Supplementary information

Asymmetric coordination activated lattice oxygen in perovskite ferrites for selective anaerobic oxidation of methane

Wenxi Chang[a,b,†], Yuming Gao[c,†], Jiahui He[a,b], Xue Xia[a,b], Chuande Huang[a,*], Yue Hu[a,d], Weibin Xu[a,d], Bo Jiang[c,*], Yujia Han[a,d], Yanyan Zhu[b,*], Xiaodong Wang[a,*]

[a]CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

[b]College of Chemical Engineering, Northwest University, Xi'an 710069, China

[c]Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian116023, China

[d]University of Chinese Academy of Sciences, Beijing 100049, China

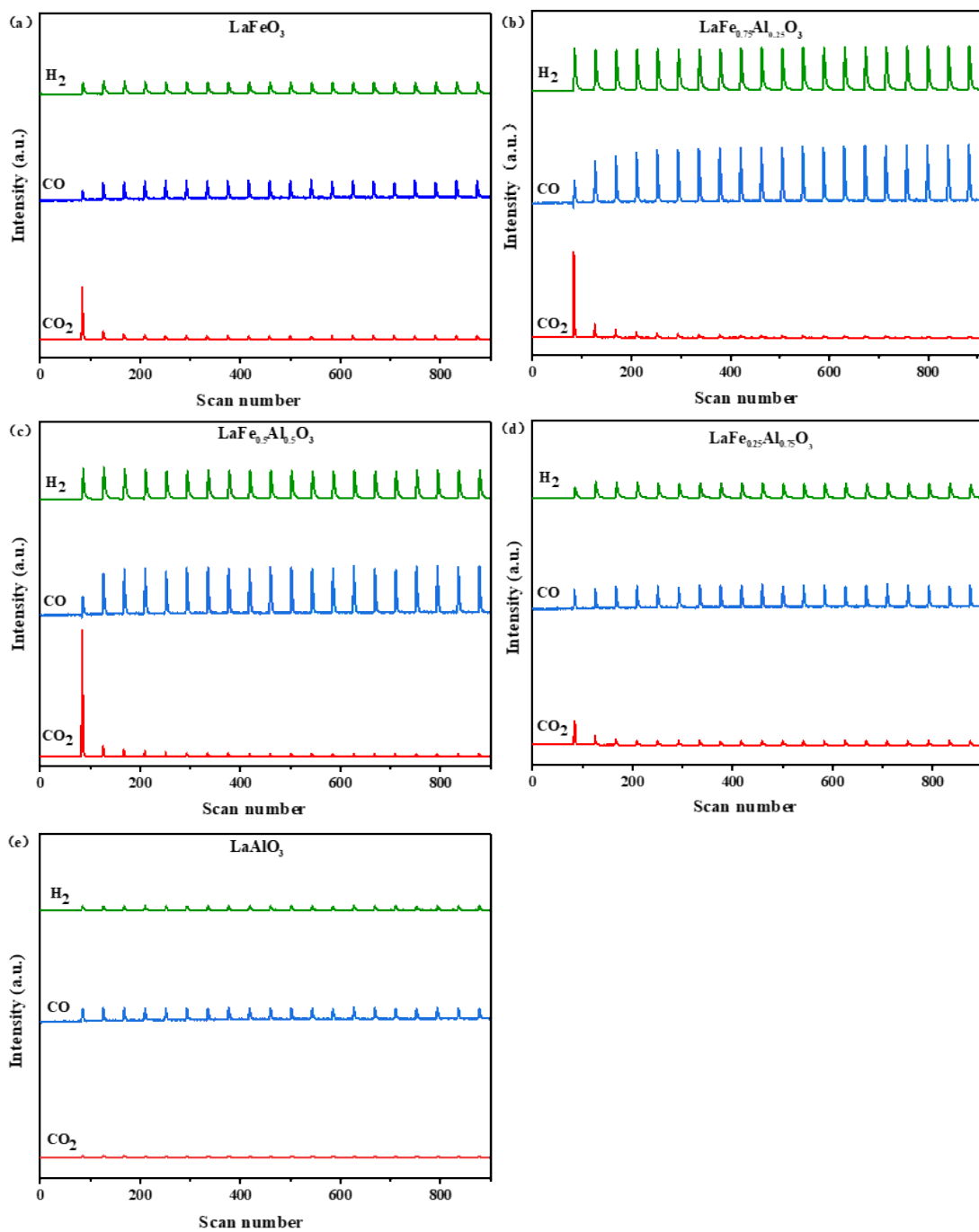[†]These authors contributed equally to this work.

