Supplementary Information

Revealing Sulfur-Resistant Pt–CeO_2 Interfacial Sites for Water–Gas Shift Catalysts toward Waste–to–Hydrogen

Ga–Ram Hong[a], *Kyoung–Jin Kim*[a], *Bong–Gyeong Shin*[a] *and Hyun–Seog Roh*[a, *]

[a] *Department of Environmental and Energy Engineering, Yonsei University, 1 Yonseidae–gil, Wonju, Gangwon 26493, Republic of Korea.*

***Corresponding Authors**

Tel.: +82 33 760 2834, E–mail: hsroh@yonsei.ac.kr (H.–S. Roh)

Number of Pages: 11

Number of Figures: 8

Number of Tables: 1

Catalysts Characterization

X–ray diffraction (XRD) patterns were recorded in a 2 θ range of 20°–80° using an Ultima IV diffractometer (Rigaku) with Cu Kα radiation (40 kV, 40 mA). The Brunauer–Emmett–Teller (BET) surface area and average pore diameter were obtained from N_2 adsorption–desorption isotherms measured at –196 °C using ASAP 2020 plus (Micromeritics). Prior to BET analysis, the samples were pretreated at 110 °C for 12 h. The Pt^0 dispersion and the amount of chemisorbed CO of the catalysts were determined by pulsed CO–chemisorption using AutoChem 2920 (Micromeritics). Before CO injection, the samples were reduced in–situ under 10% H_2/Ar at 400 °C for 1 h, followed by cooling to 50 °C in an Ar atmosphere. CO pulses were repeatedly introduced until the areas of successive CO uptake peaks became identical. The CO–to–surface Pt stoichiometry was assumed to be unity (CO/Pt = 1) for the calculation of Pt dispersion. The reduction behavior of the catalysts was investigated by H_2–temperature–programed reduction (H_2–TPR) using AutoChem 2920 (Micromeritics). Each sample was exposed to 10% H_2/Ar and heated from 50 °C to 800 °C at a rate of 10 °C/min. Raman spectroscopy was conducted using LabRam Aramis spectrometer (Horiba Jobin Yvon) with ND:YAG laser operating at an excitation wavelength of 532 nm. X–ray photoelectron spectroscopy (XPS) was carried out on a a K–Alpha spectrometer (Thermo Fisher Scientific) with a monochromatic Al Kα radiation source. The obtained spectra were adjusted using the C 1s line (284.6 eV) as a reference. To analyze the OSC of the catalysts, H_2–O_2 pulse chemisorption was performed through AutoChem 2920 (Micromeritics). The samples were pretreated in a 10% O_2/He atmosphere for 1 h while heating at 400 °C prior to the pulse chemisorption. Subsequently, H_2 pulses (5% H_2/Ar) were introduced at 400 °C until the sample was fully saturated with hydrogen. Thereafter, O_2 pulses (1.5% O_2/He) were injected until complete oxygen saturation was achieved. The OSC value was calculated from the amount of consumed O_2._In situ CO diffuse reflectance infrared fourier transform spectroscopy (CO–DRIFTS) was employed to obtain the infrared spectra of the catalysts under reaction conditions. A Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific) fitted with a liquid–nitrogen–cooled mercury cadmium telluride (MCT) detector and a Praying Mantis kit (Harrick) was attached. The spectra were collected by accumulating 64 scans at 8 cm^{-1} resolution. 35 mg of the catalyst was placed in a high–temperature reaction chamber with ZnSe windows and activated under a 5% H_2/N_2 at 400 °C for 1 h. After activation, the chamber cooled down to 50 °C under N_2 flow. The reaction was then carried out with 2% CO/N_2 gas introduced at a rate of 20 sccm for 1 h.

