Supplementary Information

Thermal Deactivation of Pd/Al_2O_3–Cu/Al_2O_3-combined Three-way Catalysts via Cu Migration and Alloying

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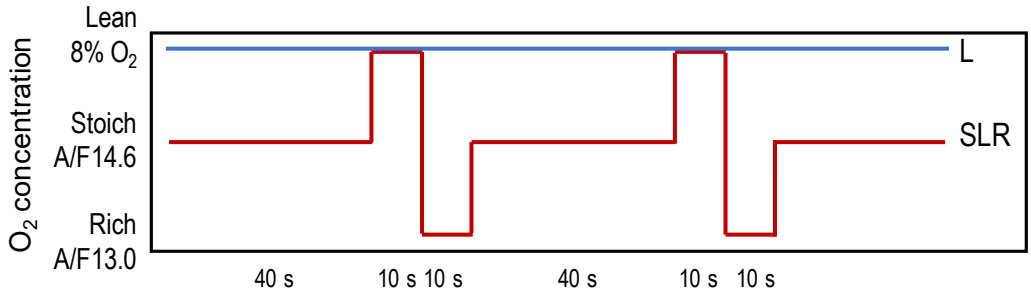

Figure S1. Schematic diagram of the gas feeds for thermal aging under SLR and L conditions. SLR: three simulated gas feeds, that is, a stoichiometric gas (S, 40 s), a fuel-lean gas (L, 10 s), and a fuel-rich gas (R, 10 s), were cycled sequentially. L: constant lean condition. Detailed gas compositions are shown below. The gas feed was supplied at a total flow rate of 100 mL min^{-1}. Gas compositions for each condition are shown below.

Aging	Stoichiometric (S) [b]	Lean (L) [b]	Rich (R) [b]	Air
Air-to-fuel ratio (A/F) [a]	14.6	-	13.0	-
Excess oxygen ratio	1.0	18.2	0.06	-
CO/%	0.50	0.50	0.50	-
C_3H_6/ppm	400	400	400	-
NO/ppm	500	500	500	-
O_2/%	0.4	8	0	18
H_2O/%	10	10	10	10
N_2	balance	balance	balance	balance

[a] The A/F value was calculated in accordance with a reported study[1] using the excess oxygen ratio of the simulated gas feed, which is calculated as follows:

$$\text{Excess oxygen ratio} = \frac{\text{Amount of oxygen in gas feed}}{\text{Amount of oxygen required for complete oxidation}} = \frac{2 \times p_{O2} + p_{NO}}{9 \times p_{C3H6} + p_{CO}}$$

[b] During SLR cycle aging, three gas feeds, that is, S (40 s), L (10 s), and R (10 s), were cycled sequentially.

Exposure to 10% H_2O/air flow without any exhaust gas mixture leads to an Air-aged Pd–Cu composite catalyst (Pd/A+Cu/A-Air). For Air aging, approximately 0.2 g of catalysts was placed into a preheated tubular furnace at the desired temperature. Following a 5-h exposure to 10% H_2O/air stream, the catalyst was removed from the furnace and cooled in air at room temperature. For L and SLR aging, approximately 0.2 g of catalysts was heated from room temperature to each

aging temperature (600°C–900°C) for 2 h under N_2 flow. When the desired aging temperature was achieved, N_2 was replaced by a simulated exhaust gas mixture as shown in the above table. Three different gas feeds, including a stoichiometric gas (A/F = 14.6, 40 s), a lean gas (8% O_2, 10 s), and a rich gas (A/F = 13.0, 10 s), were cycled sequentially, ending with the stoichiometric portion of the cycle at the end of the aging period of 5 h for L and SLR aging. After L and SLR aging, the catalyst bed was cooled under N_2 flow, and Pd/A+Cu/A-L and Pd/A+Cu/A-SLR catalysts were obtained, respectively.

