 mL pulse of 5% CO_2/Ar was introduced to the quadrupole mass spectrometer after each measurement, and the signal intensity was corrected based on the peak response. This procedure enabled consistent comparison of the desorption profiles among samples.

1.4 Scanning Transmission Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (STEM-EDXS). High-angle annular dark-field images and elemental maps were obtained using a Themis Z system (Thermo Fisher Scientific Inc., USA) at an accelerating voltage of 300 kV.

1.5 X-Ray Absorption Spectroscopy. X-ray absorption fine-structure spectra were measured at the beamline BL01B1 of the SPring-8 synchrotron radiation facility in Japan and beamline BL11S2 of the Aichi Synchrotron Radiation Center in Japan. Rh K- and Ir L_2-edge X-ray absorption fine structure spectra were recorded at room temperature in air using either a Si(311) or Si(111) monochromator. Data were analyzed using Athena software (ver. 0.9.26) and Artemis software (ver. 0.9.26).

1.6 H_2-temperature Programmed Reduction (H_2-TPR). H_2-temperature programmed reduction was performed using a fixed-bed flow reactor system. First, the catalysts were pretreated with 5% O_2 diluted with Ar at 600 °C for 10 min, and then the residual O_2 was purged with Ar at the same temperature. After cooling to room temperature, 5% H_2 diluted with Ar was introduced into the reactor, and the signal of the thermal conductivity detector was stabilized. The catalysts were then heated in increments of 10 °C/min to 600 °C, and the changing signal of the thermal conductivity detector was continuously monitored.

1.7 Fourier Transform Infrared (IR) Spectroscopy. Fourier-transformed IR spectra with probe molecules were measured with an FT/IR-4400 instrument (JASCO, Japan) with a mercury-cadmium-telluride detector at a resolution of 4 cm^{-1}. The catalyst powder was pressed into a pellet with a diameter of 10 mm, and the pellet was placed in a glass cell equipped with CaF_2 windows. The glass cell was connected to a gas flow system; the catalyst pellets were pretreated with 5% H_2 diluted with Ar at 400 °C for 30 min; and then residual H_2 was purged with Ar at the same temperature. After cooling to the set temperature, probe gases were introduced into the glass cell, and the IR spectrum was measured in transmittance mode.

2. Supplemental results

Table S1. Comparison of catalyst weight and metal amounts used in catalyst evaluation.

Catalyst	Rh loading (wt%)	Ir loading (wt%)	Total loading (wt%)	Used catalyst wight (mg)	Used Rh amount (μmol)	Used Ir amount (μmol)	Used total metal amount (μmol)
Rh/0-ZrO_2	0.50	0.00	0.50	50.0	2.43	0.00	2.43
Ir/0-ZrO_2	0.00	0.50	0.50	50.0	0.00	1.30	1.30
Rh+Ir/0-ZrO_2[a]	0.17	0.33	0.50	50.0	0.85	0.85	1.70
RhIr/0-ZrO_2	0.17	0.33	0.50	50.0	0.85	0.85	1.70

[a] 0.5 wt% Rh/0-ZrO_2 and 0.5 wt% Ir/0-ZrO_2 were mixed at a weight ratio of 1.87.

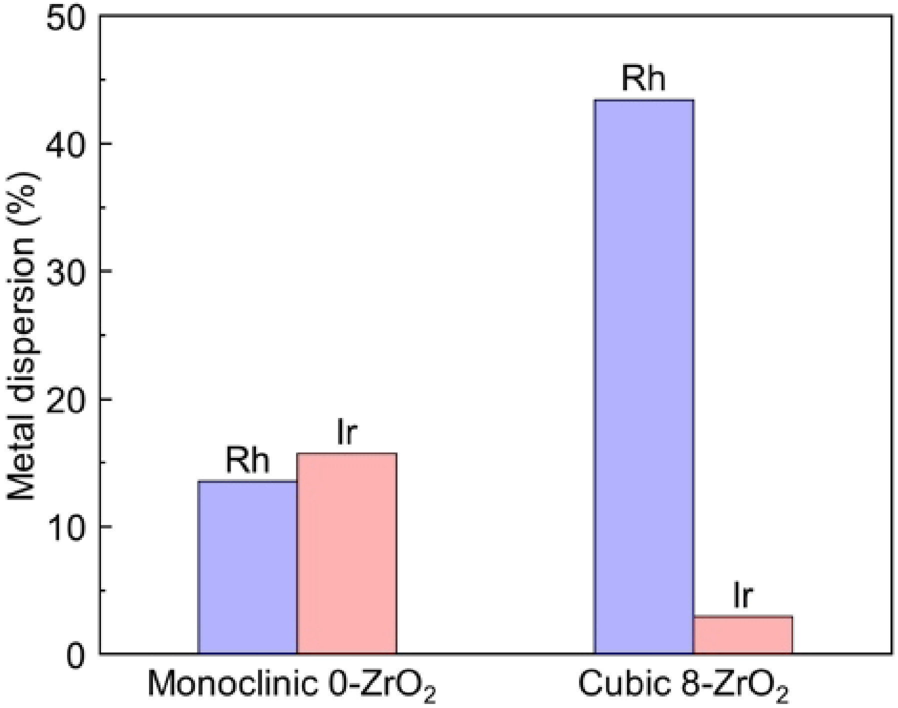


Figure S1. Metal dispersion of monometallic Rh and Ir catalysts. Before CO chemisorption, the catalysts were pretreated with 5% H_2 diluted with He at 400 °C for 60 min, and then residual H_2 was purged with He at the same temperature.

