

## Supporting Information

# Enhanced chemical looping CO<sub>2</sub> conversion activity and thermal stability of perovskite LaCo<sub>1-x</sub>Al<sub>x</sub>O<sub>3</sub> by Al substitution

*Yoshihiro Goto,<sup>\*</sup> Kiyoshi Yamazaki,<sup>\*</sup> Masashi Kikugawa, and Masakazu Aoki*

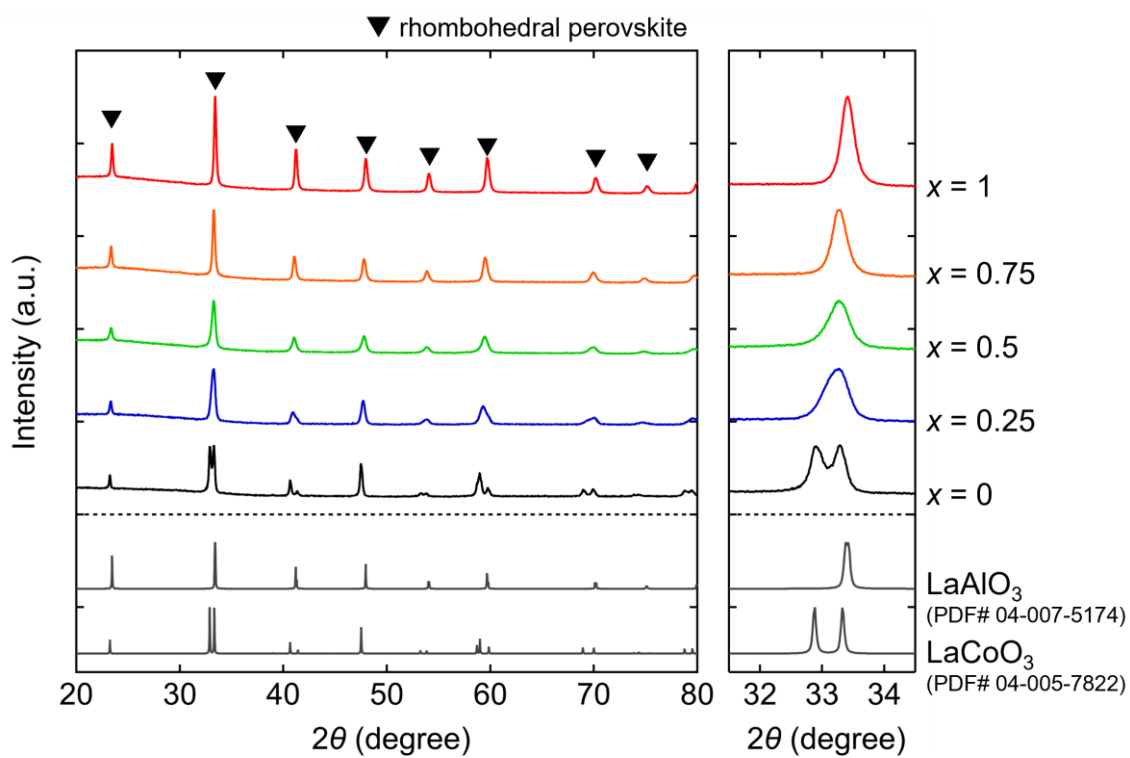
<sup>†</sup>*Toyota Central R&D Labs., Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan.*

<sup>\*</sup>*E-mail: yoshihiro-goto@mosk.tytlabs.co.jp (Y. Goto), e0936@mosk.tytlabs.co.jp (K. Yamazaki)*