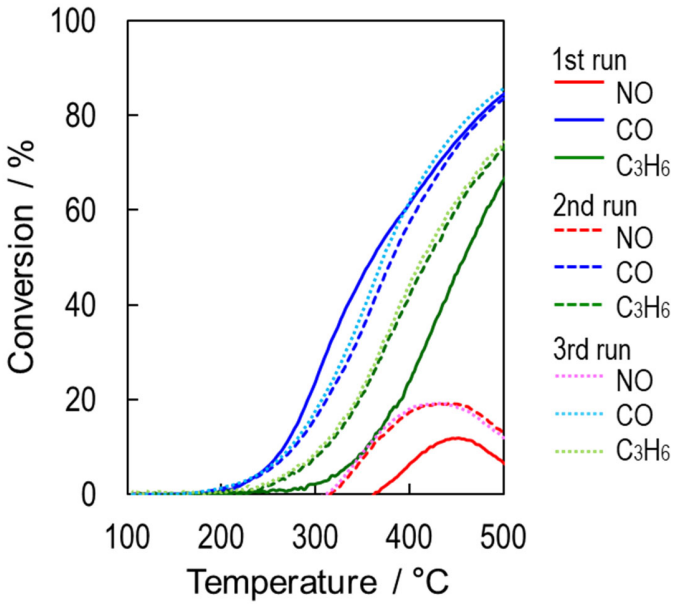

Figure S2. Light-off curves of NO, CO, and C_3H_6 during the first, second, and third light-off runs in the simulated TWC reaction over Cu/A after thermal aging under air.