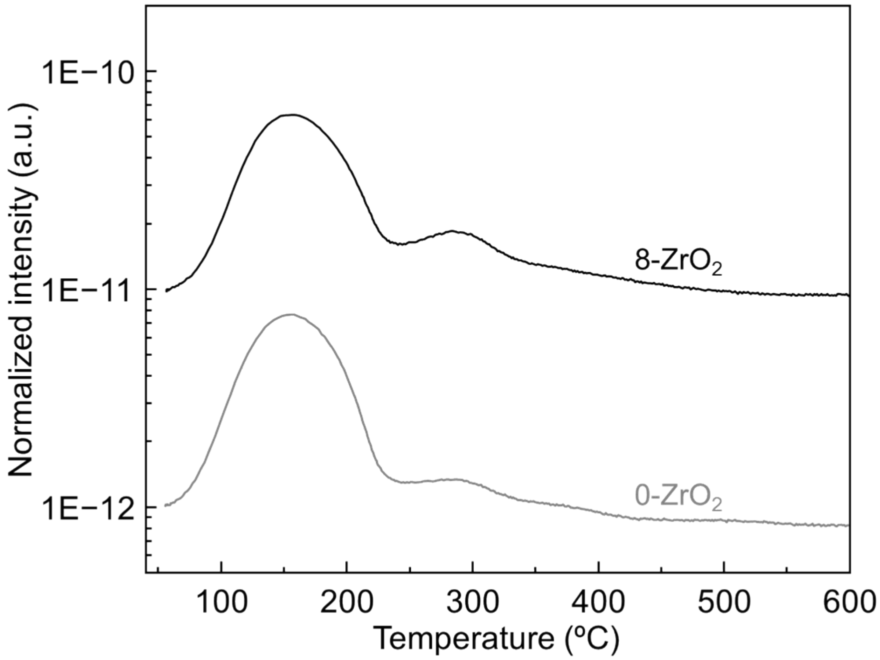


Figure S2. CO_2-TPD profiles of monoclinic 0-ZrO_2 and cubic 8-ZrO_2. Before the measurements, the sample was pretreated with 5% O_2 diluted with Ar at 600 °C for 10 min, and then the residual O_2 was purged with Ar at the same temperature.

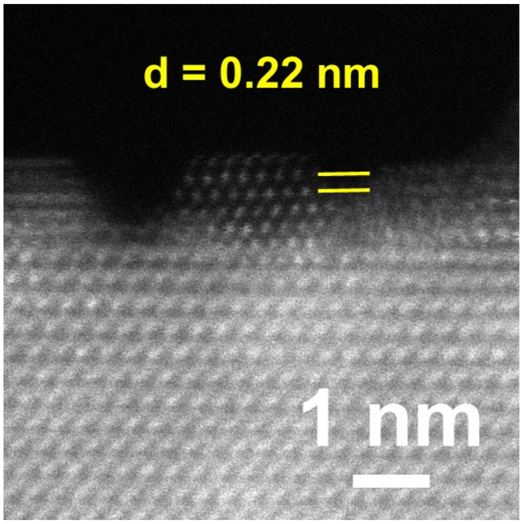
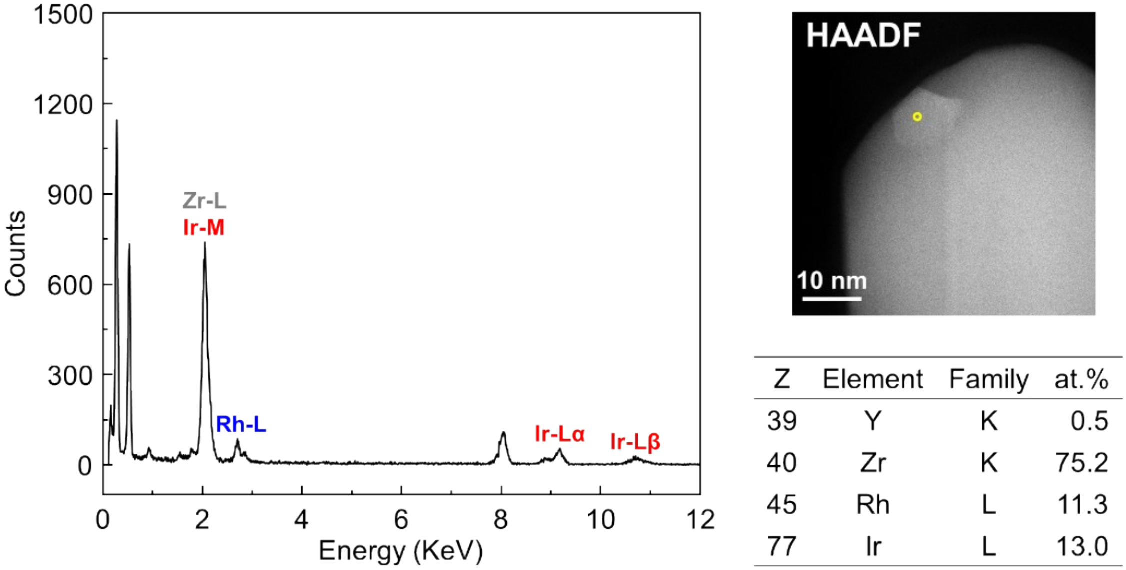


Figure S3. High-resolution HAADF image of H_2-pretreated RhIr/cubic 8-ZrO_2.



Z	Element	Family	at.%
39	Y	K	0.5
40	Zr	K	75.2
45	Rh	L	11.3
77	Ir	L	13.0

Figure S4. Elemental analysis results at selected point in STEM–EDXS analysis of calcined RhIr/monoclinic 0-ZrO_2.