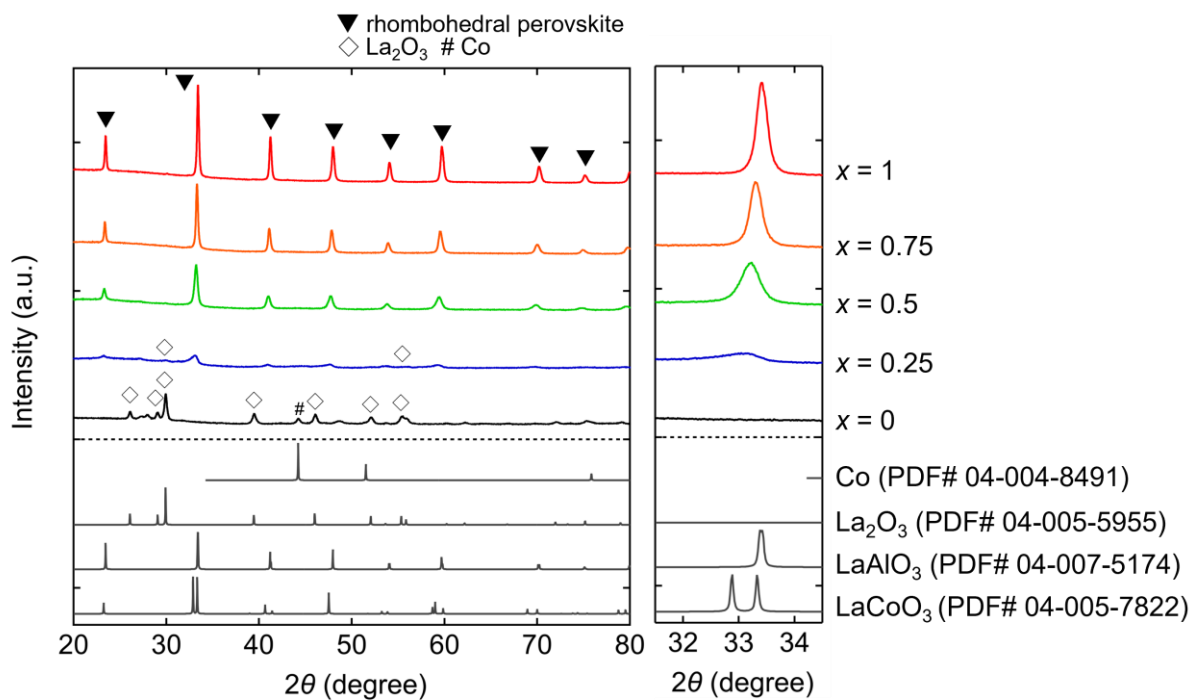
### 1. Preparation of benchmark reverse water–gas shift reaction chemical looping materials

La<sub>0.6</sub>Ca<sub>0.4</sub>Fe<sub>0.4</sub>Mn<sub>0.6</sub>O<sub>3</sub> was prepared using the polymerized complex method. La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.9%, FUJIFILM Wako Chemicals), Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (99%, Sigma-Aldrich), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99.999%, Sigma-Aldrich), Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.9%, FUJIFILM Wako Chemicals), citric acid (98%, FUJIFILM Wako Chemicals), and ethylene glycol (99%, FUJIFILM Wako Chemicals) were dissolved in a minimum amount of deionized water in a molar ratio of 0.6:0.4:0.4:0.6:6:6. The prepared solution was stirred on a hotplate at 90 °C for 7 h; the obtained gel was preheated at 450 °C for 2 h followed by calcination twice at 950 °C for 5 h in air. Co/In<sub>2</sub>O<sub>3</sub> was prepared using the wet impregnation method with In<sub>2</sub>O<sub>3</sub> (99.9%, FUJIFILM Wako Chemicals) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.9%, FUJIFILM Wako Chemicals) in a molar ratio of In:Co = 2:1, followed by calcination at 500 °C for 5 h in air.

