Supporting Information

Insights into the Mechanism of Methanol Steam Reforming Tandem Reaction over CeO₂ Supported Single-site Catalysts

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Contents

1. Experimental Section	S3-S4
2. Supplementary results	S5-S11
Figure S1. X-ray powder diffraction (XRD) of pure CeO ₂ support, Pt ₁ /CeO ₂ , Pd ₁ /CeO ₂ , Rh ₁ /CeO ₂ and Ru ₁ /CeO ₂ .	S5
Figure S2. High resolution TEM image of porous CeO ₂ supports.	S5
Table S1. The best-fit EXAFS parameters of M_1 /CeO ₂ catalysts.	S5
Figure S3. (a) EXAFS spectra of Ru foil, RuO ₂ , and Ru ₁ /CeO ₂ at Ru <i>K</i> -edge and (b) k space EXAFS of Ru ₁ /CeO ₂ .	S6
Figure S4. <i>In situ</i> DRIFTS of CO adsorption and desorption on Ru ₁ /CeO ₂ single-site catalyst.	S6
Figure S5. High resolution TEM image of (a) Pt_1/CeO_2 , (b) Pd_1/CeO_2 and (c) Rh_1/CeO_2 .	S6
Figure S6. Corresponding energy spectrum of Pt ₁ /CeO ₂ , Pd ₁ /CeO ₂ , Rh ₁ /CeO ₂ , and Ru ₁ /CeO ₂ EDS mapping.	S7
Figure S7. (a) XANES spectra and (b) EXAFS spectra of Pt foil, PtO ₂ , and Pt ₁ /CeO ₂ at Pt L_3 -edge. (c) k space EXAFS of Pt ₁ /CeO ₂ .	S7
Figure S8. (a) XANES spectra and (b) EXAFS spectra of Pd foil, PdO, and Pd ₁ /CeO ₂ at Pd <i>K</i> -edge. (c) k space EXAFS of Pd ₁ /CeO ₂ .	S8
Figure S9. (a) XANES spectra and (b) EXAFS spectra of Rh foil, Rh ₂ O ₃ , and Rh ₁ /CeO ₂ at Rh <i>K</i> -edge. (c) k space EXAFS of Rh ₁ /CeO ₂ .	S8
Figure S10. XPS spectra and corresponding fitting curves of Ce 3d in (a) CeO ₂ , (b) CeO ₂ -commercial, (c) Pt ₁ /CeO ₂ , (d) Pd ₁ /CeO ₂ , (e) Rh ₁ /CeO ₂ and (f) Ru ₁ /CeO ₂ . The green peaks are attributed to Ce ³⁺ species (881.2, 884.9, 899.3 and 903.1 eV) while the orange peaks are attributed to Ce ⁴⁺ species (882.2, 888.2, 898.1, 900.7, 907.3 and 916.7 eV).	S8
Table S2. Proportions of Ce^{3+} and Ce^{4+} species in different samples.	S 8
Figure S11. EPR spectra of original CeO ₂ and CeO ₂ after AA reduction (CeO ₂ -AA) with the microwave frequency of 9.22 GHz; 20 mW at room temperature.	S9
Figure S12. Raman spectra of original CeO ₂ and CeO ₂ after AA reduced (CeO ₂ -AA).	S9
Figure S13. Comparison of M ₁ /CeO ₂ with other reported catalysts (the red squares are measured in this work). ^a TOF and CO ₂ selectivity were measures at 300 °C; ^b TOF and CO ₂ selectivity were measured at 220 °C.	S10
Table S3. Comparison of M_1 /CeO ₂ catalysts with other transition metal catalysts at different temperature.	S10
Figure S14. Hydrogen generation rate and CO ₂ selectivity of methanol steam reforming over Ru ₁ /CeO ₂ at 350 °C during 72 hours of reaction. Reaction condition:100 mg Ru ₁ /CeO ₂ mixed with 500 mg sand; He: 30 mL/min; liquid $(V_{methanol}/V_{water} = 1:3)$ feeding rate 0.05 mL/min.	S11
Figure S15. CO-TPD curves of Pt ₁ /CeO ₂ , Pd ₁ /CeO ₂ , Rh ₁ /CeO ₂ and Ru ₁ /CeO ₂ .	S11
3. References	S12