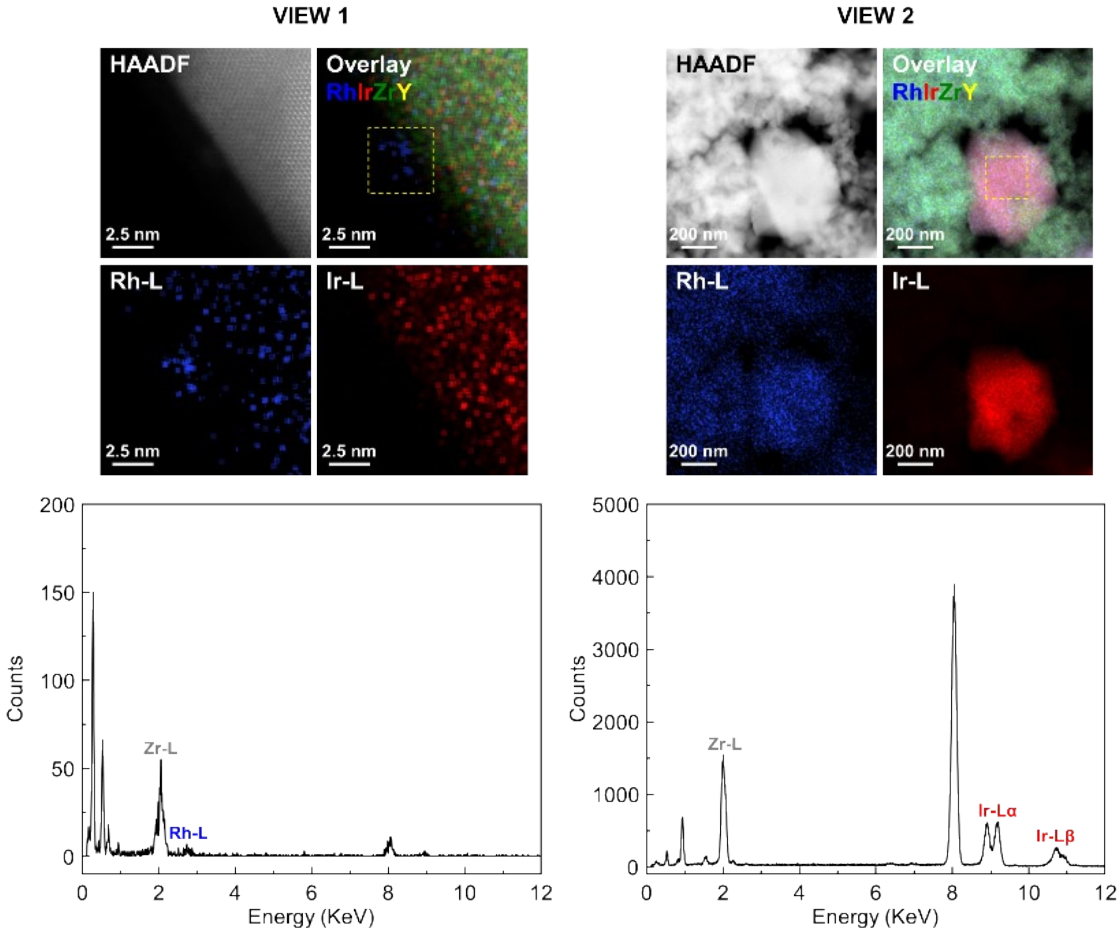


Figure S5. HAADF images, EDXS maps, and elemental analysis result for a selected area (outlined by the dotted square) in STEM–EDXS analysis of calcined RhIr/cubic 8-ZrO_2.

