Electronic Supplementary Information

Catalytic Partial Oxidation of Methane over Oxide-Ion-Conductive Lanthanum Silicate Apatites

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Contents

Catalyst preparation

La_2O_3 (High Purity Chemicals, Japan, 99.99%), SiO_2 (High Purity Chemicals, 99.9%), $CaCO_3$ (High Purity Chemicals, 99.99%), Na_2CO_3 (FUJIFILM Wako Chemicals, ≥99.8%), Ba_2CO_3 (FUJIFILM Wako Chemicals, 99.9%), In_2O_3 (High Purity Chemicals, 99.99%), Bi_2O_3 (High Purity Chemicals, 99.9%), Y_2O_3 (FUJIFILM Wako Chemicals, 99.99%), $SrCO_3$ (FUJIFILM Wako Chemicals, 99.99%), Ga_2O_3 (High Purity Chemicals, 99.99%), MgO (FUJIFILM Wako Chemicals, 99.9%), TiO_2 (High Purity Chemicals, 99%), $Ca(NO_3)_2{\cdot}4H_2O$ (FUJIFILM Wako Chemicals, 99.9%), $Al(NO_3)_3{\cdot}6H_2O$ (FUJIFILM Wako Chemicals, 99.99%), and citric acid (FUJIFILM Wako Chemicals, ≥98.0%) were used as starting materials. The appropriate amounts of raw materials were mixed in an agate mortar followed by an addition of ethanol to facilitate homogeneous mixing. The mixture was subsequently fired in a muffle furnace with intermediate grinding according to the conditions listed in Table S1. $LaCaAl_3O_7$ was prepared with a wet chemical route. Each starting material was dissolved in ultra-pure water (HNO_3 was added to La solution). The solutions were mixed in a molar ratio of La:Ca:Al:citric acid 1:1:3:15, followed by evaporation at 120 °C in an oven. Then, the resulting solid was heated at 450 °C using a heating mantle. The result was ground into powder and fired at 900 °C.

Table S1. Conditions for catalyst preparation.

Target Compounds	Starting Materials	Synthesis Conditions
$La_{9.33}Si_6O_{26}$	La_2O_3, SiO_2	Fired at 1300 °C and 1400 °C for 12 h
$La_9NaSi_6O_{26}$	La_2O_3, SiO_2, Na_2CO_3	Fired at 900 °C and 1350 °C for 6 h
$La_8Ca_2Si_6O_{26}$	La_2O_3, SiO_2, $CaCO_3$	Fired at 1300 °C and 1400 °C for 12 h
La_2SiO_5	La_2O_3, SiO_2	Fired at 1600 °C for 3 h
$Ba_2In_2O_5$	$BaCO_3$, In_2O_3	Fired at 1000 °C and 1200 °C for 10 h
$Bi_{1.4}Y_{0.6}O_3$	Bi_2O_3, Y_2O_3	Fired at 1000 °C for 12 h
$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.55}$	La_2O_3, $SrCO_3$, Ga_2O_3, MgO	Fired at 1000 °C and 1500 °C for 6 h
$Y_2Ti_2O_7$	Y_2O_3, TiO_2	Fired at 1000 °C and 1200 °C for 12 h
$LaCaAl_3O_7$ *	La_2O_3, $Ca(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}6H_2O$, citric acid	Fired at 900 °C

*Wet chemical route

Table S2. Lattice parameters of LSO compared to the reference.

a (Å)	*c* (Å)	*V* (Å^3)	Ref.
9.700(3)	7.168(6)	584.2	This work
9.719(5)	7.17(2)	586.5	[S1]

Table S3. Detailed results of the catalytic activity test for LSO.