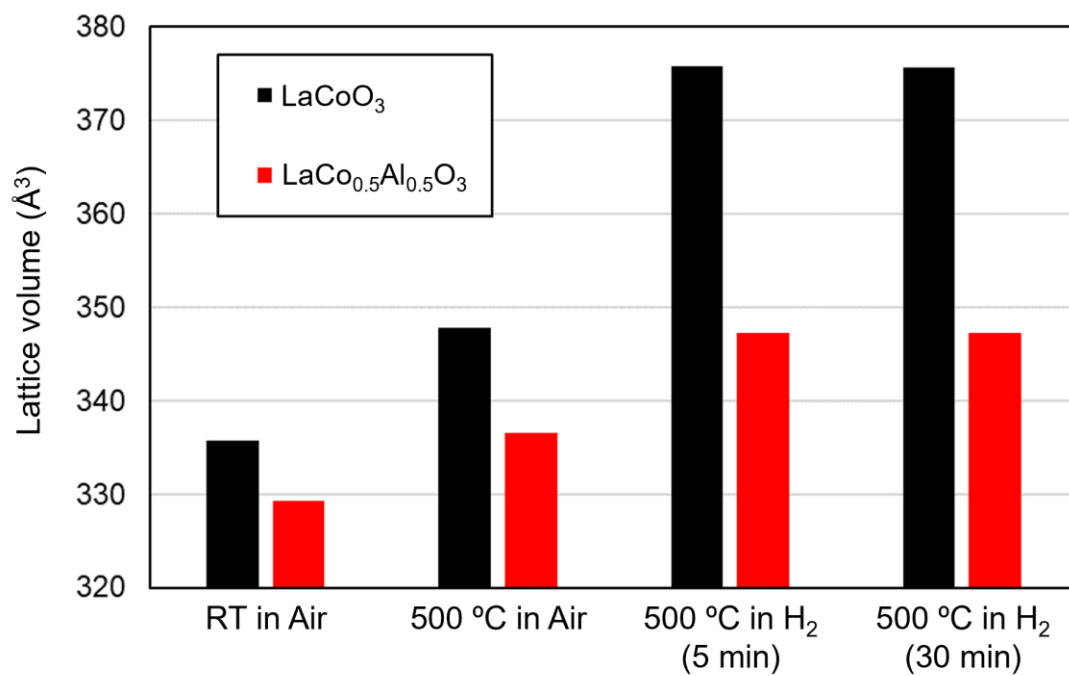
## 2. Supplementary figures



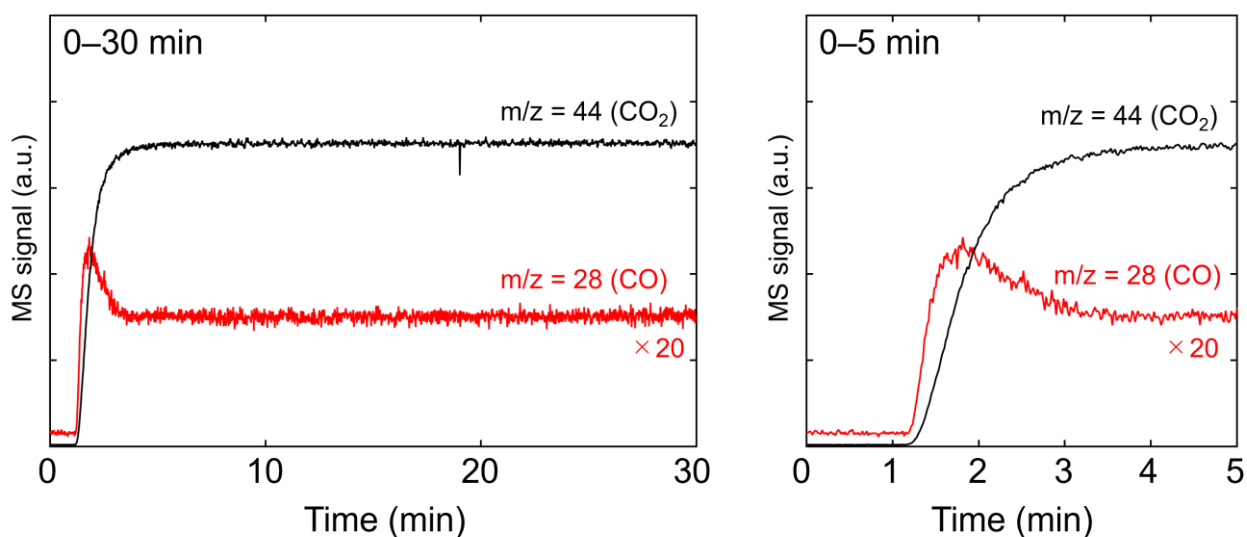
**Figure S1.** X-ray diffraction (XRD) patterns of  $\text{LaCo}_{1-x}\text{Al}_x\text{O}_3$  ( $0 \leq x \leq 1$ ) quenched at 500 °C under 5%  $\text{H}_2/\text{N}_2$  flow.