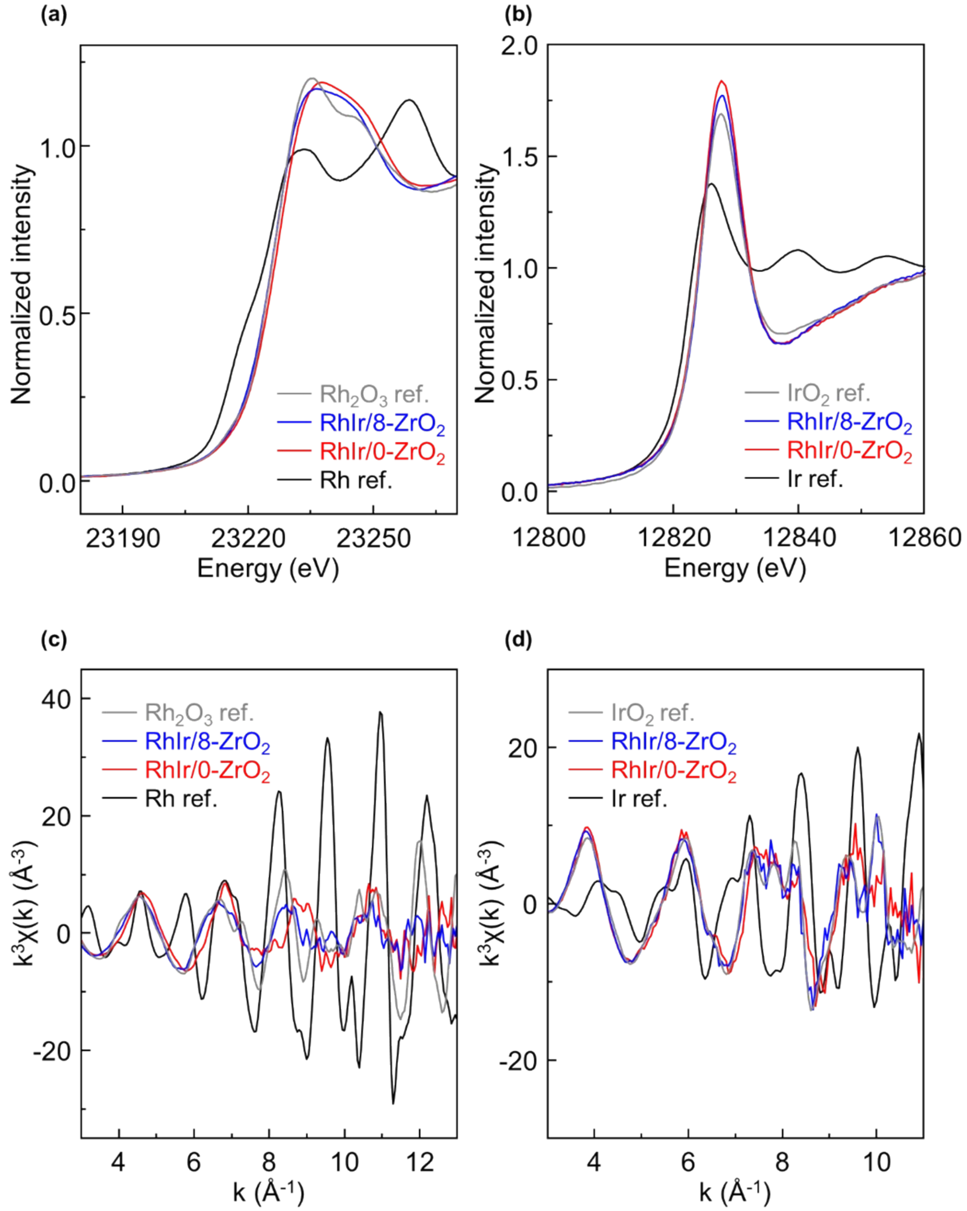


Figure S6. (a) Rh K-edge and (b) Ir L_2-edge X-ray absorption near-edge structure spectra of calcined RhIr/monoclinic 0-ZrO_2 and RhIr/cubic 8-ZrO_2. (c) Rh K-edge and (d) Ir L_2-edge extended X-ray absorption fine-structure oscillations of calcined RhIr/monoclinic 0-ZrO_2 and RhIr/ cubic 8-ZrO_2.

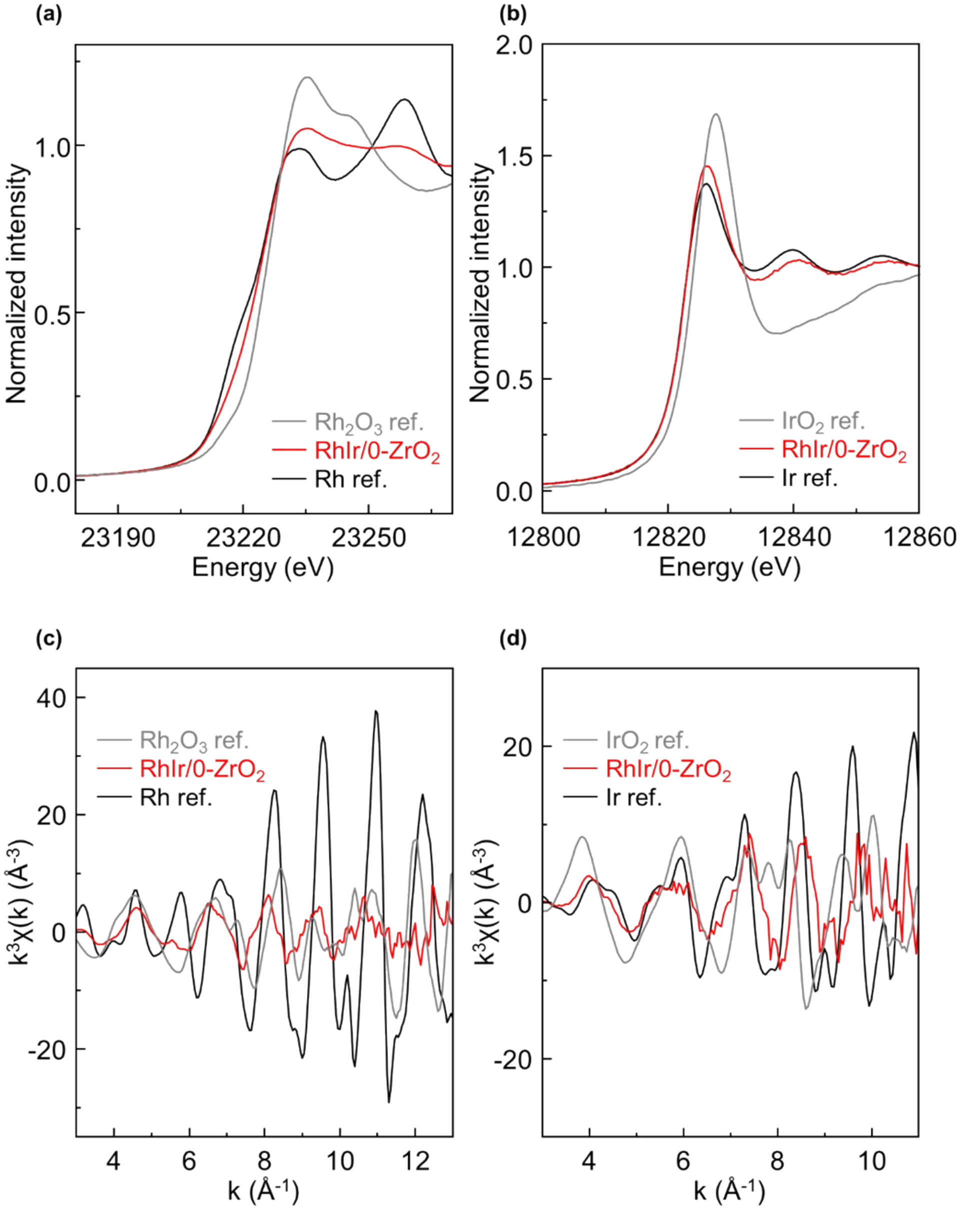


Figure S7. (a) Rh K-edge and (b) Ir L_2-edge X-ray absorption near-edge structure spectra of H_2-pretreated RhIr/monoclinic 0-ZrO_2. (c) Rh K-edge and (d) Ir L_2-edge X-ray absorption fine-structure oscillations of H_2-pretreated RhIr/monoclinic 0-ZrO_2.