Temperature	CH_4	Selectivity (%)					Yield (%)	
(°C)	Conversion (%)	H_2	CO	CO_2	C_2H_4	C_2H_6	H_2	CO
500	0.9	39.2	58.0	42.0	0	0	0.3	0.5
600	6.4	37.0	55.2	42.0	0	2.9	2.3	3.5
700	22.1	19.2	34.0	43.3	10.0	12.8	4.2	7.5

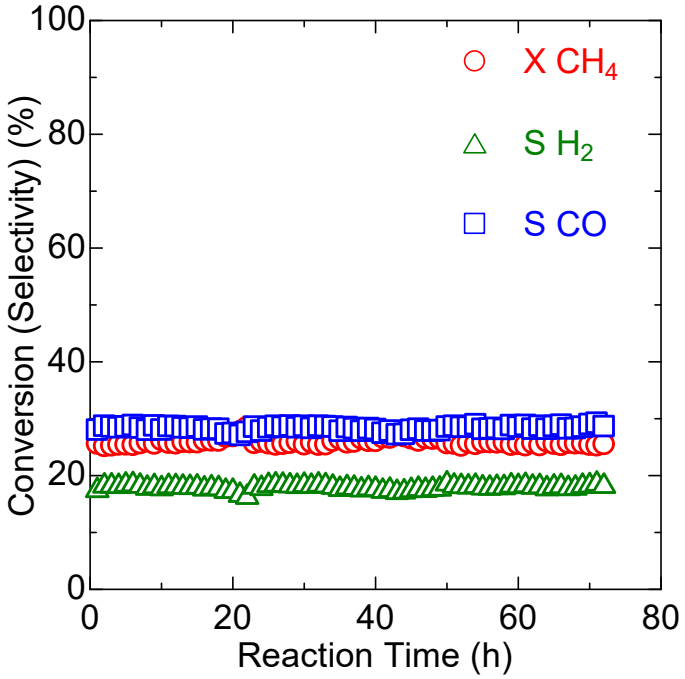

Figure S1. Long-term catalytic test over LSO for 72 h at 700 °C.

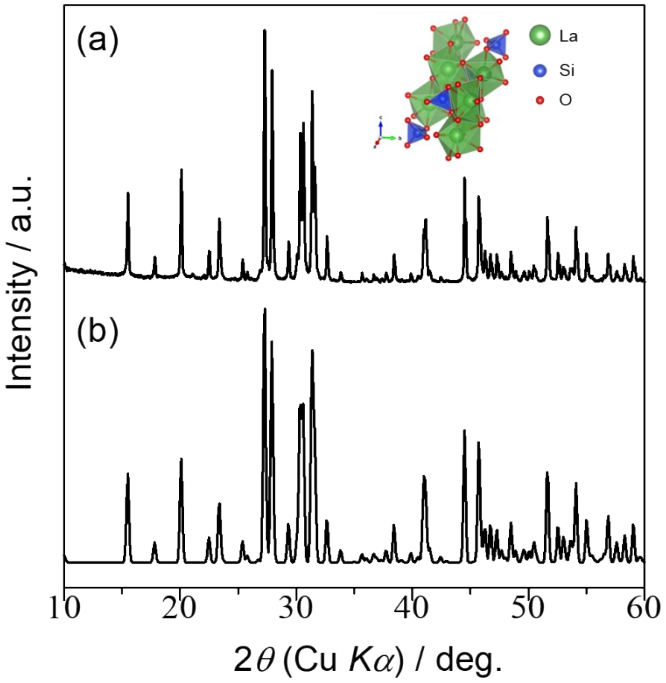

Figure S2. (a) XRD pattern for La_2SiO_5. (b) Simulated pattern for La_2SiO_5 from ICSD#157892 [S2].

Table S4. Lattice parameters of La_2SiO_5 compared to the reference.

a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	Ref.
9.329(4)	7.507(4)	7.030(5)	466.4	This work
9.332(0)	7.508(8)	7.033(2)	466.9	[S2]

Table S5. Detailed results of the catalytic activity test for La_2SiO_5.