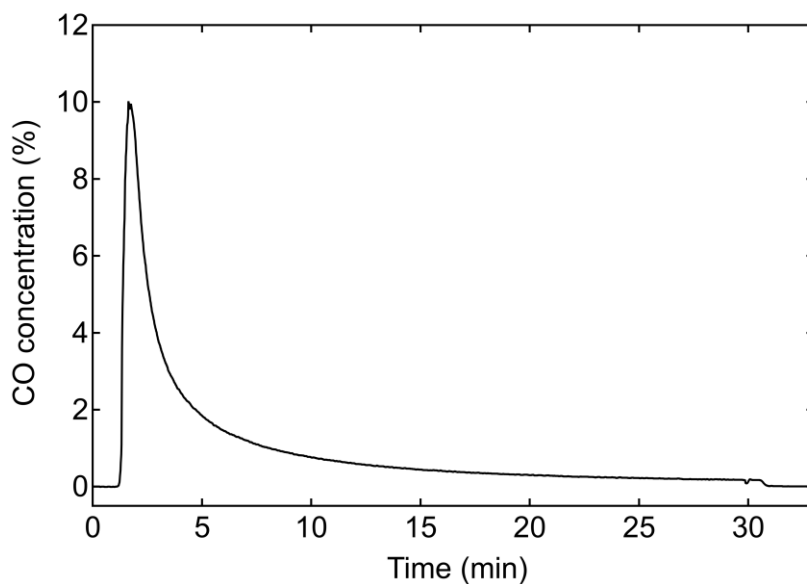
**Figure S2.** XRD patterns of LaCo<sub>1-x</sub>Al<sub>x</sub>O<sub>3</sub> ( $0 \leq x \leq 1$ ) quenched at 800 °C under 5% H<sub>2</sub>/N<sub>2</sub> flow.



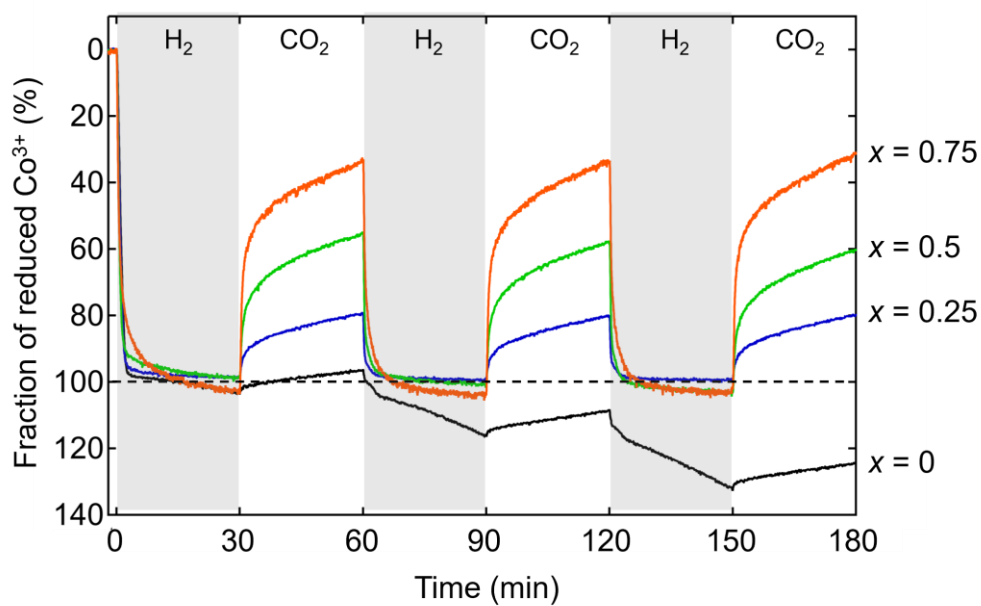
**Figure S3.** Lattice volumes of LaCoO<sub>3</sub> and LaCo<sub>0.5</sub>Al<sub>0.5</sub>O<sub>3</sub> at room temperature in air, 500 °C in air, and 500 °C in 100% H<sub>2</sub> (5 and 30 min) estimated from in situ synchrotron XRD patterns.



