Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Low-temperature NO Oxidation Using Lattice Oxygen in Fe-site Substituted $SrFeO_{3-\delta}$

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NO_x desorption profiles from the specimens

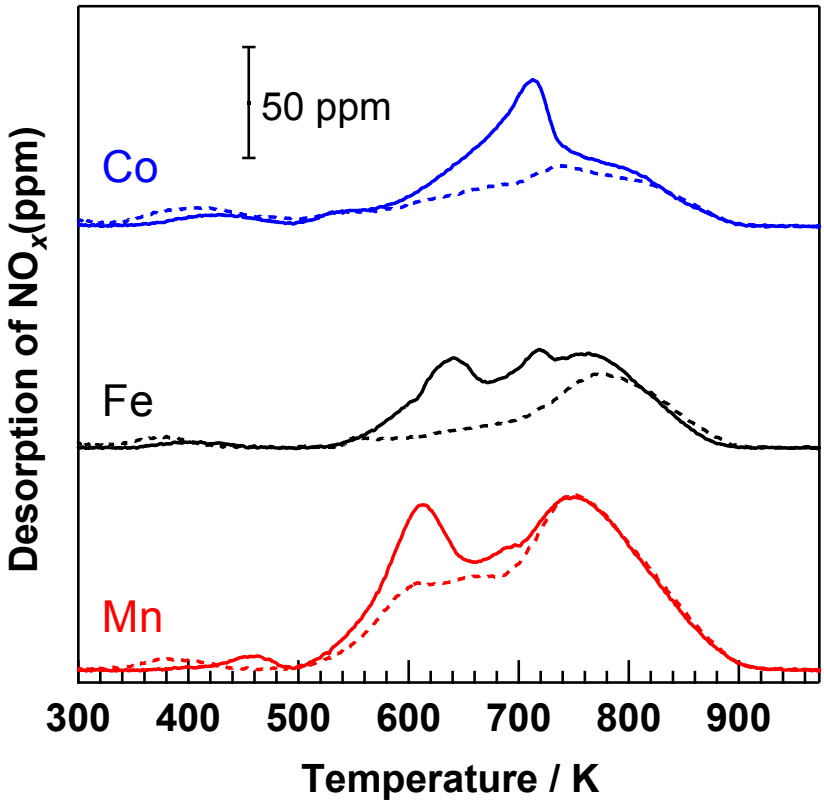

Figure S1. NO_x-TPD profiles for $SrFe_{0.8}M_{0.2}O_{3-\delta}$ (M = Mn, Fe, or Co) after NO_x storage at 423 K (solid lines) and 573 K (dash lines) for 1 h.

SEM images of the specimens

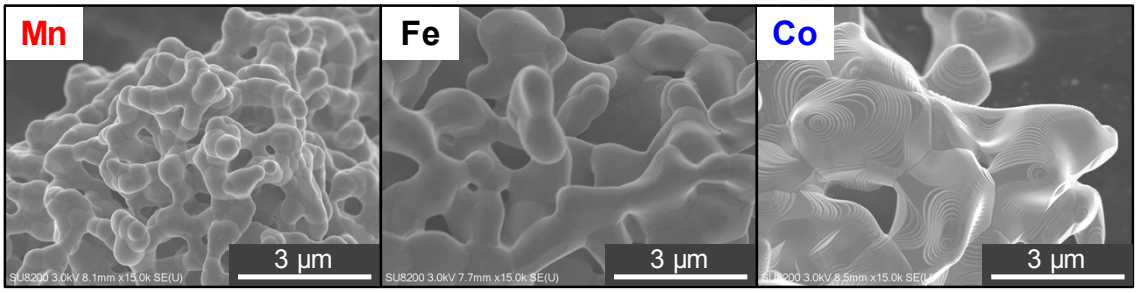

Figure S2. SEM images of the as-synthesized SFMO, SFO, and SFMO.