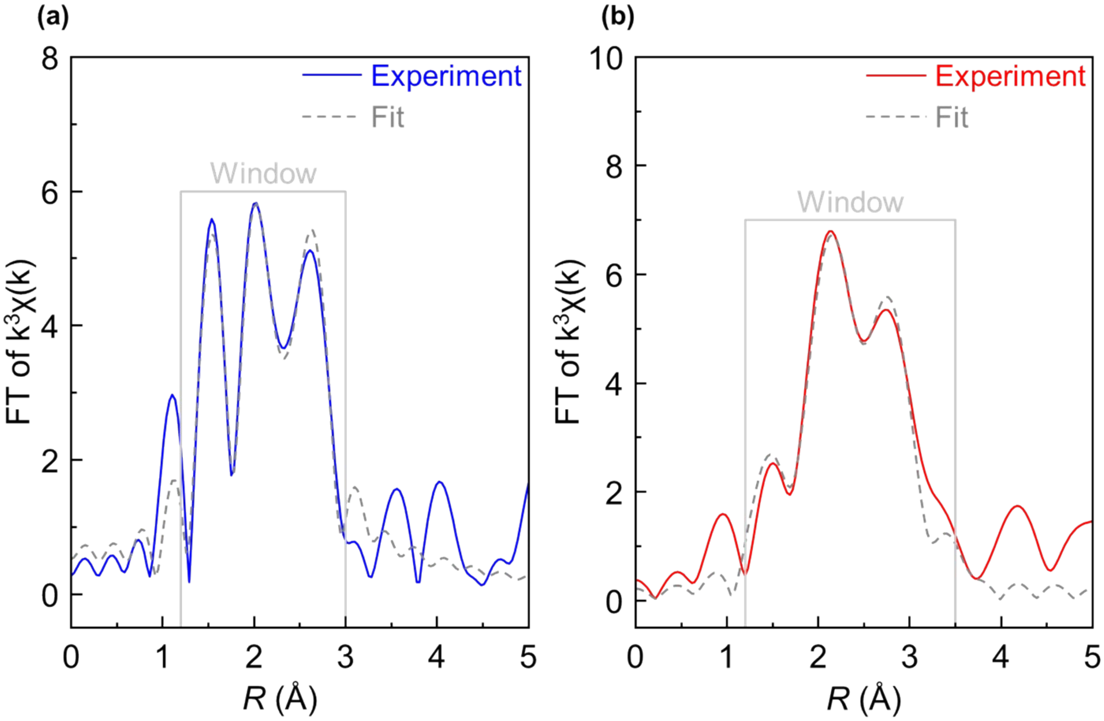


Figure S8. Curve-fitting results of (a) Rh K-edge and (b) Ir L_2-edge Fourier-transformed (FT) extended X-ray absorption fine structure spectra of H_2-pretreated RhIr/monoclinic 0-ZrO_2.

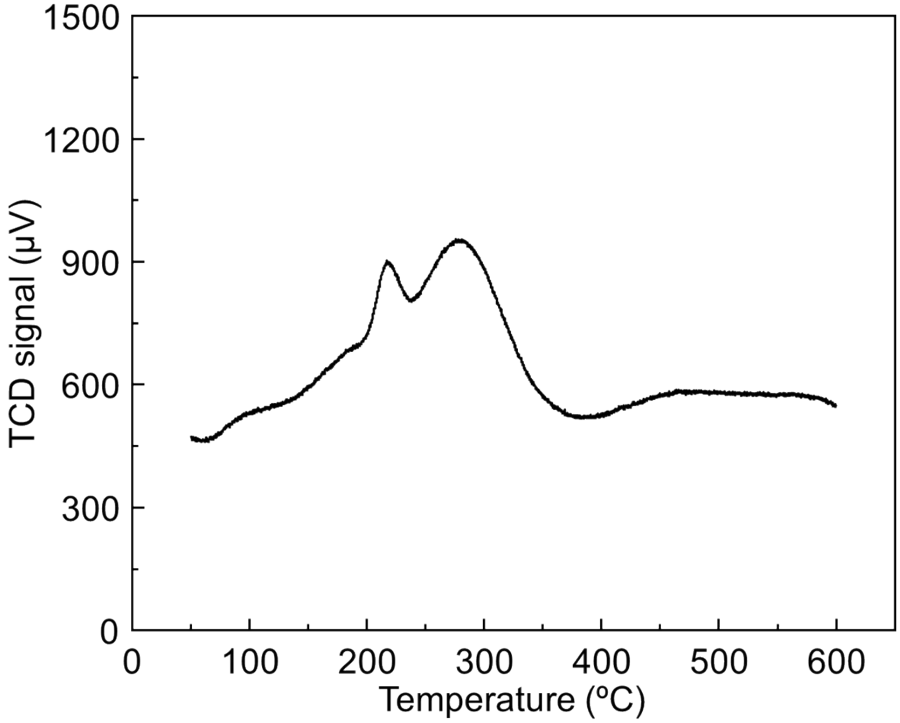


Figure S9. The H_2-TPR profile of RhIr/monoclinic ZrO_2, with a relatively high specific surface area (100 m^2/g). Before the measurements, the catalyst was pretreated with 5% O_2 diluted with Ar at 600 °C for 10 min, and then the residual O_2 was purged with Ar at the same temperature.