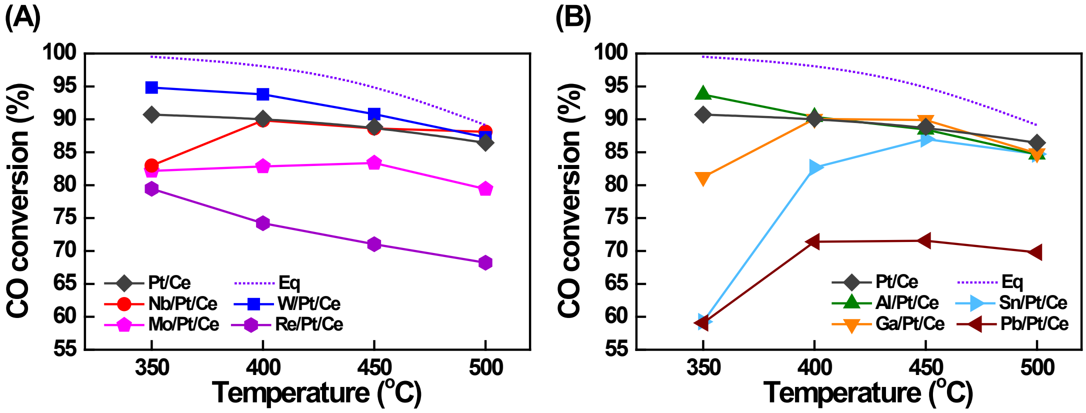

Figure S1. Catalytic performance of Pt/Ce catalysts with various metal promoters as a function of temperature. (A) Transition metal promoted catalysts; (B) Non–transition metal promoted catalysts. Reaction conditions: $H_2O/(CH_4 + CO + CO_2) = 2.0$; $T = 400$ °C; GHSV = 46,000 $mL \cdot g^{-1} \cdot h^{-1}$.

