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Supplementary information

Enhanced C_{2+} Selectivity in Plasma-assisted Chemical Looping Oxidative Coupling of Methane using (Na, Li, and K) doped $LaMnO_3$

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Table S1. Fixed bed experimental procedure.

	Gas	Gas flow rate (ml/min)	Reaction time	Reaction type
1	N_2	100	30 min	Purging
2	Pure CH_4	50	30 s	Reduction reaction
3	N_2	100	30 min	Purging
4	Air	100	20 min	Oxidation reaction

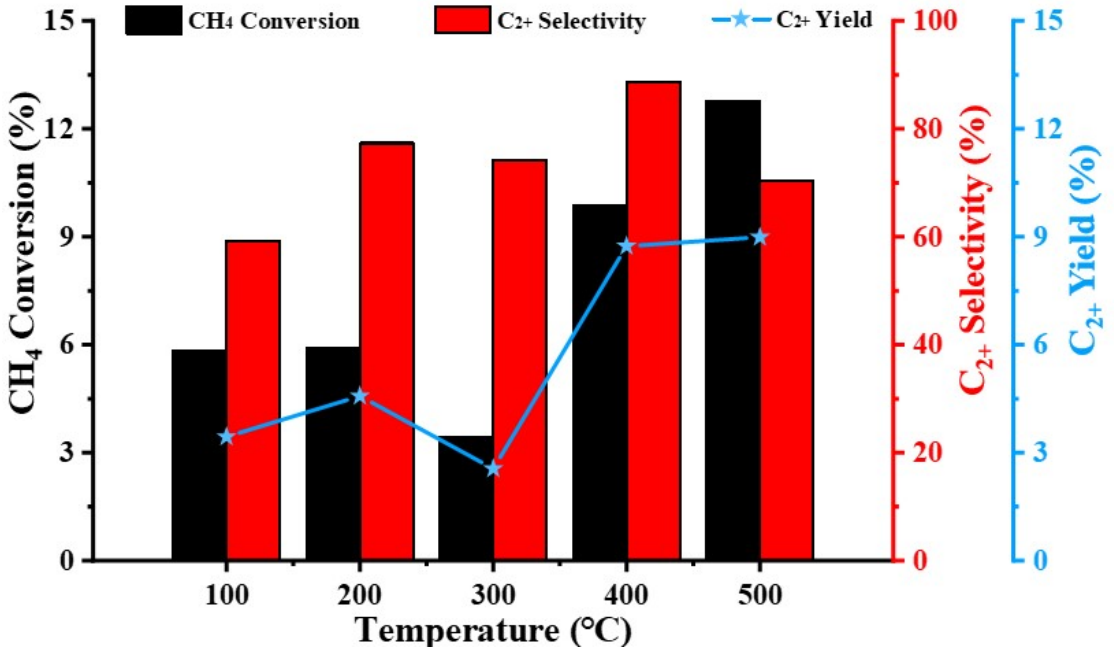

Fig. S1. Plasma-assisted CLOCM performance of K-$LaMnO_3$ at different temperatures (plasma discharge power: 50 W).

Table S2. Comparison of oxidative coupling of methane performance in the work with Those with similar systems.