1. Experimental Section

1.1. Chemicals and Materials. Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99%), sodium hydroxide (NaOH, 97%), ascorbic acid (AA, $C_6H_8O_6$, 99%), ruthenium(III) chloride hydrate (RuCl₃·xH₂O, 99.98%), chloroplatinic acid hexahydrate (H₂PtCl₆· 6H₂O, 99.9%), palladium(II) chloride (PdCl₂, 99%), rhodium(III) chloride (RhCl₃, 98%) and methanol (CH₄O, 99.9%), were purchased from Sigma-Aldrich. All reagents were used without further purification.

1.2. Synthesis of porous CeO₂. Porous CeO₂ nanorods were synthesized according to previous literature.^[S1] 4 mmol Ce(NO₃)₃· 6H₂O (1.736 g) and 0.48 mol NaOH (19.2 g) were dissolved in 80 ml distilled water and stirred for 30 min at room temperature. Then the solution was transferred to 100 ml Teflon-lined stainless-steel autoclave. After reacting at 100 °C for 12 h, the products were collected by centrifugation and washed with distilled water for several times. Upon drying in a vacuum for 12 h at 60 °C, the products were calcined at 400 °C in air for 1 h.

1.3. Characterization of samples. The morphology of products was imaged using high-resolution TEM (ThemIS), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy dispersive X-ray spectroscopy (EDS) operated at 300 kV at the National Center for Electron Microscopy of Lawrence Berkeley National Laboratory. The composition of products was determined by powder X-ray diffraction (XRD) on a Rigaku D/max X-ray diffractometer (Cu Ka radiation, 0.15418 nm). X-ray photoelectron spectroscopy (XPS) measurements were conducted to analyze the chemical states of the elements. X-ray spectroscopy (EDS, Oxford, UK) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher, USA) configured with Al K_a excitation source with a fixed spot size of 400 μ m. Before collecting XPS spectrum, ion flood source is adopted for charge neutralization. The continuous wave EPR spectra were performed using electron Paramagnetic Resonance (EPR) using a Varian E109 EPR spectrometer equipped with a Model 102 Microwave bridge. The following spectrometer conditions were used: microwave frequency, 9.22 GHz; 20 mW at room temperature. Raman spectra were obtained by LabRAM with a 532 nm laser.

1.4. In Situ DRIFTS Study. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was measured by Thermo Nicolet 6700 equipped with an *in situ* reaction chamber covered by KBr filters and mercury-cadmium-telluride (MCT) detector. The sample was first in situ pretreated at 300 °C for 30 min under 50 mL/min N₂ flow. After cooling down to room temperature under 50 mL/min N₂ flow for 10 min, the background was collected. Then 30 mL/min CO was purged into the cell for 10 min. For the CO adsorption step, CO (99.99%) gas was fed into the cell at a flow rate of 30 mL/min for 10 min. Upon CO adsorption, 50 mL/min N₂ was purged into the cell to remove the adsorbed CO, and the spectra were recorded at desired times.

1.5. X-ray absorption spectroscopy (XAS) measurements. The Ru *K*-, Pt *L*₃-, Rh *K*- and Pd *K*edge X-ray absorption fine structure (XAFS) spectra were measured at the TPS 44A beamline of the National Synchrotron Radiation Research Center (NSRRC) Taiwan.^[S2] The data were collected in fluorescence mode by using 7-element silicon drift detector and the standard metal foils (Ru, Pt, Rh and Pd) were employed as references for the energy calibration of incident photons.^[S3,S4] The edge-jump of all spectra were normalized to compare the feature at XANES region. The EXAFS $\chi(k)$ data was obtained from raw data via the following two equations:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E_0)}, \ k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

where $\mu(E)$ is the measured absorption coefficient, $\mu_0(E)$ is a smooth background function representing the absorption of an isolated atom, and $\Delta \mu_0$ is the measured jump in the absorption μ (*E*) at the threshold energy E₀, *k* is the wave number of the photon-electron, m is the electron mass and \hbar is Planck's constant. The list of the atomic Cartesian coordinates of standard metal-oxide from crystallographic structure data were used for the construction of the scattering potentials and enumeration of scattering paths. Then the theoretical calculation of EXAFS scattering factors was used to fit the EXAFS data to obtain the structure parameters such as coordination number, bond length and Debye-Waller factor. The data processing was dealt with the Demeter software package.^[S5]