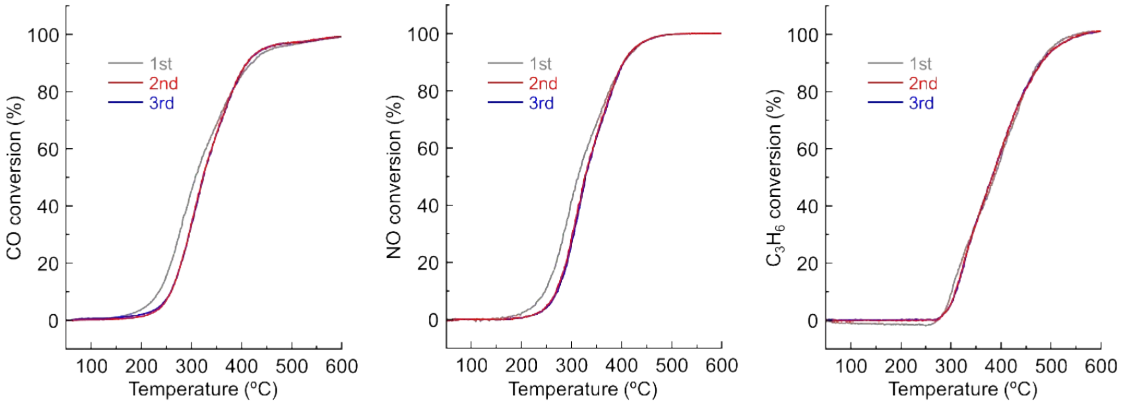


Figure S10. Three-way catalytic performance of the representative alloyed RhIr/monoclinic 0-ZrO_2 measured over three consecutive light-off cycles. Before the evaluation, the catalyst was pretreated with 5% H_2 diluted with N_2 at 400 °C for 30 min, and then the residual H_2 was purged with N_2 at the same temperature.

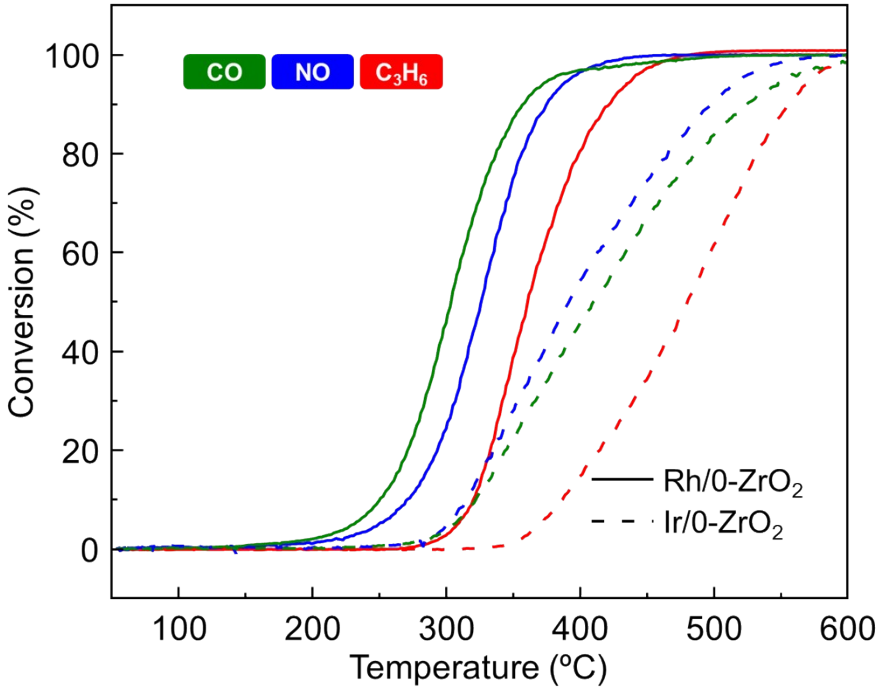


Figure S11. Three-way catalytic performance of monometallic Rh and Ir/monoclinic 0-ZrO$_2$. Before the evaluation, the catalysts were pretreated with 5% H_2 diluted with N_2 at 400 °C for 30 min, and then the residual H_2 was purged with N_2 at the same temperature.

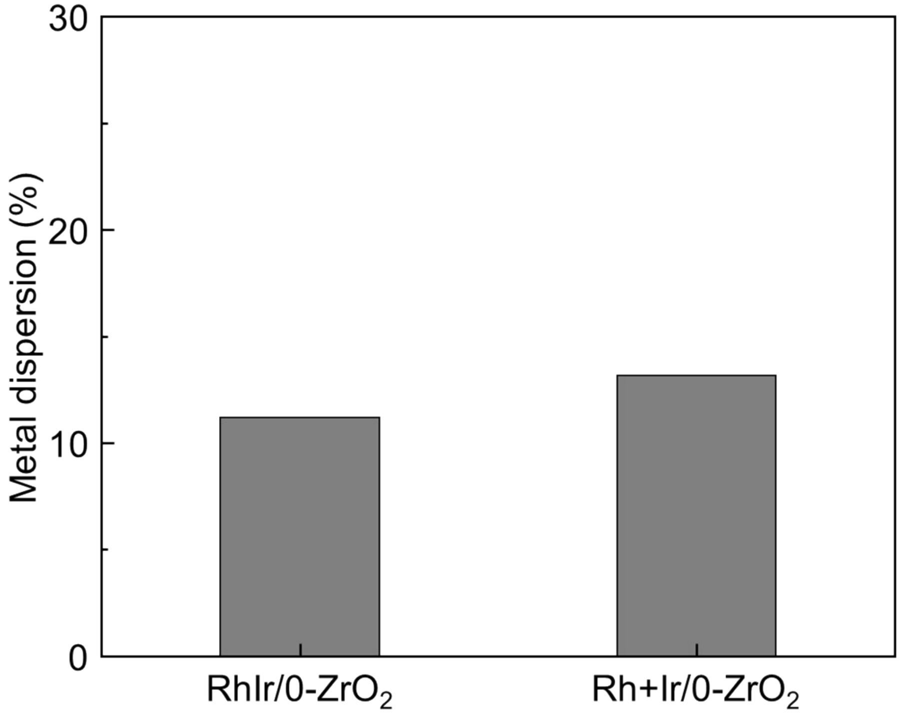


Figure S12. Metal dispersion of alloyed RhIr/monoclinic 0-ZrO_2 and physically mixed Rh+Ir/monoclinic 0-ZrO_2. Before CO chemisorption, the catalysts were pretreated with 5% H_2 diluted with He at 400 °C for 60 min, and the residual H_2 was purged with He at the same temperature.

