Supporting Information

Efficient oxygen storage property of Sr-Fe mixed oxide as automotive catalyst support

Kosuke Beppu,[a] Saburo Hosokawa,*[ab] Hiroyuki Asakura,[ab] Kentaro Teramura, [ab] and Tsunehiro Tanaka*[ab]

Affiliations and full postal addresses

[a] *Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

[b] *Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8245, Japan*

Experimental methods

Catalyst preparation: $Sr_3Fe_2O_{7-\delta}$ of which Fe was partially substituted with other transition metals ($Pd/Sr_3(Fe_{1-x}M_x)_2O_{7-\delta}$, where M = Mn, Co, Ni, or Cu) and CeO_2-ZrO_2 solid solution were synthesized by a polymerized complex method. Citric acid (400 mmol) (98.0%, Wako Pure Chemical Industries Ltd. Osaka, Japan (abbreviated as Wako)) was dissolved into 180 mL of water at 353 K. Next, calculated amounts of $SrCO_3$ (99.9%, Wako), $Fe(NO_3)_3$•$9H_2O$ (99.9%, Wako), $Mn(NO_3)_2$•$6H_2O$ (98%, Wako), $Co(NO_3)_2$•$6H_2O$ (99.0%, Wako), $Ni(NO_3)_2$•$6H_2O$ (99.9%, Wako), and $Cu(NO_3)_2$•$3H_2O$ (99%, Wako) were added, and the mixture was stirred for 2 h to obtain a solution of the desired metal oxide complexes, containing a total amount of 16.67 mmol cations. In particular, complexes in which 20 mol% of Fe was replaced by Mn, Co, and Cu and complexes containing various amounts of Ni were prepared. To this solution, 400 mmol of ethylene glycol (99.5%, Wako) was added, and the solution was stirred at 403 K for 4 h to form a gelatinous solution. After heating the gel in a mantle heater at 623 K for 3 h, the obtained brown powder was calcined at 1273 K for 2 h. CeO_2-ZrO_2 solid solution was synthesized by the same method above, and $Ce(NO_3)_3$•$6H_2O$ (98.0%, Wako) and $ZrO(NO_3)_2$ (Wako) were used as the starting materials. Ce/Zr ratio was fixed to 1. $Sr_3(Fe_{1-x}M_x)_2O_{7-\delta}$ or CeO_2-ZrO_2-supported Pd catalysts were synthesized by the impregnation method using Pd acetate (99.9%, Sigma-Aldrich) as the Pd source. Pd acetate was dissolved in ethyl acetate (99.5%, Wako), and the support was added. The solution was evaporated at 353 K, and the powder obtained was calcined at 1073 K or 1273 K for 5 h. The loading amount of Pd was 1.0 wt% or 5.0 wt% on metal basis. Unless otherwise noted, the loading amount of Pd was 1.0 wt%, and the calcination temperature after Pd loading was 1073 K.

Catalytic reaction: Three types of catalytic reaction were performed: a lean/rich/lean transition test, a lean-rich cycle test, and a temperature programmed reaction under λ = 1. The catalytic reaction was carried out in a fixed-bed flow reactor, as described in our previous report.[31] The catalyst sample (200 mg, 25/50 mesh) was placed in a tubular reactor, and the total gas flow rate was 100 mL min^{-1}. The catalyst was pretreated by heating to 773 K under He flow (30 mL min^{-1}) for 1 h. The gas concentration was analyzed using a Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector (TCD) and MS-5A and Porapak-Q columns. The temperature programmed reaction was carried out by increasing the temperature from 373 K to 773 K in a stepwise manner (50 K intervals) under stoichiometric conditions (λ = 1.0): NO, 1000 ppm; CO, 1000 ppm; C_3H_6, 250 ppm; O_2, 1125 ppm. The catalytic activity for lean/rich/lean