1.6. CO-temperature-programmed desorption study. CO-temperature-programmed desorption (CO-TPD) was carried out by AutoChem 2920 instrument. 100 mg M_1 /CeO₂ was first heated at 300 oC in air for 1 hour and then cooled down to room temperature. The CO (20 mL min⁻¹) gas was introduced into sample chamber for 5 min. After full adsorption of CO, the He gas flow (40 mL min⁻¹) purged into the chamber for 30 min to remove CO gas. The chamber temperature was raised at the rate of 10 °C min⁻¹; and the signal was recorded by a MS detector.

2. Supplementary results



2 Theta (°) Figure S1. X-ray powder diffraction (XRD) of pure CeO₂ support, Pt₁/CeO₂, Pd₁/CeO₂, Rh₁/CeO₂ and Ru₁/CeO₂.



Figure S2. High resolution TEM image of porous CeO₂ supports.

Sample	Scattering Path	Ν	R (Å)	σ ² (Å ²)	Rf
Ru foil	Ru-Ru bond	12	2.67	0.003	0.003
RuO ₂	Ru-O bond	6	1.97	0.002	0.0007
Ru_1/CeO_2	Ru-O bond	5.15	2.03	0.006	0.0003
Pt foil	Pt-Pt bond	12	2.77	0.004	0.0004
PtO ₂	Pt-O bond	6	2.02	0.003	0.006
Pt ₁ /CeO ₂	Pt-O bond	5.96	1.97	0.002	0.0002
Pd foil	Pd-Pd bond	12	2.74	0.005	0.003
PdO	Pd-O bond	4	2.02	0.004	0.006
Pd ₁ /CeO ₂	Pd-O bond	4	1.99	0.002	0.007
Rh foil	Rh-Rh bond	12	2.69	0.003	0.008
Rh ₂ O ₃	Rh-O bond	6	2.04	0.002	0.009
Rh ₁ /CeO ₂	Rh-O bond	6	2.04	0.002	0.007

Table S1. The best-fit EXAFS parameters of M₁/CeO₂ catalysts.



Figure S3. (a) EXAFS spectra of Ru foil, RuO₂ and Ru₁/CeO₂ at Ru *K*-edge and (b) k space EXAFS of Ru₁/CeO₂.



Figure S4. In situ DRIFTS of CO adsorption and desorption on Ru1/CeO2 single-site catalyst.



Figure S5. High resolution TEM image of (a) Pt₁/CeO₂, (b) Pd₁/CeO₂ and (c) Rh₁/CeO₂.



Figure S6. Corresponding energy spectrum of Pt₁/CeO₂, Pd₁/CeO₂, Rh₁/CeO₂, and Ru₁/CeO₂ EDS mapping.



Figure S7. (a) XANES spectra and (b) EXAFS spectra of Pt foil, PtO₂, and Pt₁/CeO₂ at Pt *L*₃-edge. (c) k space EXAFS of Pt₁/CeO₂.



Figure S8. (a) XANES spectra and (b) EXAFS spectra of Pd foil, PdO, and Pd₁/CeO₂ at Pd *K*-edge. (c) k space EXAFS of Pd₁/CeO₂.



Figure S9. (a) XANES spectra and (b) EXAFS spectra of Rh foil, Rh₂O₃, and Rh₁/CeO₂ at Rh *K*-edge. (c) k space EXAFS of Rh₁/CeO₂.



Figure S10. XPS spectra and corresponding fitting curves of Ce 3d in (a) CeO₂, (b) CeO₂commercial, (c) Pt1/CeO₂, (d) Pd1/CeO₂, (e) Rh1/CeO₂ and (f) Ru1/CeO₂. The green peaks are attributed to Ce³⁺ species (881.2, 884.9, 899.3 and 903.1 eV) while the orange peaks are attributed to Ce⁴⁺ species (882.2, 888.2, 898.1, 900.7, 907.3 and 916.7 eV).^[S6]

Table S2. Proportions of Ce^{3+} and Ce^{4+} species in different samples.