Catalyst	Temperature (°C)	CH_4 Conversion（%）	C_{2+} Selectivity (%)	C_{2+} Yield（%）	Method	Author
Na-$LaMnO_3$	400	9.9	73.9	7.3	Plasma-assisted CLOCM	This work
Li-$LaMnO_3$	400	2.2	43.8	0.9	Plasma-assisted CLOCM	This work
K-$LaMnO_3$	400	9.8	88.7	8.7	Plasma-assisted CLOCM	This work
FeMnO3-Na2WO4	800	20	80	16	Chemical looping OCM	Sun[1]
Na-Mg_6MnO_8	850	27.9	82.9	23.2	Chemical looping OCM	Huang[2]
$La_2Ce_2O_7$	750	26.6	62.4	16.6	Oxidative coupling of methane	Xu[3]
Na_2WO_4/Mn/SiO_2	850	32	45	14.4	OCM	Lee[4]
Ag/SiO_2	385	27.3	35.7	9.7	Plasma-assisted OCM	Lee[5]
Ag/Glass bead	385	\	\	4.5	Plasma-assisted OCM	Lee[5]
Ag/γ-Al_2O_3	385	\	\	4.0	Plasma-assisted OCM	Lee[5]
Ag/TiO_2	385	\	\	1.9	Plasma-assisted OCM	Lee[5]
Ag/$BaTiO_3$	385	\	\	1.8	Plasma-assisted OCM	Lee[5]
La/ZrO_2	150	3	31.2	0.9	Thermal catalytic	Oshima[6]
Ba/La_2O_3	150	6.3	32.3	2.0	Thermal catalytic	Oshima[6]
Na_2WO_4/La_2O_3	750	2	50	1.0	Oxidative coupling of methane	Yildiz[7]
(Li, W)-Mg_6MnO_8	850	49	58.4	26.8	Chemical looping OCM	Baser[8]
Li/$BaSrTiO_3$	800	37	59.5	22.0	Oxidative coupling of methane	Farzaneh[9]
CaO/SiO_2	800	40	50	20.0	Oxidative coupling of methane	An et al.
$LaInO_3$	800	15.4	53.6	8.3	Oxidative coupling of methane	Tanaka[10]
$La_{0.6}Ba_{0.4}InO_{3-x}$	800	21.4	61.1	13.1	Oxidative coupling of methane	Tanaka[10]
Li/$SmzO_3$/MgO	800	24	64.0	15.4	Oxidative coupling of methane	Elkins[11]
Li/MgO	800	38.05	35.2	13.4	Oxidative coupling of methane	Raouf[12]

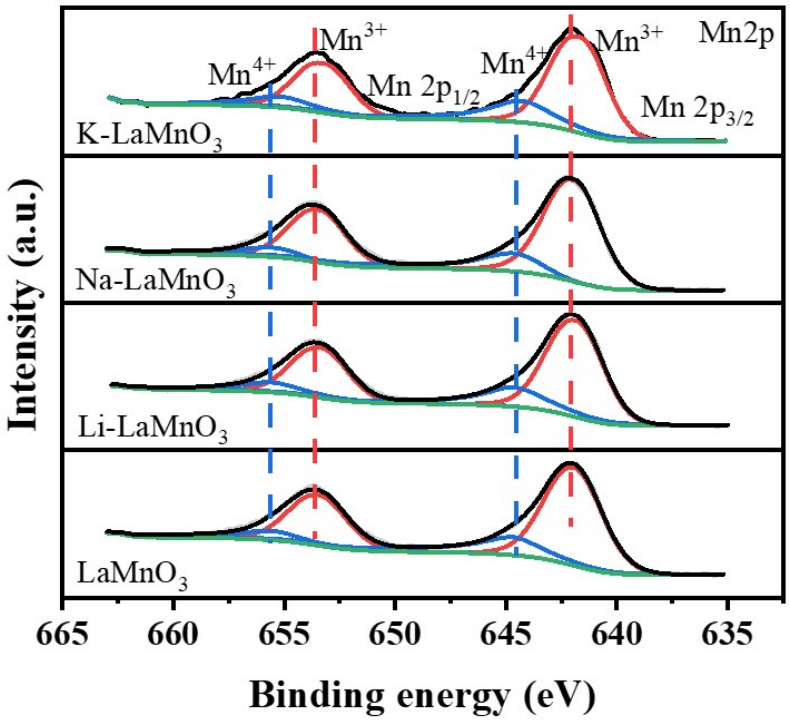

Fig. S2. Mn 2p XPS spectra of the corresponding X-$LaMnO_3$ (X=Na, Li, and K) and undoped $LaMnO_3$ oxygen carriers.

Table S3. The quantitative analysis results of Manganese distribution.

Sample	Manganese distribution (%)		
	Mn^{4+}	Mn^{3+}	Mn^{4+}/ Mn^{3+}
$LaMnO_3$	23.57	76.43	0.31
Li- $LaMnO_3$	24.48	75.52	0.32
Na- $LaMnO_3$	21.93	78.07	0.28
K- $LaMnO_3$	27.11	72.89	0.37

The Mn 2p XPS spectra showed that K doping increased the relative content of Mn^{4+} in the oxygen carrier, which in turn enhanced the redox properties of the oxygen carrier[2]. The ratio of Mn^{4+}/Mn^{3+} follows the trend of K-$LaMnO_3$ > Li- $LaMnO_3$ > $LaMnO_3$ > Na- $LaMnO_3$.

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