Wide-range XRD patterns of oxygen-released specimens

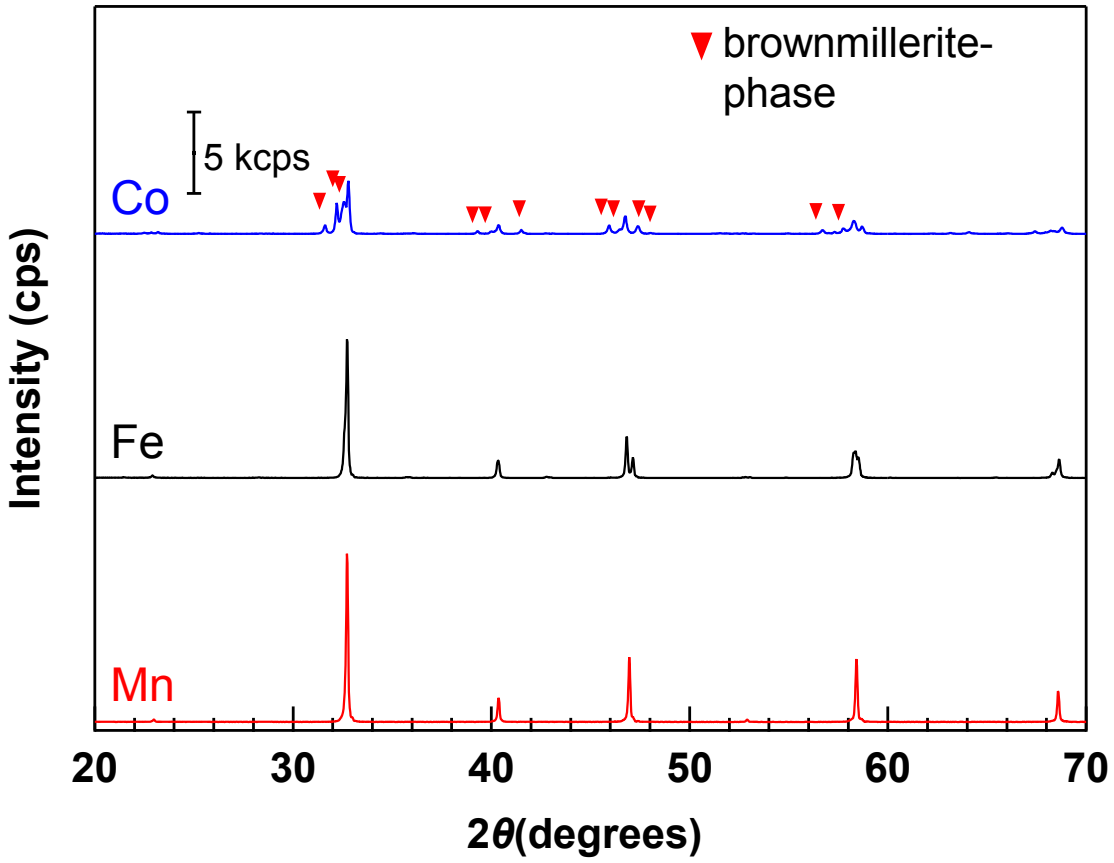

Figure S3. XRD patterns of the oxygen-released SFMO, SFO, and SFCO after the reaction with NO at 573 K.

Fe K-edge XANES of oxygen-stored SFO, SFMO, and SFCO

SFO with different oxygen amounts were synthesized by heating under pure O_2 at 873 K, under 1% NO/He at 573 K, and under 5% H_2/Ar at 823 K. The determined amount of oxygen was $SrFeO_{2.876}$, $SrFeO_{2.746}$, and $SrFeO_{2.501}$, respectively. **Figure S4** plots the Fe K-edge position of these specimens against the valence of Fe determined by the iodometric titrations. The linear relationship was observed between the edge position of Fe K-edge XANES, where the normalized absorption is 0.5. By using this approximate line, the average valence of Fe species in SFMO and SFCO was estimated from the Fe K-edge position.