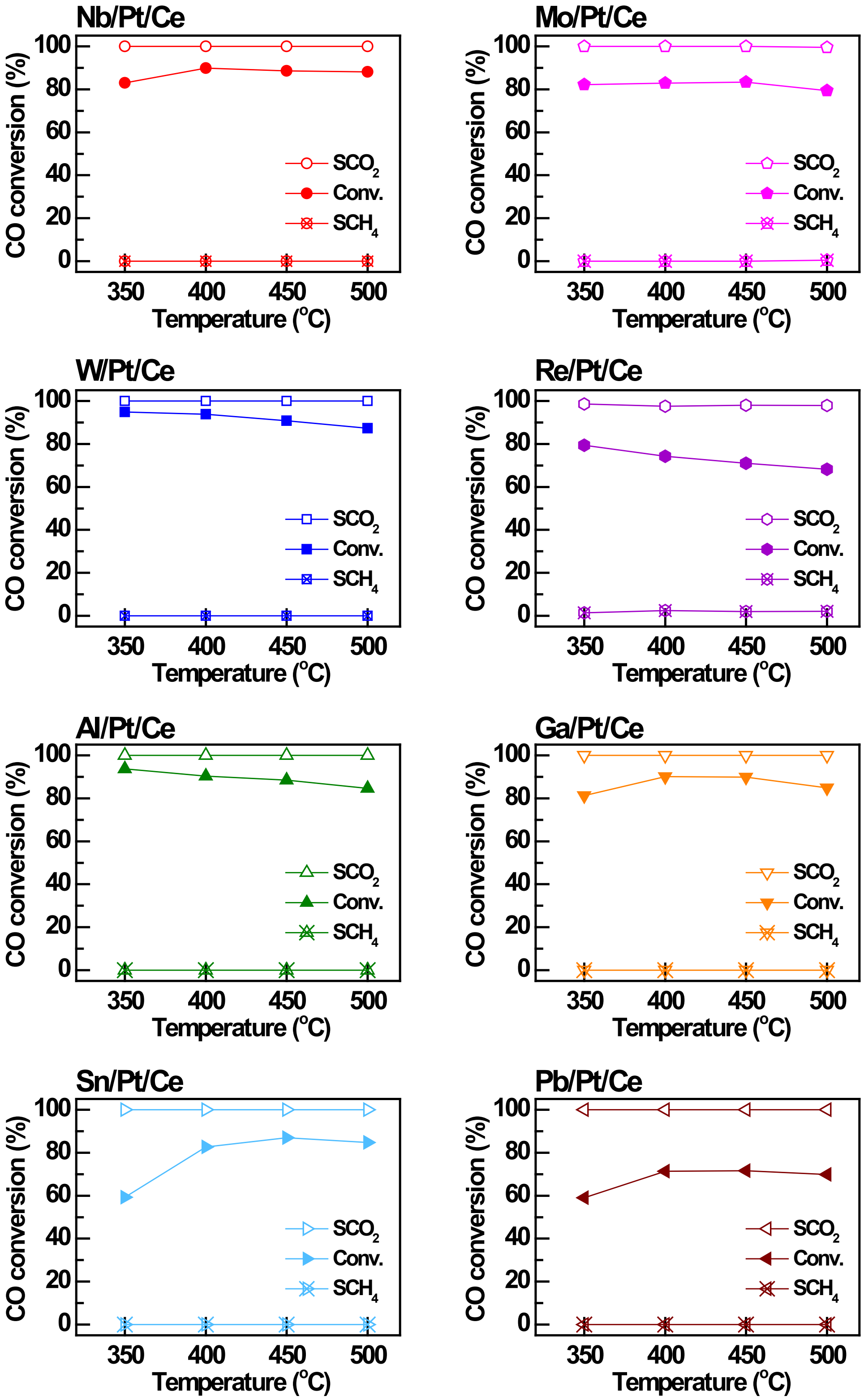

Figure S2. CO conversion, CO_2 and CH_4 selectivity of Pt/Ce catalysts with various metal promoters as a function of temperature. Reaction conditions: $H_2O/(CH_4 + CO + CO_2) = 2.0$; $T = 400$ °C; GHSV $= 46{,}000\ \mathrm{mL \cdot g^{-1} \cdot h^{-1}}$.

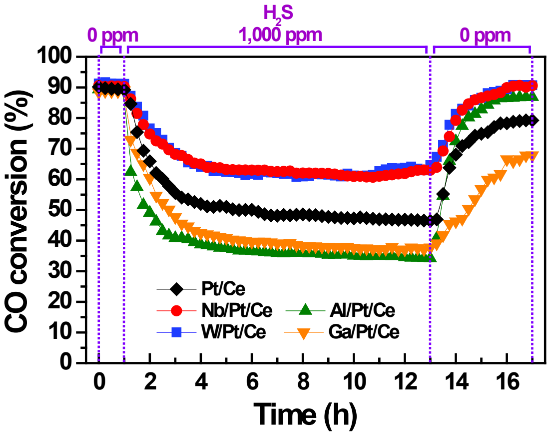

Figure S3. Catalytic performance with time on stream over the Pt/Ce catalysts with various metal promoters. Reaction conditions: $H_2O/(CH_4 + CO + CO_2) = 2.0$; $T = 400$ °C; GHSV = 46,000 $mL \cdot g^{-1} \cdot h^{-1}$; H_2S = 1,000 ppm.