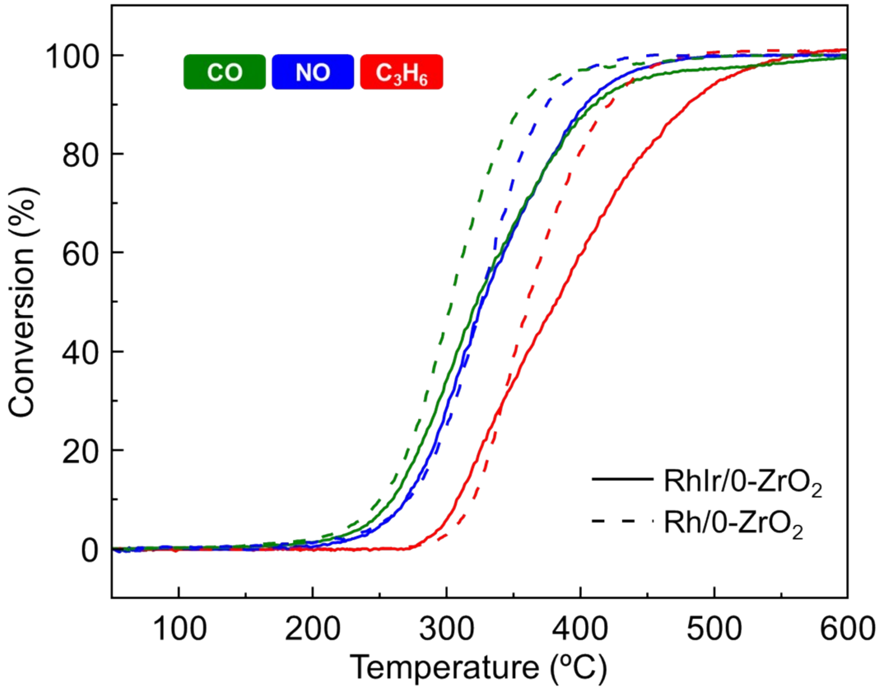


Figure S13. Comparison of the three-way catalytic performance of alloyed RhIr/monoclinic 0-ZrO_2 and monometallic Rh/monoclinic 0-ZrO_2. Before the evaluation, the catalysts were pretreated with 5% H_2 diluted with N_2 at 400 °C for 30 min, and then the residual H_2 was purged with N_2 at the same temperature.

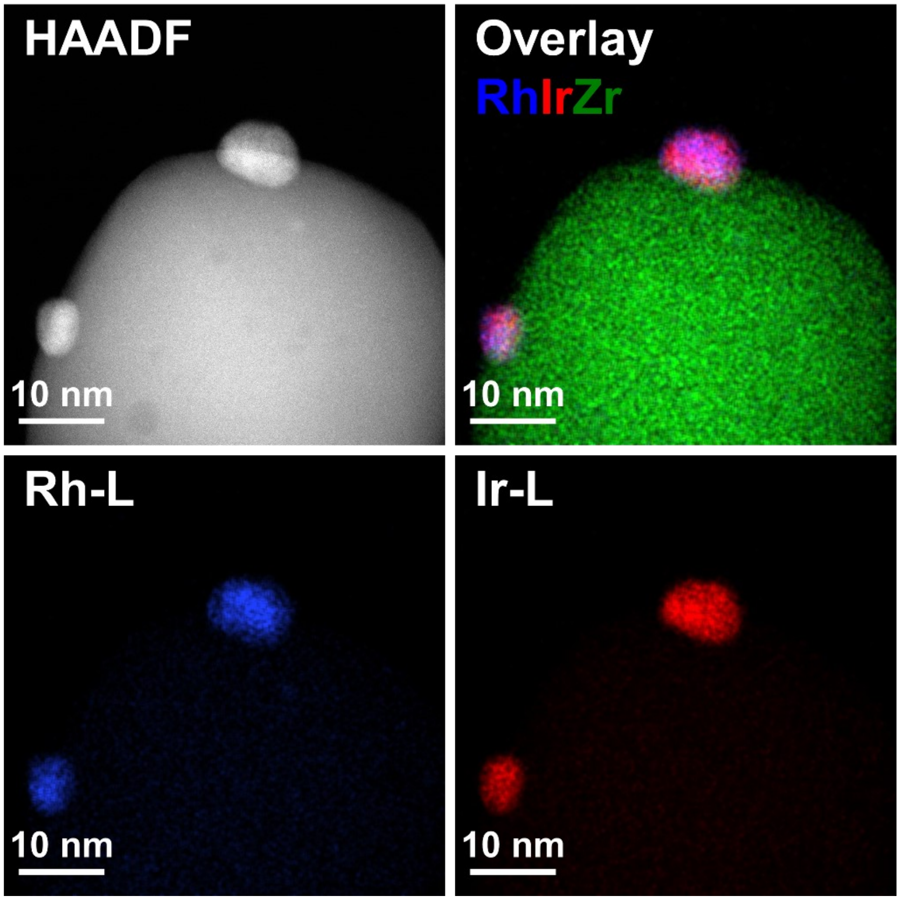


Figure S14. HAADF image and EDXS maps of RhIr/monoclinic 0-ZrO_2 after the second light-off cycle.