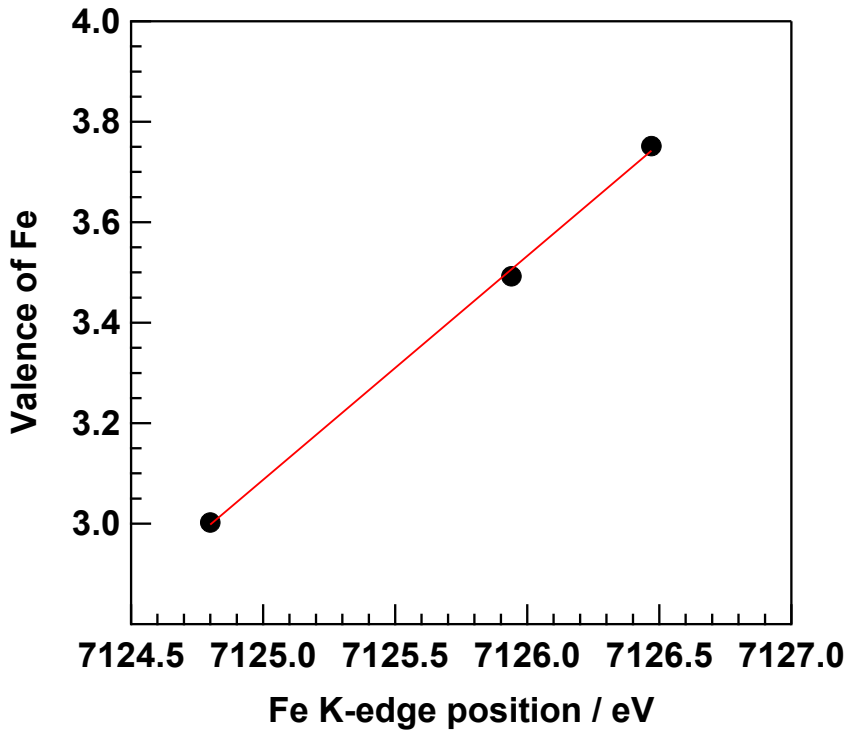

Figure S4. Relationship between the valence state of Fe and the position of XANES at Fe K-edge in SFO with various oxygen contents.