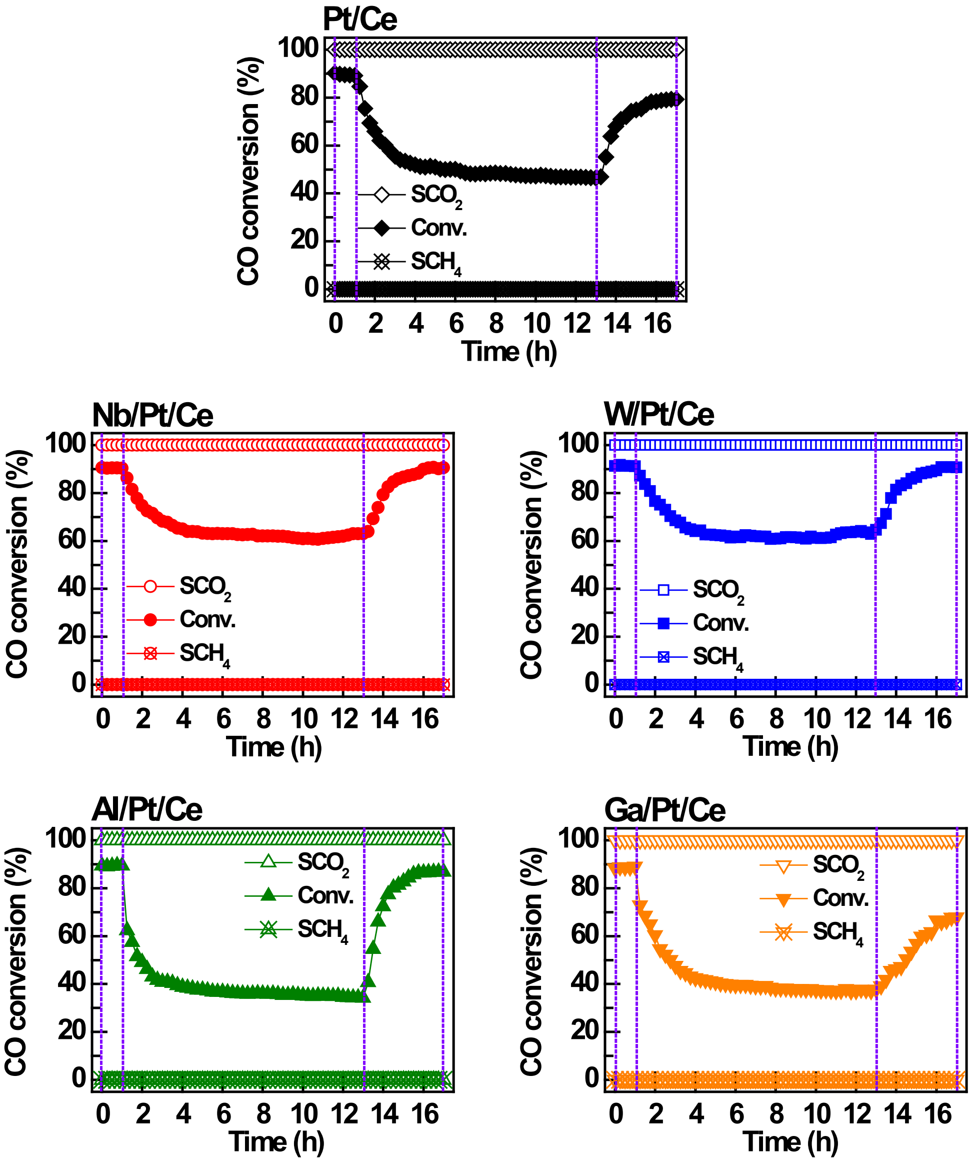

Figure S4. CO conversion, CO_2 and CH_4 selectivity with time on stream over the Pt/Ce catalysts with various metal promoters. Reaction conditions: $H_2O/(CH_4 + CO + CO_2) = 2.0$; $T = 400$ °C; GHSV = 46,000 $mL \cdot g^{-1} \cdot h^{-1}$.