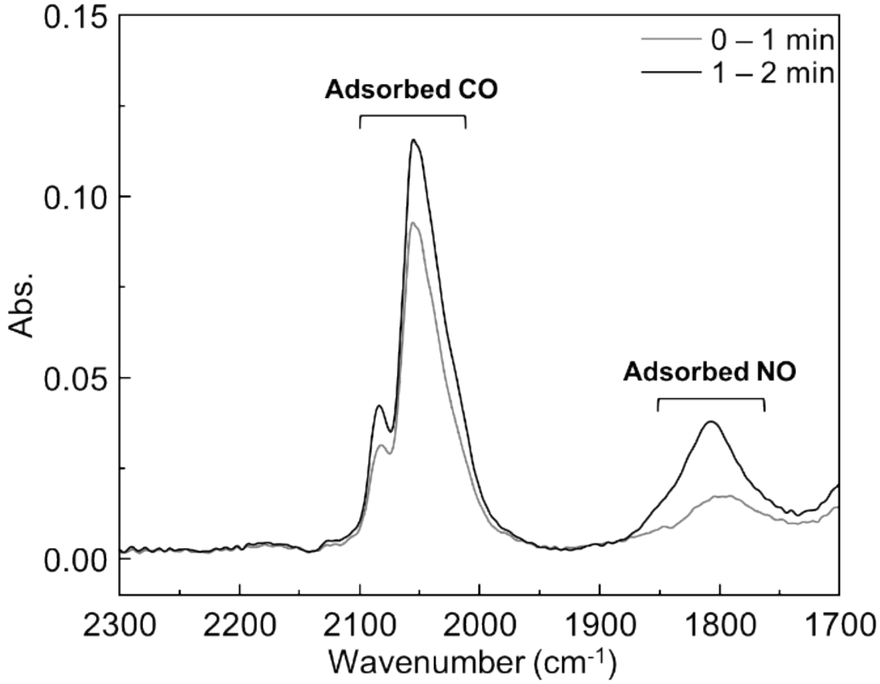


Figure S15. Initial IR spectra recorded at room temperature after flowing stoichiometric model gases composed of 0.35% CO, 0.15% NO, 0.33% C_3H_6, and 0.25% O_2 diluted with Ar through the alloyed RhIr/monoclinic 0-ZrO_2. Before the measurements, the catalyst was pretreated with 5% H_2 diluted with Ar at 400 °C for 30 min, and then the residual H_2 was purged with Ar at the same temperature.

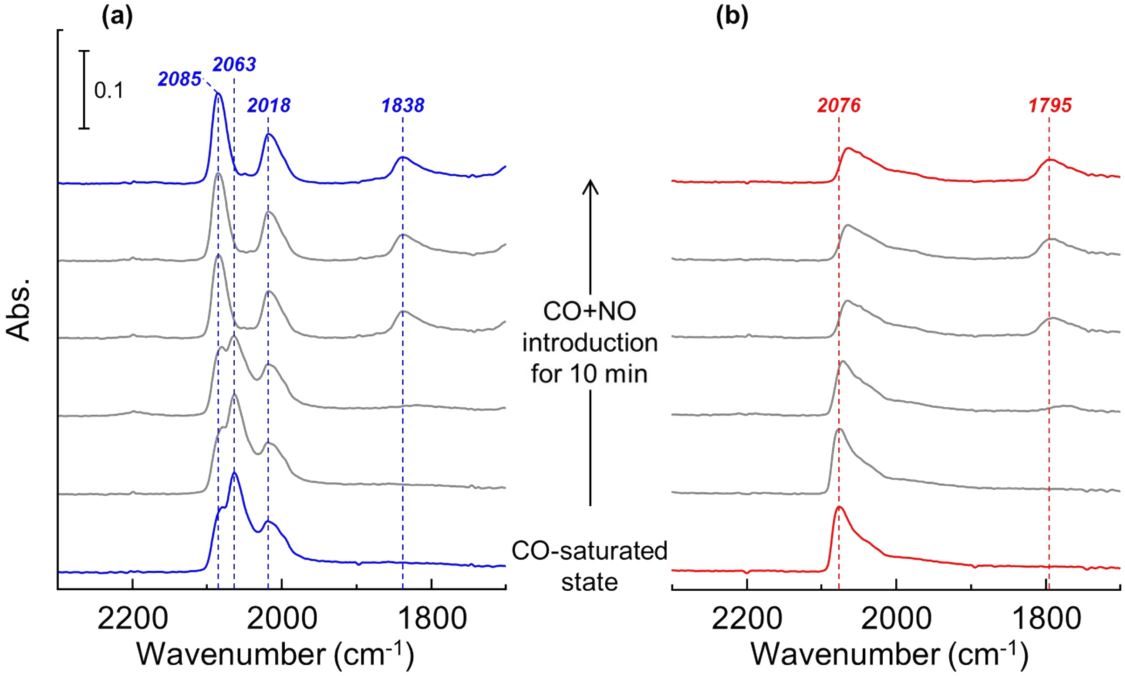


Figure S16. IR spectra recorded at 150 °C after flowing mixed gases composed of 0.15% CO+ 0.15% NO diluted with Ar through (a) monometallic Rh/monoclinic 0-ZrO_2 and (b) monometallic Ir/monoclinic 0-ZrO_2. Before the measurement, the catalysts were pretreated with 5% H_2 diluted with Ar at 400 °C for 30 min, and then the residual H_2 was purged with Ar at the same temperature.