EXAFS oscillations and FT-EXAFS

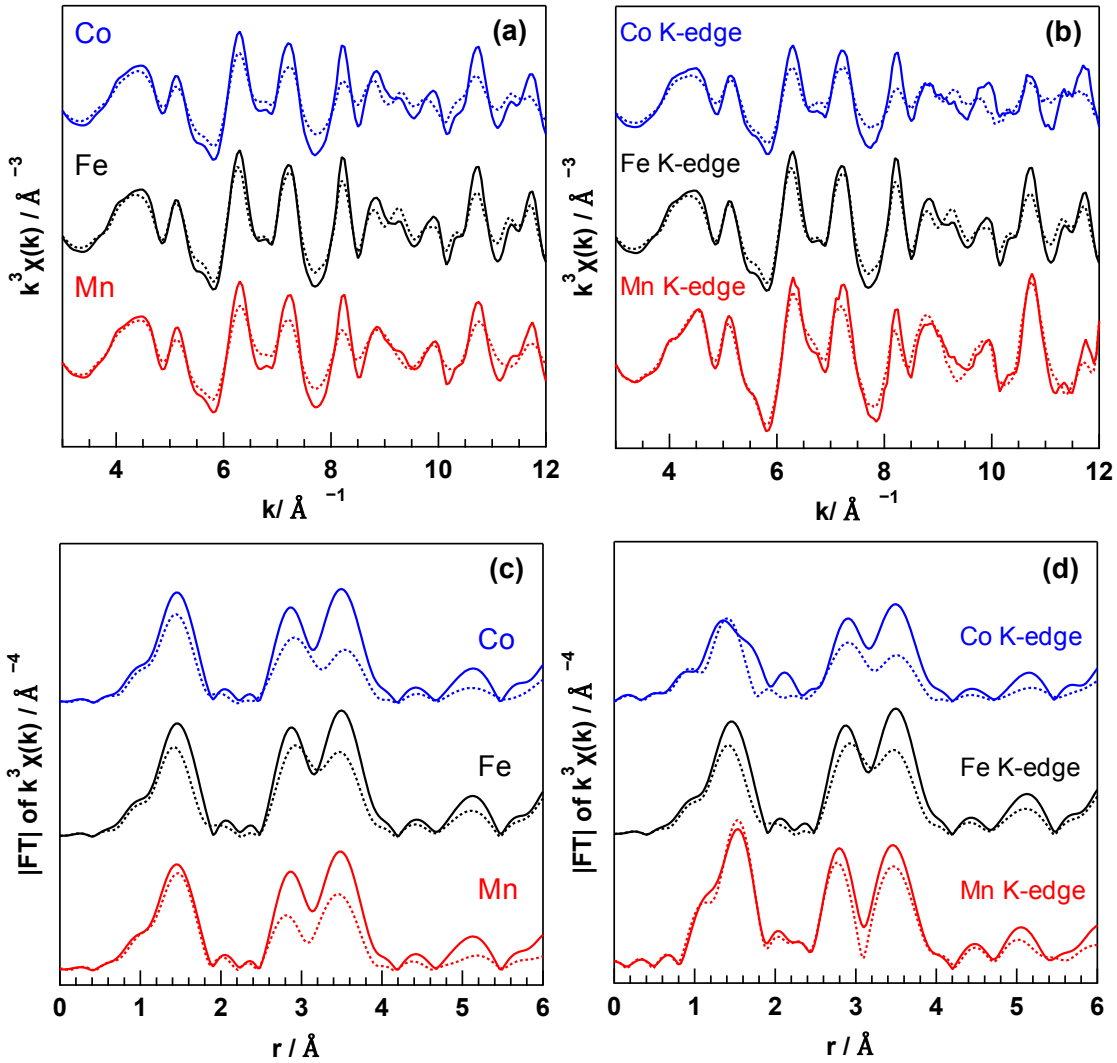

Figure S5. (a, b) EXAFS oscillations, and (c, d) Fourier-transformed EXAFS spectra of $SrFe_{0.8}M_{0.2}O_{3-\delta}$ (M = Mn, Fe, or Co) at (a, c) the Fe K-edge, and (b, d) the M K-edge of the dopant species. The solid lines represent spectra after oxidizing treatment, while the dashed lines show the spectra obtained after reaction with NO at 573 K.

XRD patterns of the specimens after O_2-TPD

XRD patterns of the specimens after O_2-TPD measurements are shown in **Figure S6**. These XRD patterns were recorded on a Rigaku Ultima IV system using Cu-Kα radiation. SFO and SFCO transformed into the BM phase, while SFMO maintained the cubic perovskite structure.