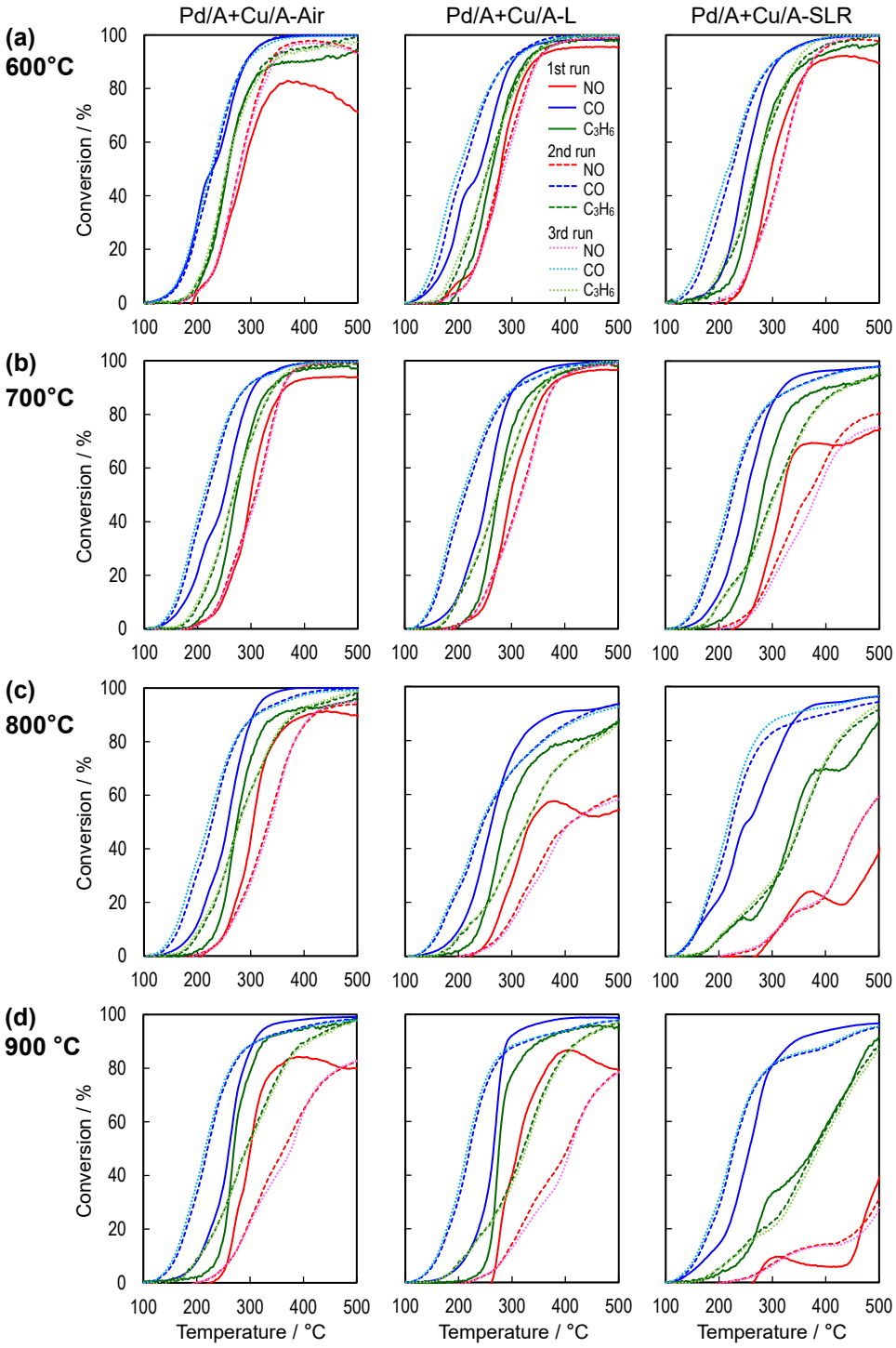

Figure S3. Light-off curves of NO, CO, and C_3H_6 during the first, second, and third light-off runs in the simulated TWC reaction over Pd/A+Cu/A-Air, Pd/A+Cu/A-L, and Pd/A+Cu/A-SLR catalysts with different aging temperatures: (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C.