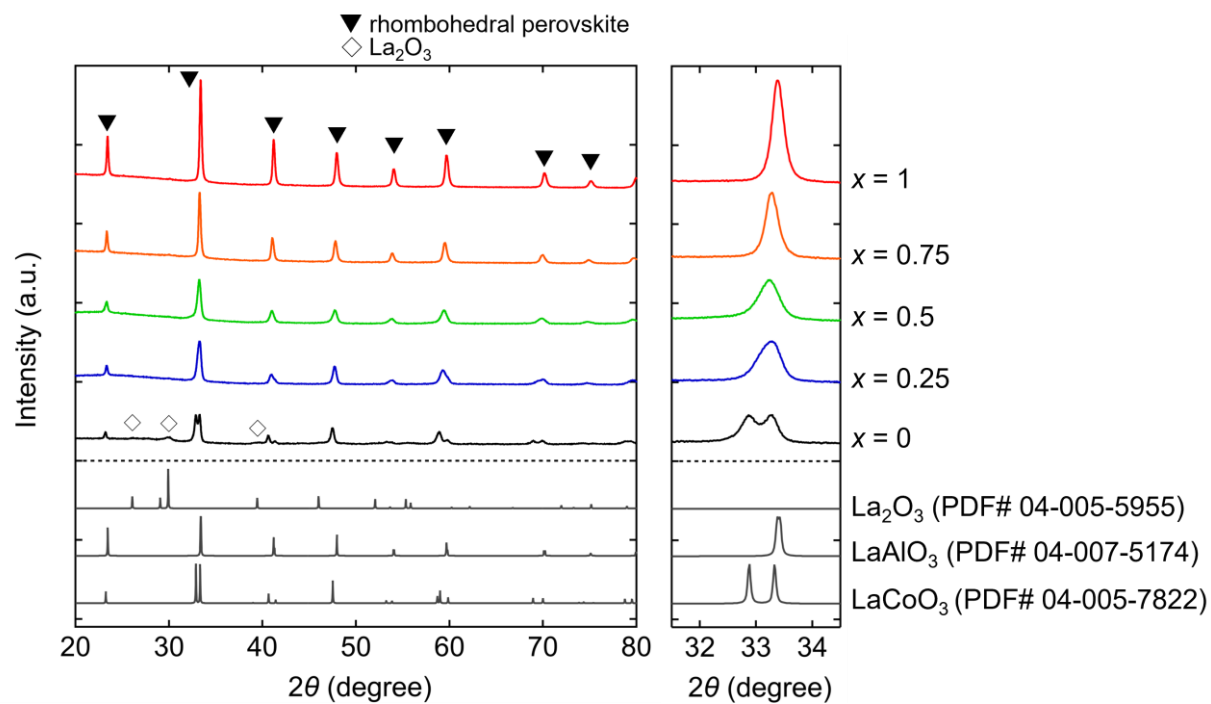
**Figure S4.** Mass spectra of CO ( $m/z = 28$ ) and CO<sub>2</sub> ( $m/z = 44$ ) in the LaCo<sub>0.5</sub>Al<sub>0.5</sub>O<sub>3</sub> outlet gas (40 mg) after switching the flow from 5% H<sub>2</sub>/He (100 mL min<sup>-1</sup>) to 5% CO<sub>2</sub>/He (100 mL min<sup>-1</sup>) at 500 °C. Pretreatment was conducted for 30 min under 5% H<sub>2</sub>/He flow. The CO intensity increased temporarily after CO<sub>2</sub> introduction and then decreased, indicating that CO was produced in the RWGS-CL reaction between LaCo<sub>0.5</sub>Al<sub>0.5</sub>O<sub>3</sub> and CO<sub>2</sub>, in addition to the fragmentation of unreacted CO<sub>2</sub>.



**Figure S5.** CO concentration in the  $\text{LaCo}_{0.5}\text{Al}_{0.5}\text{O}_3$  outlet gas (2.00 g) after switching the flow from 50%  $\text{H}_2/\text{He}$  ( $50 \text{ mL min}^{-1}$ ) to 50%  $\text{CO}_2/\text{He}$  ( $50 \text{ mL min}^{-1}$ ) at  $500 \text{ }^\circ\text{C}$ . Pretreatment was conducted for 30 min under 5%  $\text{H}_2/\text{He}$  flow. The CO concentration was determined by Fourier-transform infrared (FT-IR) spectroscopy. The maximum concentration of CO was 10.0%. The CO production amount was  $3.31 \times 10^{-4} \text{ CO-mol g}^{-1}$ .