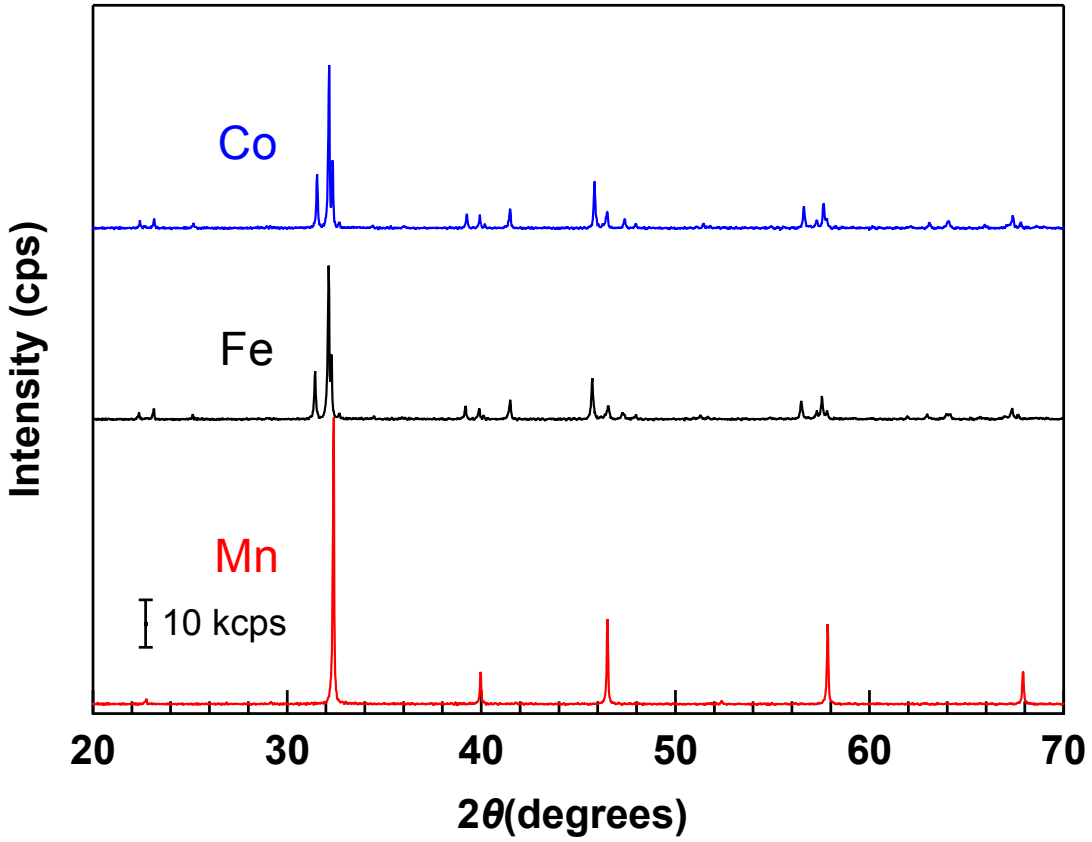

Figure S6. XRD patterns of the oxygen-released SFMO, SFO, and SFCO after O_2-TPD measurements.

Fitting parameters for oxygen release/storage obtained by DXAFS

Table S1-1. Parameters for the fitting of the oxygen release profiles using eq. 2

T/K	SFMO				SFO			
	A_1	k_1	A_2	k_2	A_1	k_1	A_2	k_2
523	−294	0.060	−466	0.010	−253	0.022	−561	0.007
573	−395	0.099	−418	0.016	−288	0.124	−653	0.034
623	−252	0.149	−332	0.021	−	−	−	−

Table S1-2 Parameters for the fitting of the oxygen release profiles using eq. 3

T/K	SFO			SFCO		
	A	k	r_l	A	k	r_l
523	−	−	−	−360	0.034	1.69
573	−	−	−	−318	0.126	4.61
623	−674	0.119	0.77	−66	0.517	6.03

Table S2-1. Parameters for the fitting of the oxygen-storage profiles using eq. 2

T/K	SFMO				SFO			
	A_1	k_1	A_2	k_2	A_1	k_1	A_2	k_2
523	−71	0.139	−283	0.003	–	–	–	–
573	−246	0.060	−345	0.005	–	–	–	–
623	−328	0.099	−336	0.009	−204	0.037	−388	0.004