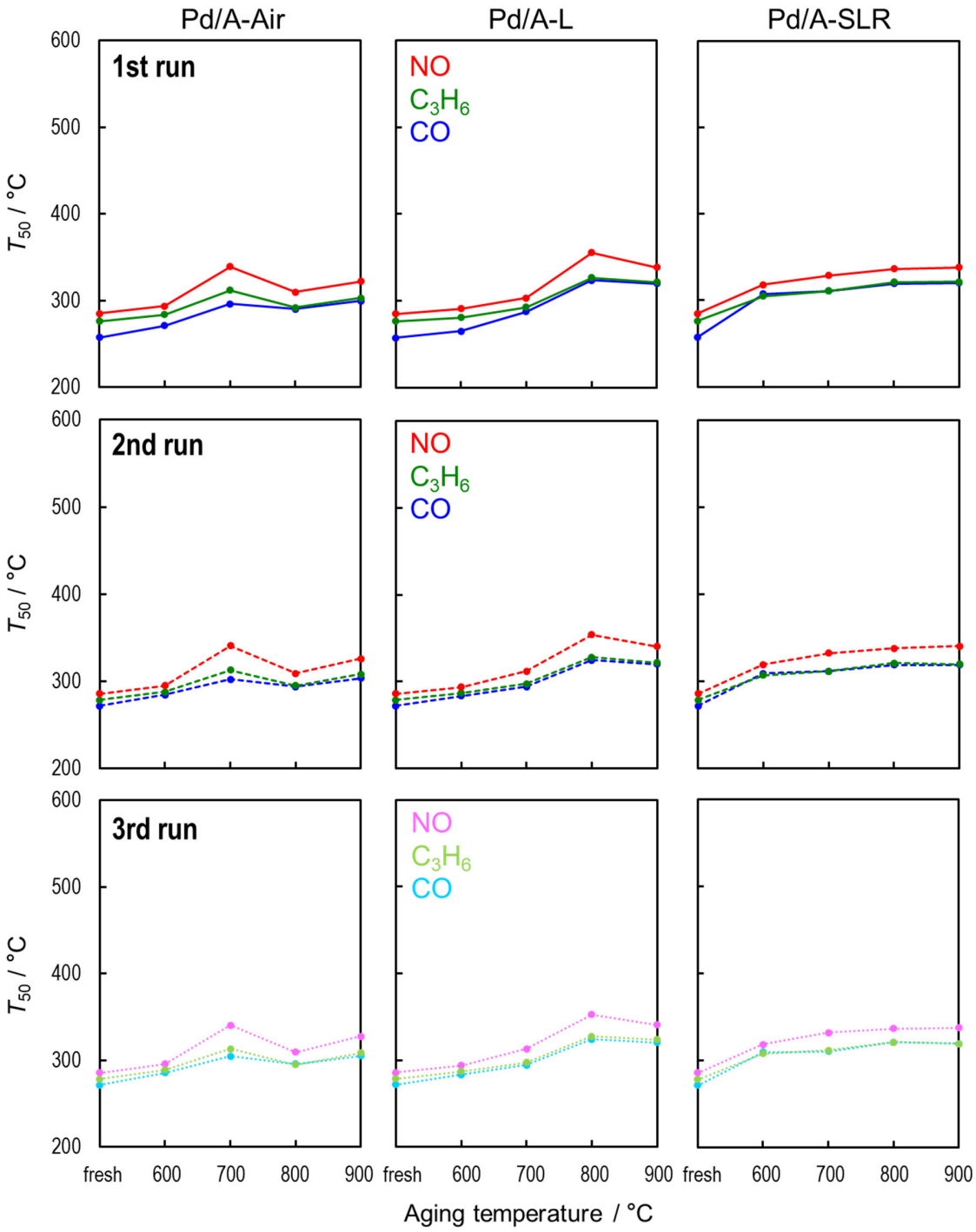

Figure S4. T_{50} values of NO, CO, and C_3H_6 during the first, second, and third light-off runs in the simulated TWC reaction for Pd/A catalysts after thermal aging at elevated temperatures under Air, L, and SLR conditions. The light-off curves for each plot are shown in Figure S5.