Figure S1. Methane pulse reaction performance over $LaFe_{1-x}Al_xO_3$ ($0 \leq x \leq 1.0$) oxides at 700 °C.
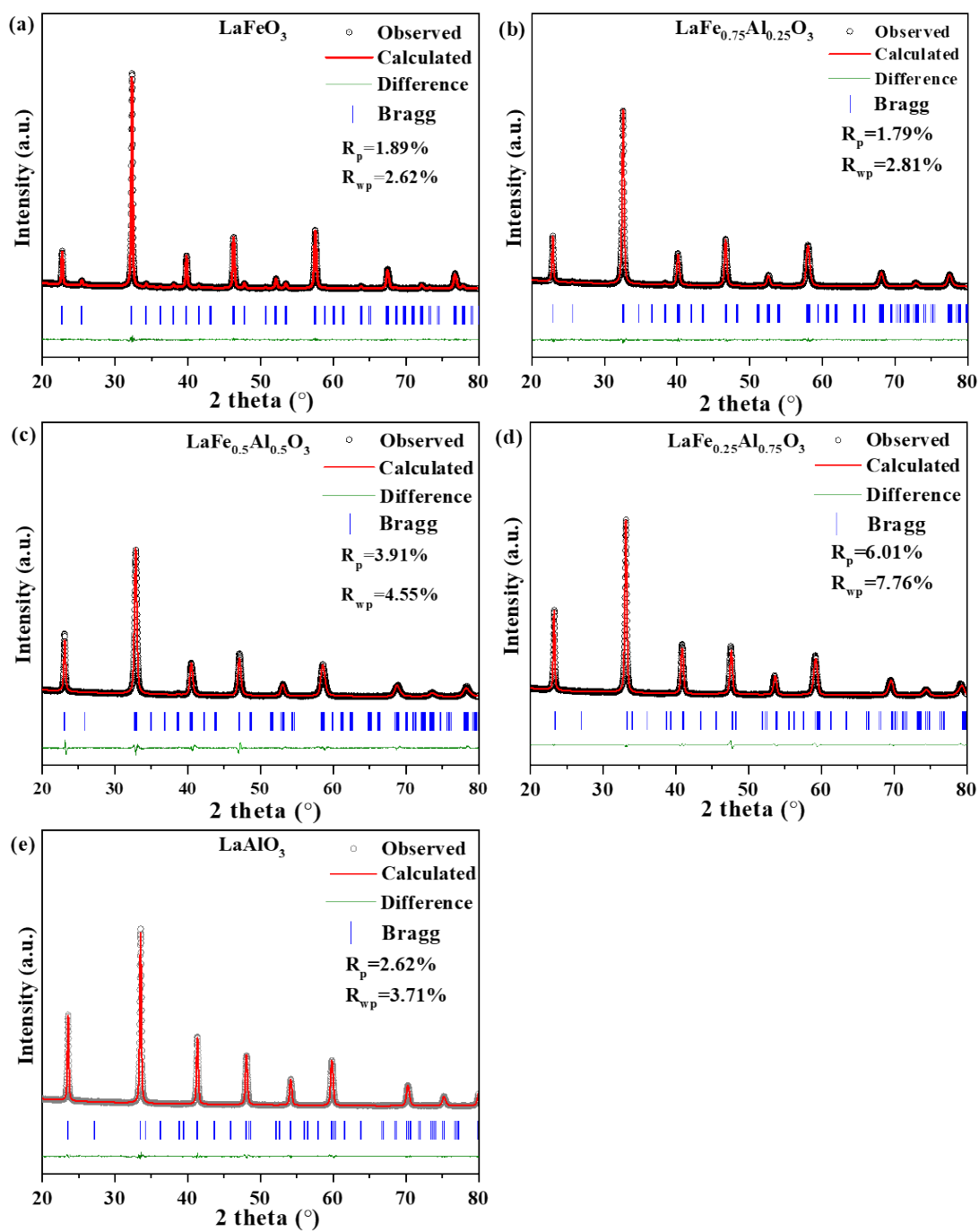
Figure S2. Rietveld refinement results of $LaFe_{1-x}Al_xO_3$ ($0 \leq x \leq 1.0$) oxides.