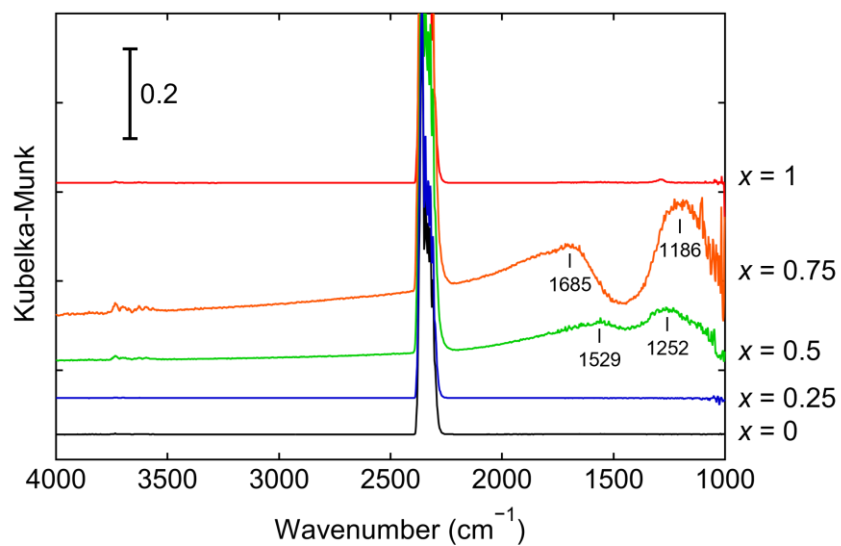


**Figure S6.** Fraction of reduced  $\text{Co}^{3+}$  ( $[\text{Co}^{2+}]/([\text{Co}^{2+}] + [\text{Co}^{3+}])$ ) in the isothermal reverse water–gas shift reaction chemical looping (RWGS-CL) reaction at 500 °C.

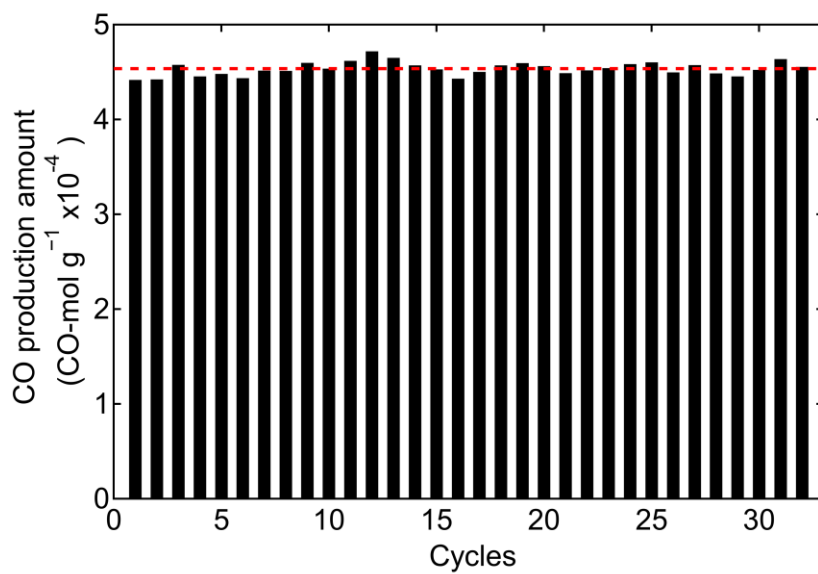


**Figure S7.** XRD patterns of LaCo<sub>1-x</sub>Al<sub>x</sub>O<sub>3</sub> ( $0 \leq x \leq 1$ ) after the RWGS-CL reaction at 500 °C.