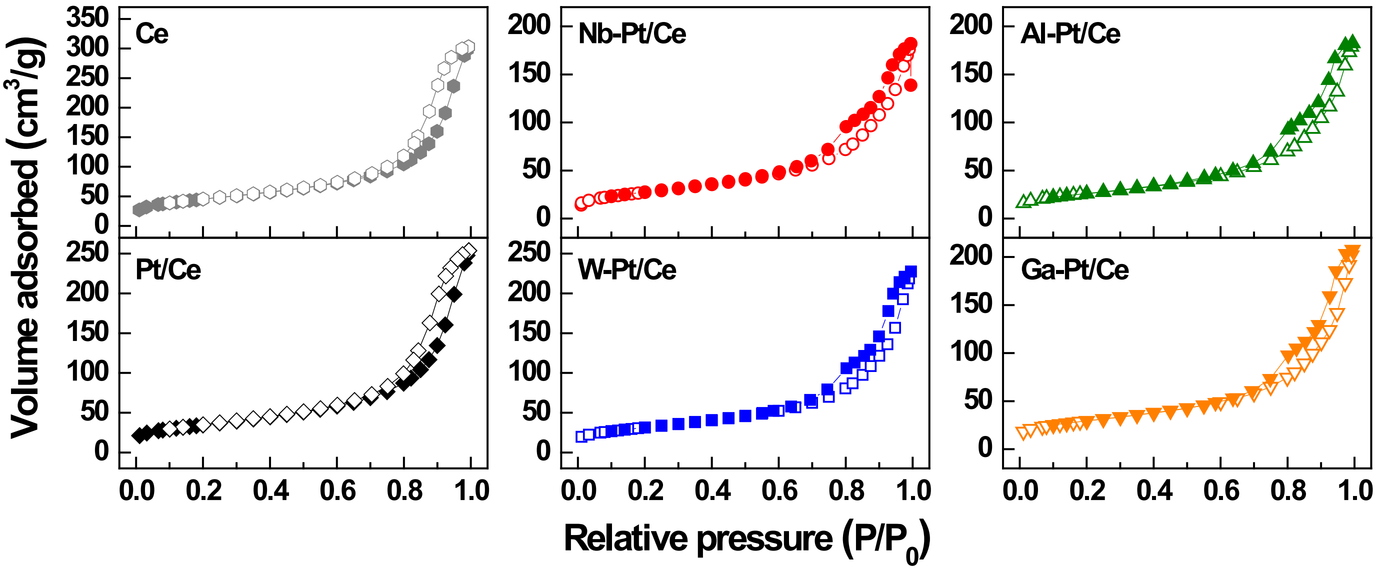

Figure S5. Adsorption–desorption curve of the CeO_2 support and Pt/Ce catalysts with various metal promoters.