Sample	Ce ³⁺ species (%)	Ce ⁴⁺ species (%)
CeO ₂	23.8	76.2
CeO ₂ -AA	41.5	58.5
Pt ₁ /CeO ₂	31.7	68.3
Pd_1/CeO_2	28.8	71.2
Rh ₁ /CeO ₂	29.3	70.7
Ru ₁ /CeO ₂	30.3	69.7

The proportion of Ce^{3+} species, P(Ce³⁺), was calculated using the following equation, of which the areas are the fitting areas in XPS:

Proportion (
$$Ce^{3+}$$
) = $\frac{area(Ce^{3+})}{area(Ce^{3+}) + area(Ce^{4+})} \times 100\%$



Figure S11. EPR spectra of original CeO₂ and CeO₂ after AA reduction (CeO₂-AA) with the microwave frequency of 9.22 GHz; 20 mW at room temperature.^[S7]



Figure S12. Raman spectra of original CeO₂ and CeO₂ after AA reduced (CeO₂-AA). The characteristic F_{2g} mode due to the *Fm3m* fluorite cubic ceria structure observed at 457 cm⁻¹ prevails in all spectra. a weak band at ~260 cm⁻¹ (due to second order transverse acoustic mode) and the so-called defect-induced band (band "D") at ~600 cm⁻¹ "leak" as result of relaxation of symmetry selection rules caused by structural perturbations of the ceria cubic lattice. Thus, the I_D/I_{F2g} ratio is commensurate to the abundance of structural defects. ^[S8]



CO₂ Selectivity (%) Figure S13. Comparison of M₁/CeO₂ with other reported catalysts (the red squares are measured in this work). ^a TOF and CO₂ selectivity were measures at 300 °C; ^b TOF and CO₂ selectivity were measured at 220 °C.

Table S3. Comparison of M_1 /CeO₂ catalysts with other transition metal catalysts at different temperature.

Catalysts	Temperature (°C)	TOF	CO ₂ selectivity
		(mol _{H2} mol _{Metal} ⁻¹ h ⁻¹)	(%)
Ru ₁ /CeO ₂ [this work]	150	83.7	>99.9
	250	3242	82.8
	350	9493	97.8
Pt ₁ /CeO ₂ [this work]	250	975	42.5
	350	11317	47.8
Pd ₁ /CeO ₂ [this work]	250	375	52.5
	350	3575	52.5
Rh1/CeO2 [this work]	250	625	57.3
	350	6952	64.0
Cu/ZnO ^[S14]	250	12.16	67.4
Cu/ZnO/ZrO ₂ [S14]	250	806.2	>99.9
CuO/ZnO/CeO ₂ /ZrO ₂ ^[S15]	260	29.4	-
CuZnGaOx ^[S16]	150	15.7	100
Cu/Zn/Ce/Al ^[S17]	260	591.2	98.9
$Cu/ZnO/Al_2O_3^{[S18]}$	250	67.6	99.0
10La-10Ni/Al ₂ O ₃ ^[S19]	300	65.7	~8.5
Ni0.78Al0.16(OH)2(CO3)0.15 ^[S20]	340	41.9	57.4
NiAl-LDH ^[S21]	350	18.0	95.0
Fe/Al ₂ O ₃ [S22]	350	27.6	-
Co/Al ₂ O ₃ [S22]	350	338.3	-
Mn/Al ₂ O ₃ [S22]	350	8.4	-
Cu/Al ₂ O ₃ [S22]	300	433.5	45.2
Zn/Al ₂ O ₃ [S22]	350	27.7	-
Ni/Al ₂ O ₃ [S22]	350	259.6	-



Figure S14. Hydrogen generation rate and CO₂ selectivity of methanol steam reforming over Ru₁/CeO₂ at 350 °C during 72 hours of reaction. Reaction condition: 100 mg Ru₁/CeO₂ mixed with 500 mg sand; He: 30 mL/min; liquid (V_{methanol}/V_{water} = 1:3) feeding rate: 0.05 mL/min.



Figure S15. CO-TPD curves of Pt1/CeO2, Pd1/CeO2, Rh1/CeO2 and Ru1/CeO2.

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