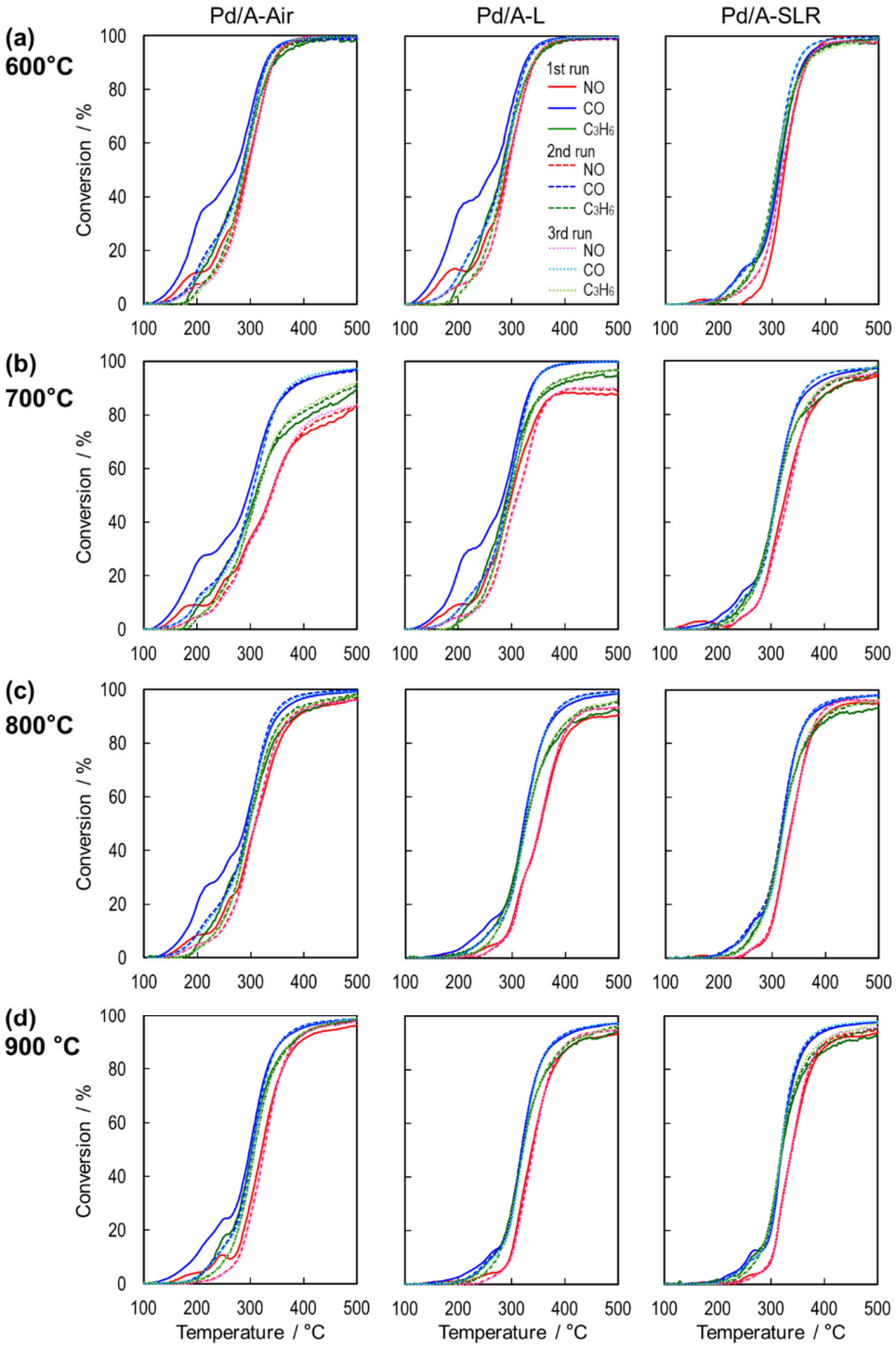

Figure S5. Light-off curves of NO, CO, and C_3H_6 during the first, second, and third light-off runs in the simulated TWC reaction over Pd/A-Air, Pd/A-L, and Pd/A-SLR catalysts with different aging temperatures: (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C.

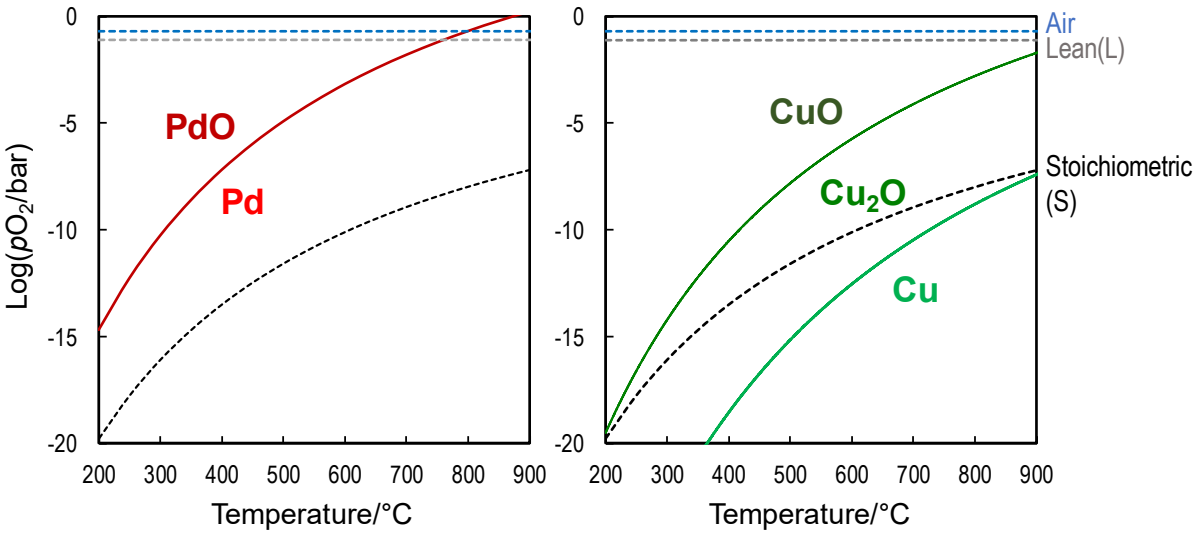

Figure S6. Phase relationships in the partial oxygen pressure versus temperature plots of the Pd–O and Cu–O systems. Red and green curves represent the equilibrium of PdO–Pd and CuO–Cu_2O–Cu, respectively, and other dashed curves correspond to the thermal aging atmosphere.