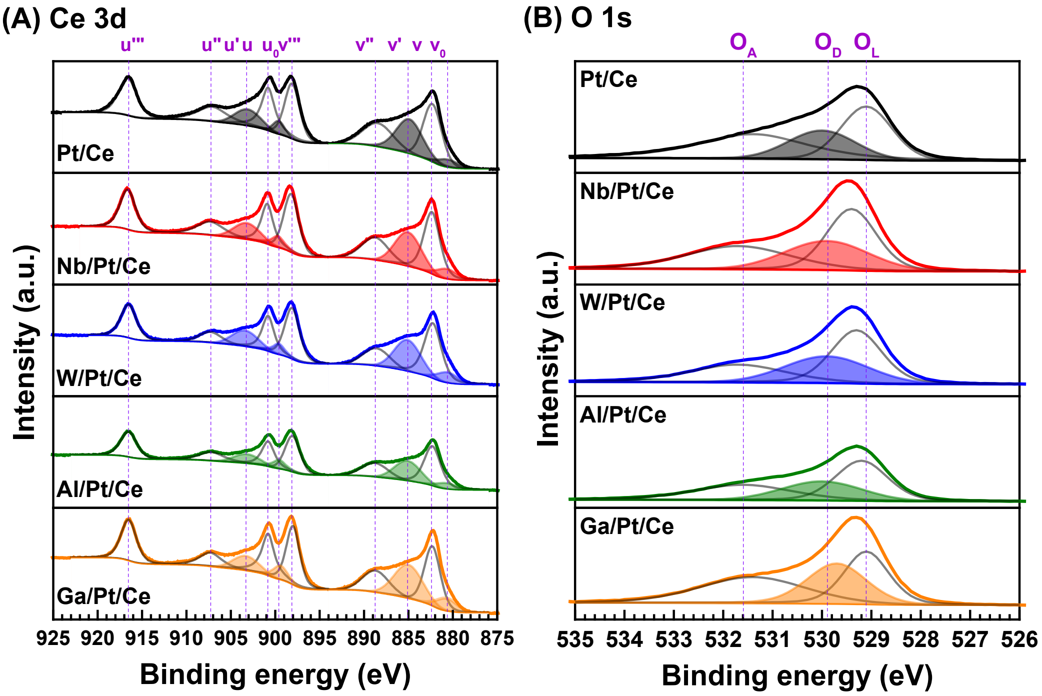

Figure S6. XPS spectra of the reduced Pt/Ce catalysts with various metal promoters.