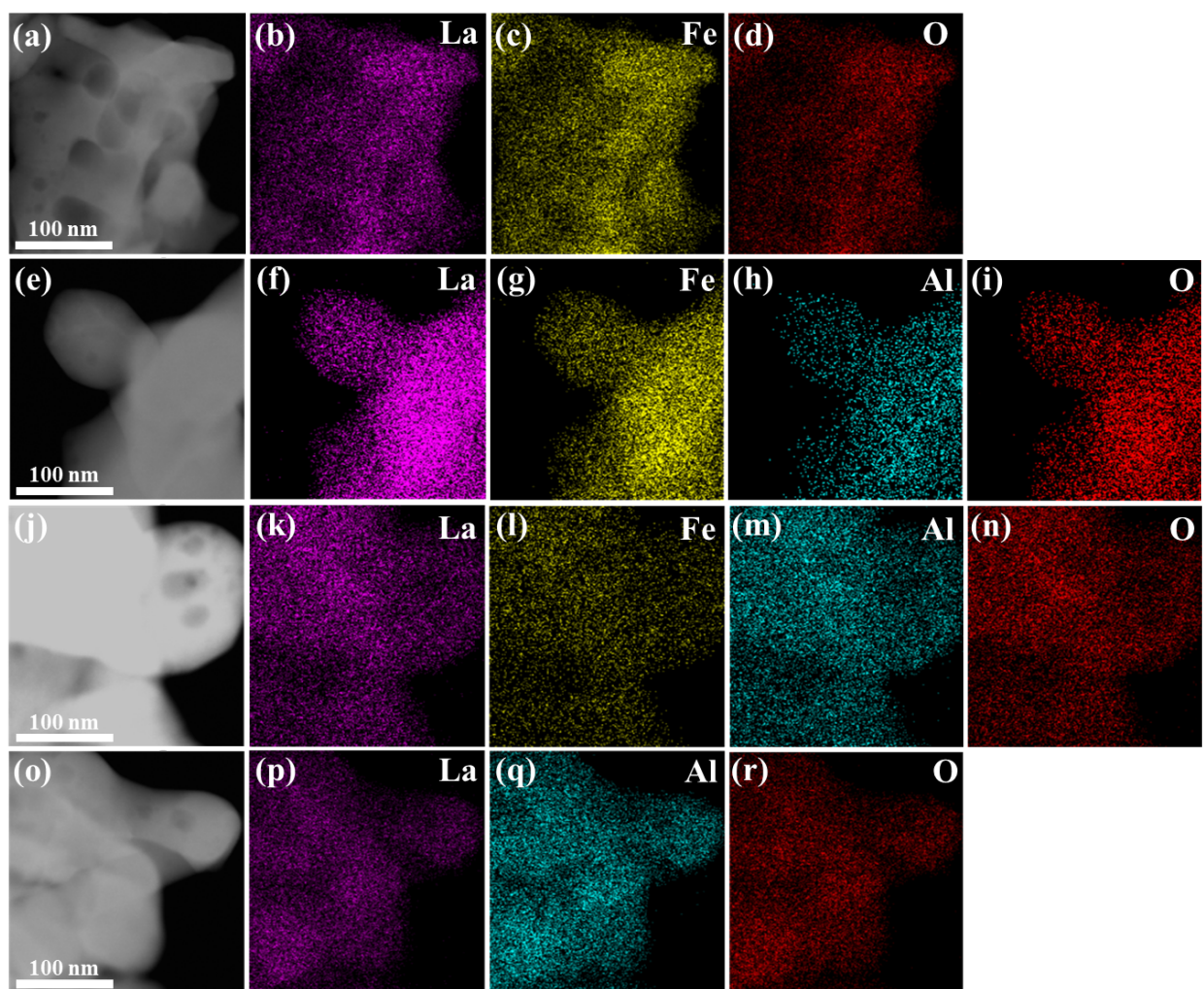**Figure S3.** STEM images and corresponding element distribution of (a-d) $LaFeO_3$, (e-i) $LaFe_{0.75}Al_{0.25}O_3$, (j-n) $LaFe_{0.25}Al_{0.75}O_3$, and (o-r) $LaAlO_3$.
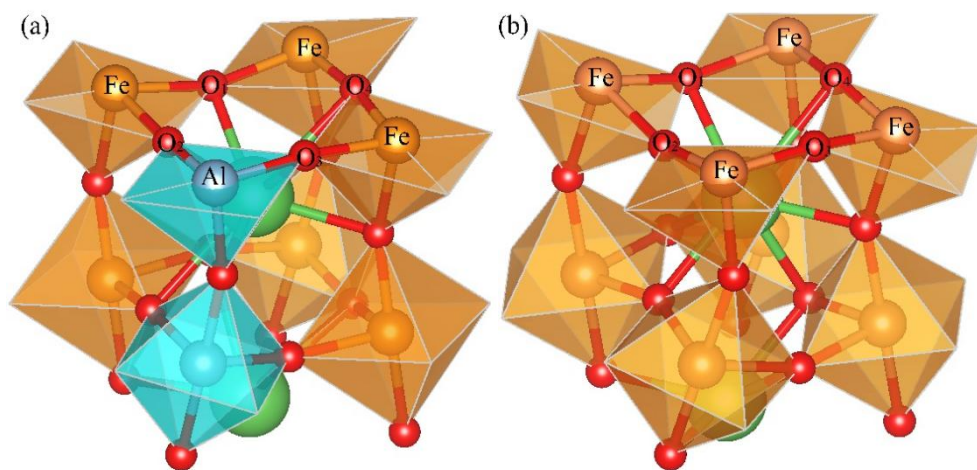
Figure S4. Schematic representations of local structures around Fe on (a) $LaFe_{0.5}Al_{0.5}O_3$ and (b) $LaFeO_3$.