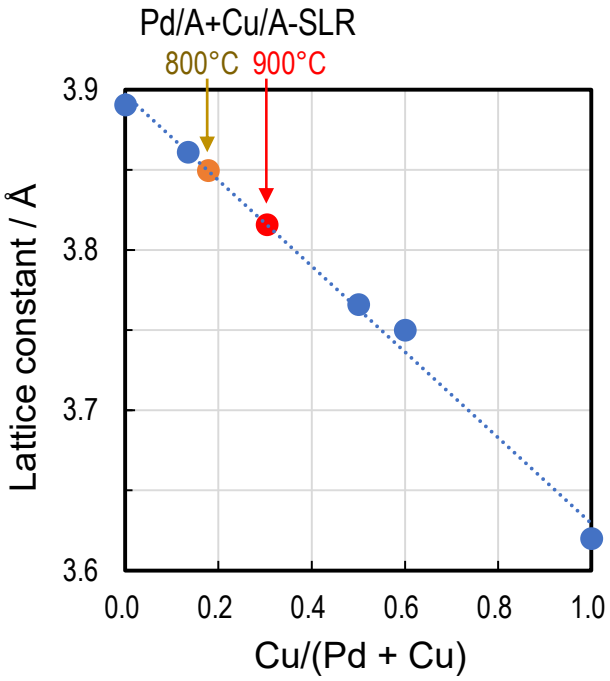

Figure S7. Lattice constant estimation of the Pd–Cu alloys formed in Pd/A+Cu/A-SLR after aging at 800°C and 900°C. The blue circles correspond to Pd−Cu alloys found in the literature data.[2-5] Pd–Cu alloys observed in Pd/A+Cu/A-SLR are shown as yellow and red circles.

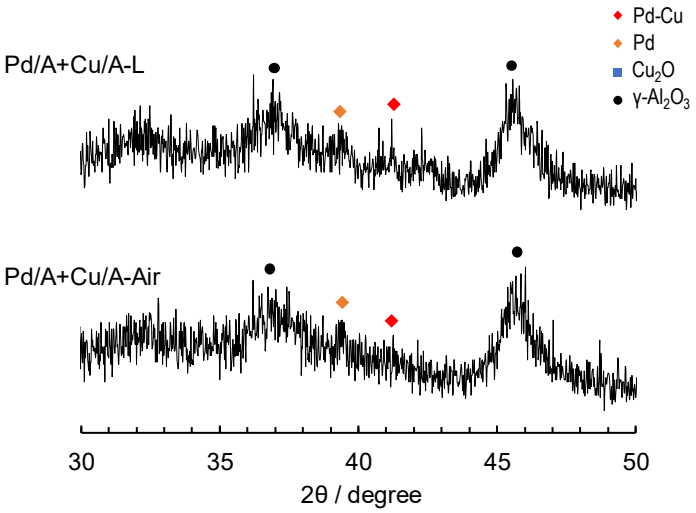

Figure S8. XRD patterns of Pd/A+Cu/A-Air and Pd/A+Cu/A-L catalysts (aged at 800°C) after stoichiometric TWC light-off runs (three runs).

REFERENCES

1. Tanaka, H.; Fujiwara, H.; Takahashi, I., Excellent Oxygen Storage Capacity of Perovskite-Pd Three-Way Catalysts. *SAE Paper* **1995**, 950256.

2. M. Friedrich and M. Armbrüster, *Chem. Mater.*, 2009, **21**, 5886-5891.

3. K. Baba, U. Miyagawa, K. Watanabe, Y. Sakamoto and T. B. Flanagan, *J. Mater Sci.*, 1990, **25**, 3910-3916.

3. O. Loebich and C. J. Raub, *J. Less Common Metals*, 1977, **55**, 67-76.

4. W. E. Krull and R. W. Newman, *J. Appl. Crystallogr.*, 1970, **3**, 519-521.