(A) XPS Ce 3d spectra; (B) XPS O 1s spectra

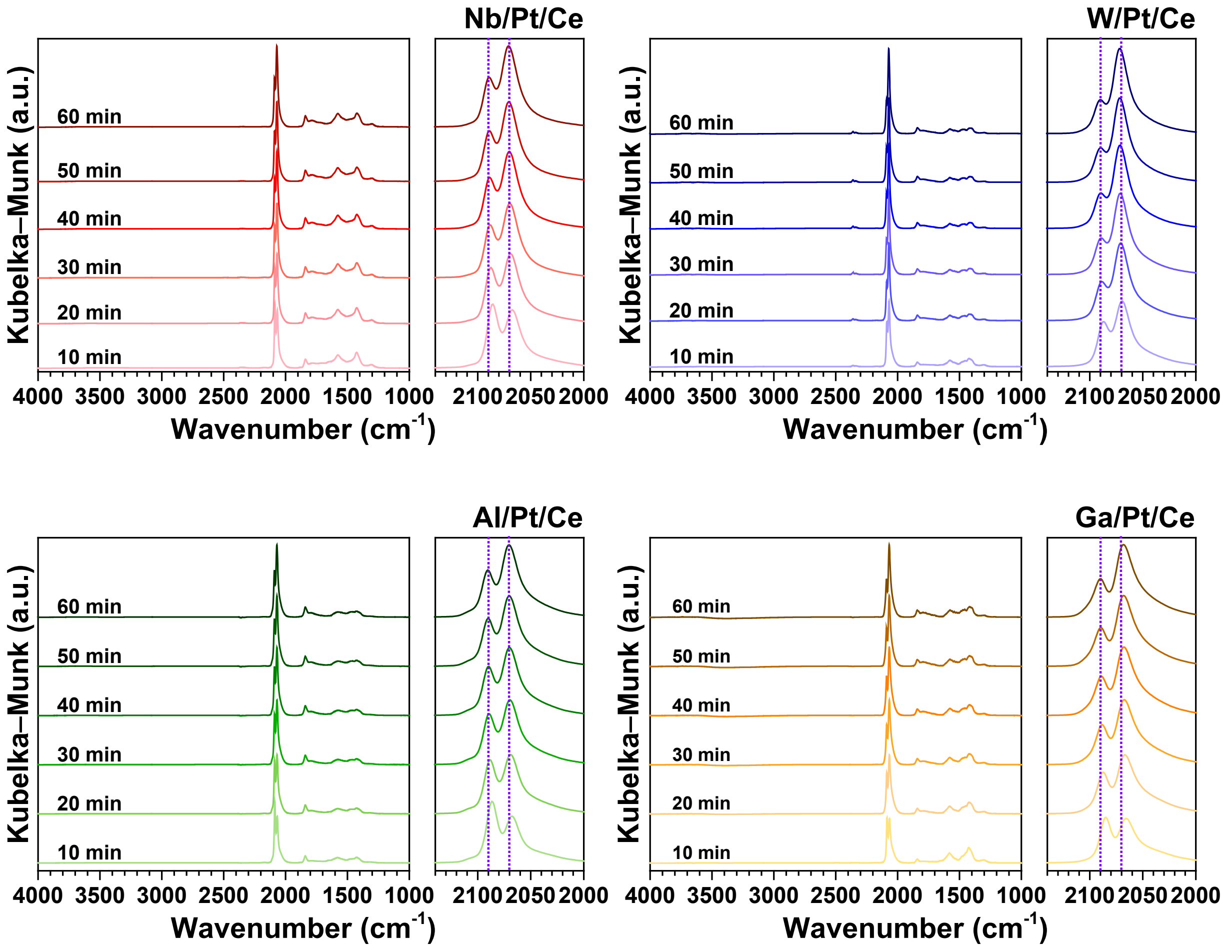

Figure S7. CO–DRIFTS spectra recorded in the 1,000–4,000 cm^{-1} range at 50 °C over 60 min at 10 min intervals of CO adsorption on reduced Me/Pt/Ce catalysts with various metal promoters.

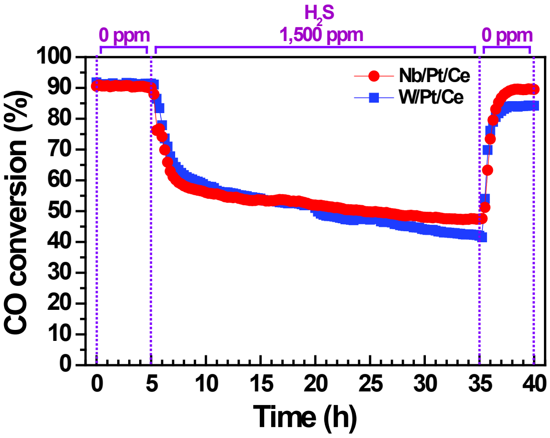

Figure S8. Catalytic performance with time on stream over Pt/Ce catalysts promoted with Nb and W. Reaction conditions: $H_2O/(CH_4 + CO + CO_2) = 2.0$; $T = 400$ °C; GHSV = 46,000 $mL \cdot g^{-1} \cdot h^{-1}$; H_2S = 1,500 ppm.

Table S1. Comparison of reported data and our results.

Catalyst	**GHSV (h^{-1})**	**H_2O/C**	**Temp. (°C)**	**CO conc. (%)**	**S conc. (ppm)**	**CO conv. (%)**
Nb/Pt/Ce	46,000	2.0	400	38.4% (dry)	1,000	63
Pt/Ce [1]	46,000	2.0	400	38.4% (dry)	500	80
CuOZnO(2)/HAP [2]	30,000	1.3	230	15% (wet)	200	16
Pt/Nb_2O_5 [3]	24,000	1.3	300	15% (wet)	50	28
Pt/$Ce_{0.25}Zr_{0.75}O_2$ [4]	24,000	1.3	300	15% (wet)	50	19
FeCe [5]	60,000	1.5	400	-	400	55

Supplementary References

1 K. J. Kim, Y. L. Lee, G. R. Hong, S. Y. Ahn, B. J. Kim, S. S. Lee, Y. Jeon and H. S. Roh, *Catal. Today*, DOI:10.1016/j.cattod.2023.114361.

2 C. C. de Souza, L. P. C. Silva, L. E. Terra, A. C. S. L. S. Coutinho, Y. Xing and F. B. Passos, *Catal. Today*, DOI:10.1016/j.cattod.2025.115480.

3 L. P. C. Silva, M. M. Freitas, R. M. Santos, G. Perez, L. E. Terra, A. C. S. L. S. Coutinho and F. B. Passos, *Int. J. Hydrogen Energy*, 2018, **43**, 3190–3202.

4 L. P. C. Silva, L. E. Terra, A. C. S. L. S. Coutinho and F. B. Passos, *J. Catal.*, 2016, **341**, 1–12.

5 G. K. Reddy, P. Boolchand and P. G. Smirniotis, *J. Catal.*, 2011, **282**, 258–269.