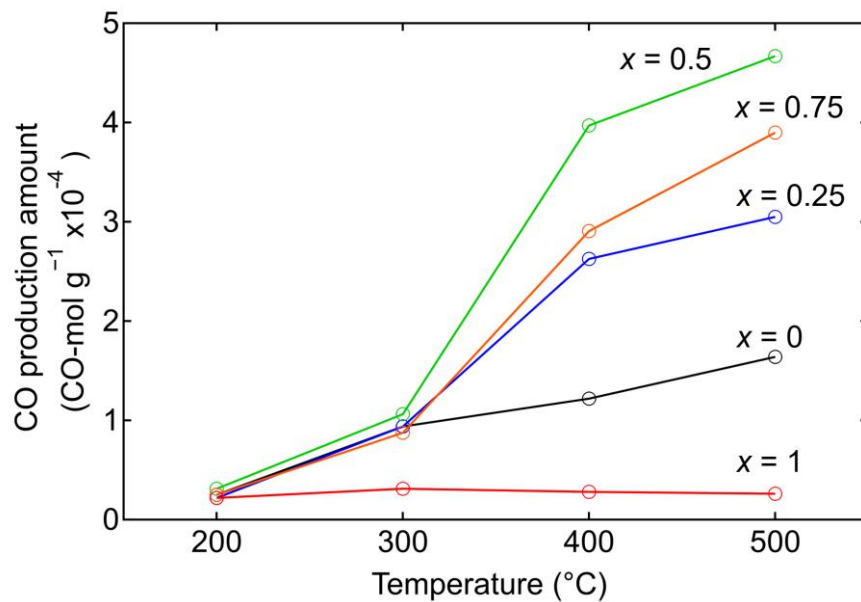




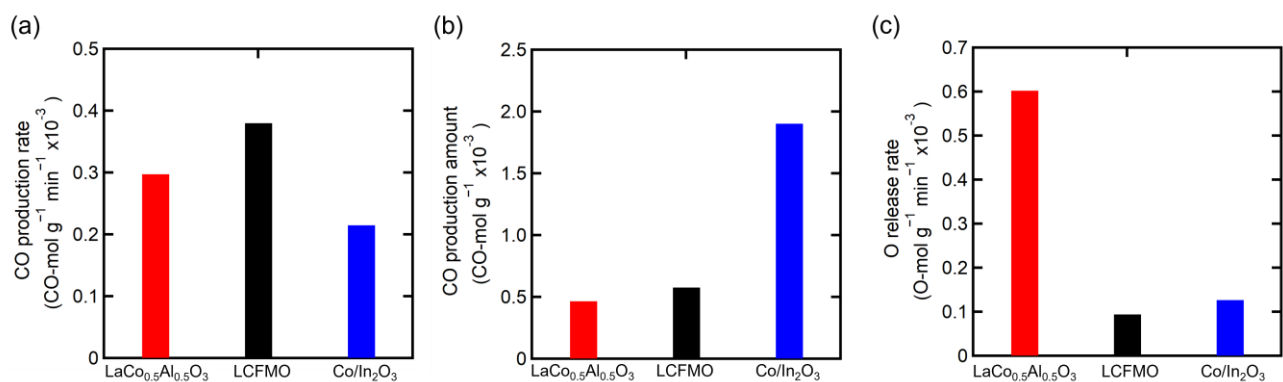
**Figure S8.** Diffuse reflectance infrared Fourier transform spectra of LaCo<sub>1-x</sub>Al<sub>x</sub>O<sub>3</sub> ( $0 \leq x \leq 1$ ) at 500 °C in 5% CO<sub>2</sub>/N<sub>2</sub>. The spectra collected after the pretreatment at 500 °C for 30 min under 5% H<sub>2</sub>/N<sub>2</sub> flow are used as background. Peaks at approximately 2300 cm<sup>-1</sup> are assigned to the CO<sub>2</sub> gas phase.<sup>S1</sup>



**Figure S9.** RWGS-CL stability test for  $\text{LaCo}_{0.5}\text{Al}_{0.5}\text{O}_3$ . The red dashed line represents the average CO production amount ( $4.54 \times 10^{-4} \text{ CO-mol g}^{-1}$ ).



**Figure S10.** Temperature dependence of the CO production amount of  $\text{LaCo}_{1-x}\text{Al}_x\text{O}_3$  estimated from the weight increase in 5%  $\text{CO}_2/\text{N}_2$  at 200–500 °C. Pretreatment was carried out for 30 min under 5%  $\text{H}_2/\text{N}_2$  flow at the same temperature as that under 5%  $\text{CO}_2/\text{N}_2$  flow (200–500 °C).



**Figure S11.** Comparison of (a) CO production rate, (b) CO production amount, and (c) O release rate on LaCo<sub>0.5</sub>Al<sub>0.5</sub>O<sub>3</sub> in this study and prepared various oxides (La<sub>0.6</sub>Ca<sub>0.4</sub>Fe<sub>0.4</sub>Mn<sub>0.6</sub>O<sub>3</sub><sup>S2</sup> and Co/In<sub>2</sub>O<sub>3</sub><sup>S3</sup>) reported in literatures.

## References

- S1 F. Azzolina-Jury and F. Thibault-Starzyk, *Top. Catal.*, 2017, **60**, 1709.
- S2 D. Maiti, B. J. Hare, Y. A. Daza, A. E. Ramos, J. N. Kuhn, and V. R. Bhethanabotla, *Energy Environ. Sci.*, 2018, **11**, 648.
- S3 J. Makiura, S. Kakihara, T. Higo, N. Ito, Y. Hirano, and Y. Sekine, *Chem. Commun.*, 2022, **58**, 4837.