Table S2-2. Oxygen-storage rates for SFCO

T/K	SFCO
	r_l
523	0.5
573	7.4
623	38.9

Arrhenius plots made from the parameters obtained by DXAFS

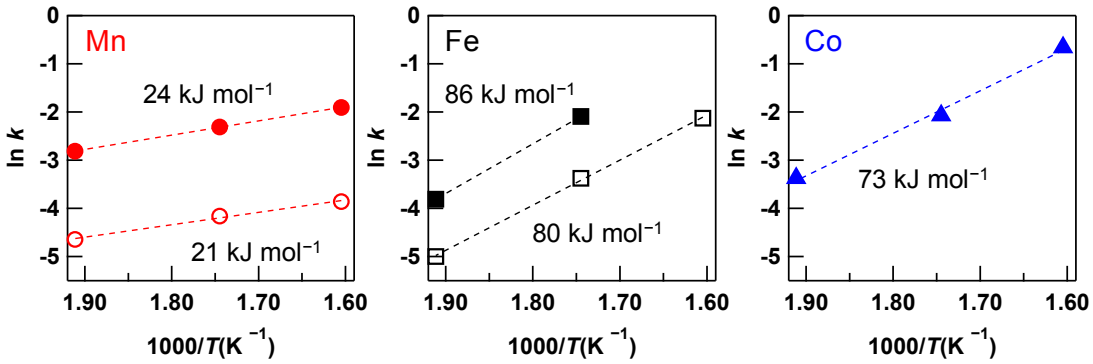

Figure S7. Arrhenius plots from the reaction rate constants (k) obtained by DXAFS during the exponential-type oxygen release. Closed marks represent larger rate constants (k_1), while open marks represent smaller rate constants (k_2).

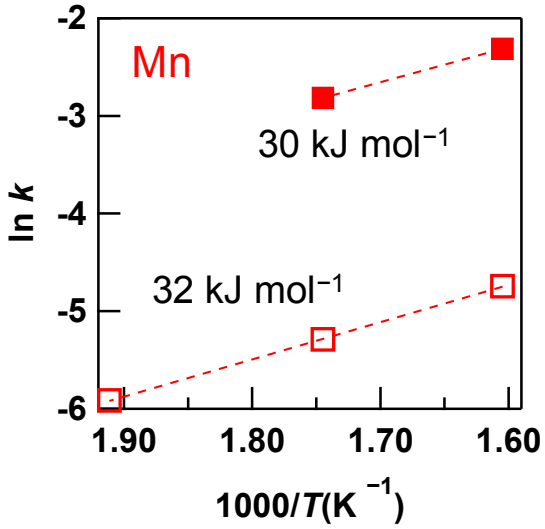

Figure S8-1 Arrhenius plots from the reaction rate constants (k) obtained by DXAFS during the exponential-type oxygen storage in SFMO. Closed marks represent the larger rate constants (k_1), while open marks represent the smaller rate constants (k_2).

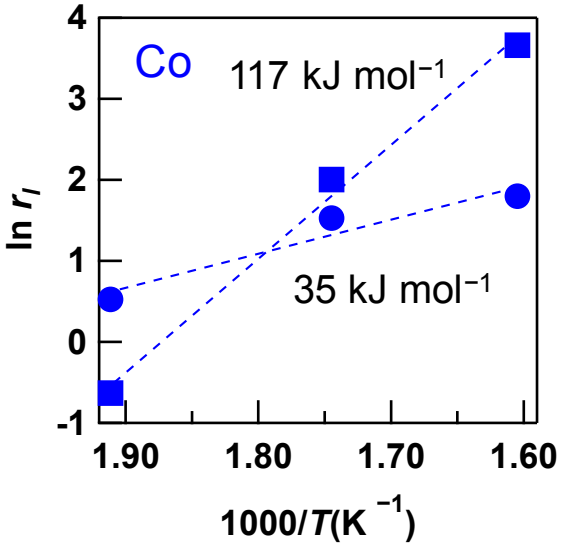

Figure S8-2. Arrhenius plots from the oxygen release (●) and storage (■) rates. The reaction rates were obtained by fitting with the linear function.