Table S1. Basic Parameters for $LaFe_{1-x}Al_xO_3$ ($0 \leq x \leq 1$) Oxides

Samples	$LaFeO_3$	$LaFe_{0.75}Al_{0.25}O_3$	$LaFe_{0.5}Al_{0.5}O_3$	$LaFe_{0.25}Al_{0.75}O_3$	$LaAlO_3$
Space Group	Pnma	Pnma	Pnma	R-3ch	R-3ch
Lattice	a= 5.5640	a= 5.4975	a= 5.4550	a= 5.3811	a= 5.3618
Parameters	b= 7.8540	b= 7.7854	b= 7.7289	b= 5.3811	b= 5.3618
(Å)	c= 5.5580	c= 5.5286	c= 5.4831	c= 13.2424	c= 13.1326
Average B-O length (Å)	2.0037	1.9696	1.9489	1.9074	1.8966
Average B-O-B Bond angle (º)	159.2	164.7	168.0	174.9	176.3
Surface area (m^2/g)	9.8	7.6	5.5	6.6	9.8

Table S2. Fitted O 1s data for $LaFe_{1-x}Al_xO_3$ ($0 \leq x \leq 1.0$) oxides.

Samples	Binding energy (eV)		Ratio of O_A/O_L
	O_A	O_L	
x = 0	531.36	529.04	1.23
x = 0.25	531.35	529.13	1.04
x = 0.5	531.37	529.26	0.87
x = 0.75	531.38	529.31	0.66
x = 1.0	531.38	529.34	0.64

Table S3. Symmetry assignment for Raman phonon modes of $LaFeO_3$.

Raman shift (cm^{-1})	Assignment	Atomic motion
139	$B_{2g}(1)$	A(z), out-of-phase
157	$B_{2g}(2)$	A(x), out-of-phase
179	$A_g(1)$	$[010]_{pc}$ FeO_6 rotation, in-phase
266	$A_g(2)$	O_1 x-z plane
294	$A_g(3)$	$[101]_{pc}$ FeO_6 bending, in-phase
415	$B_{2g}(3)$	O-Fe-O scissor like bending
432	$A_g(4)$	Fe-O stretching

Table S4. Basic parameters for $LaFe_{0.5}Al_{0.5}O_3$ and $LaFeO_3$ obtained by DFT calculations

Parameters		$LaFe_{0.5}Al_{0.5}O_3$	$LaFeO_3$
bond length (Å)	$Fe-O_1$	1.96 Å	1.97 Å
	$Fe-O_2$	2.02 Å	2.10 Å
	$Fe-O_3$	1.91 Å	2.10Å
	$Fe-O_4$	1.89 Å	1.89 Å
	average	1.95 Å	2.02 Å
bond angle (deg)	$Fe-O_1-Fe$	159.88	158.80
	$Fe-O_2-Fe$	172.53	158.80
	$Fe-O_3-Fe$	172.54	162.31
	$Fe-O_4-Fe$	172.22	162.31
	average	169.30	160.55

Table S5. Calculated stability of chemisorbed *CH$_3$ and *H on Fe-O or Al-O of Fe-O-Fe and Fe-O-Al motif.

Interaction	Energy (eV)
*CH$_3$ on Fe and *H on O of Fe-O-Fe	-3.21
*CH$_3$ on Fe and *H on O of Fe-O-Al	-3.71
*CH$_3$ on Al and *H on O of Fe-O-Al	-1.72