Temperature	CH_4	Selectivity (%)					Yield (%)	
(°C)	Conversion (%)	H_2	CO	CO_2	C_2H_4	C_2H_6	H_2	CO
500	0.5	37.0	67.1	32.9	0.0	0.0	0.2	0.3
600	3.0	37.0	66.5	33.5	0.0	0.0	1.1	2.0
700	13.3	22.9	46.7	38.3	4.3	10.7	3.0	6.2

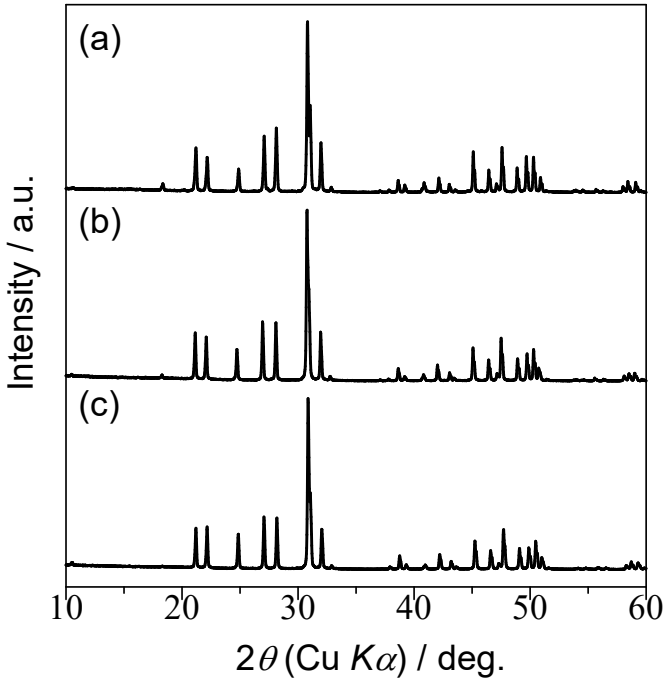

Figure S3. (a) XRD patterns for LSO, (b) sodium-substituted LSO ($La_9NaSi_6O_{26}$, LNSO), and (c) calcium-substituted LSO ($La_8Ca_2Si_6O_{26}$, LCSO).

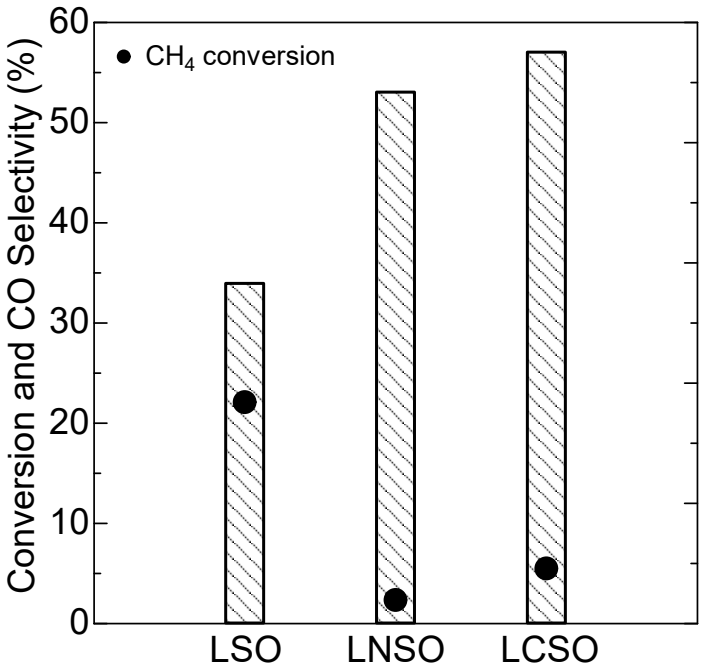

Figure S4. Catalytic activity data at 700 °C for LSO ($La_{9.33}Si_6O_{26}$), LNSO ($La_9NaSi_6O_{26}$), and LCSO ($La_8Ca_2Si_6O_{26}$).

References

[S1] K. Fujii, M. Yashima, K. Hibino, M. Shiraiwa, K. Fukuda, S. Nakayama, N. Ishizawa, T. Hanashima, T. Ohhara, *J Mater Chem A Mater*. **2018**, *6* (23), 10835–10846. DOI: 10.1039/C8TA02237B.

[S2] K. Fukuda, T. Iwata, E. Champion, *Powder Diffr*. **2006**, *21* (4), 300–303. DOI: 10.1154/1.2383066.