transition test was evaluated at 773 K under the following atmospheric conditions: NO, 1000 ppm; CO, 1000 ppm; C_3H_6, 250 ppm; O_2, various concentrations (675−1462.5 ppm); and He as a balance gas. The λ value was defined as the number of oxygen atoms in the reaction system ([NO] + [CO] + [O_2] × 2) divided by the number of oxygen atoms under stoichiometric conditions ([NO] + [CO] + [O_2] × 2 = 4250 ppm). The catalytic reaction was started under lean conditions (O_2, 1462.5 ppm), and the oxygen concentration was decreased to 625 ppm (rich conditions) in a stepwise manner while maintaining the NO and CO concentrations constant. Next, the oxygen concentration was changed back to lean conditions. The reaction gas was kept for 30 min at each oxygen concentration. Lean-rich cycle test for the NO reduction was performed at 773 K by instantaneously alternating the atmospheric conditions between lean (λ = 1.15; NO, 1000 ppm; CO, 1000 ppm; C_3H_6, 250 ppm; O_2, 1444 ppm) and rich (λ = 0.85; NO, 1000 ppm; CO, 1000 ppm; C_3H_6, 250 ppm; O_2, 806 ppm) conditions. The catalyst was pre-treated under He flow at 773 K, and the reaction gases corresponding to the lean conditions was introduced at 773 K for 30 min to the pre-treated catalyst. Then, the reaction conditions were alternated between rich and lean every 1 h. The outlet gases were detected using a micro gas chromatograph (Varian CP-4900 Micro GC) fitted with MS-5A and PoraPLOT Q columns.

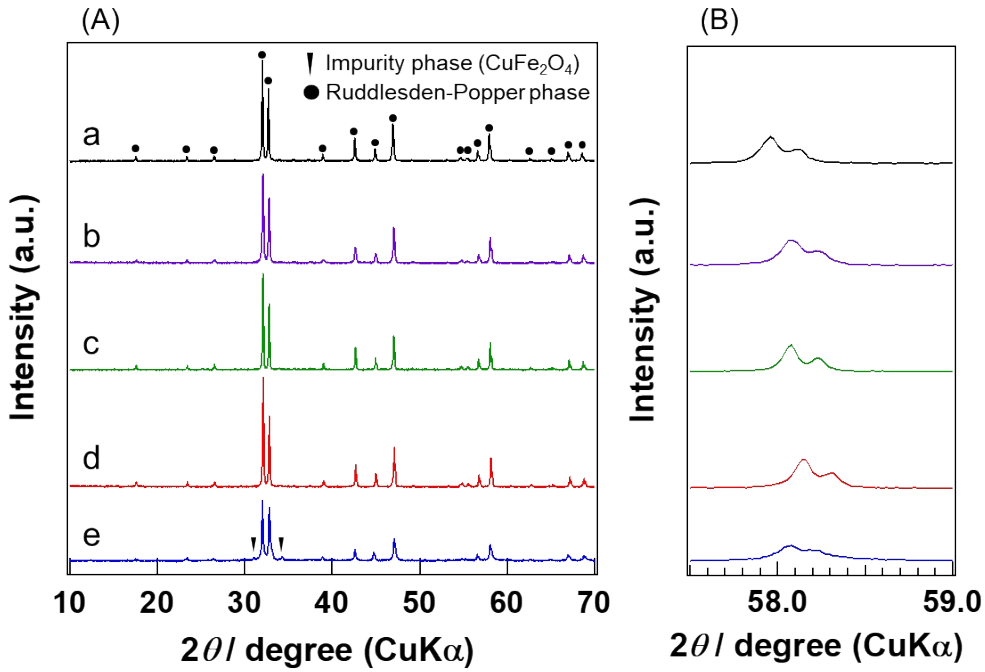

Figure S1 XRD patterns of $Pd/Sr_3Fe_2O_{7-\delta}$ in which 20 mol% of Fe atoms was replaced by other transition metals. a, Fe (unreplaced); b, Mn; c, Co; d, Ni; e, Cu. (A) Overall view and (B) magnified view.

Table S1 Ionic radii of transition metals*

Valence	Ionic radius (pm)				
	Mn	Fe	Co	Ni	Cu
4+	67 (6 coordination)	72.5 (6 coordination)	67 (6 coordination)	62 (6 coordination)	-
3+	72 (5 coordination)	72 (5 coordination)	68.5 (6 coordination)	70 (6 coordination)	68 (6 coordination)
2+	80 (4 coordination)	77 (4 coordination)	72 (4 coordination)	69 (4 coordination)	71 (4 coordination)

*These ionic radii were referred by ref. 33.

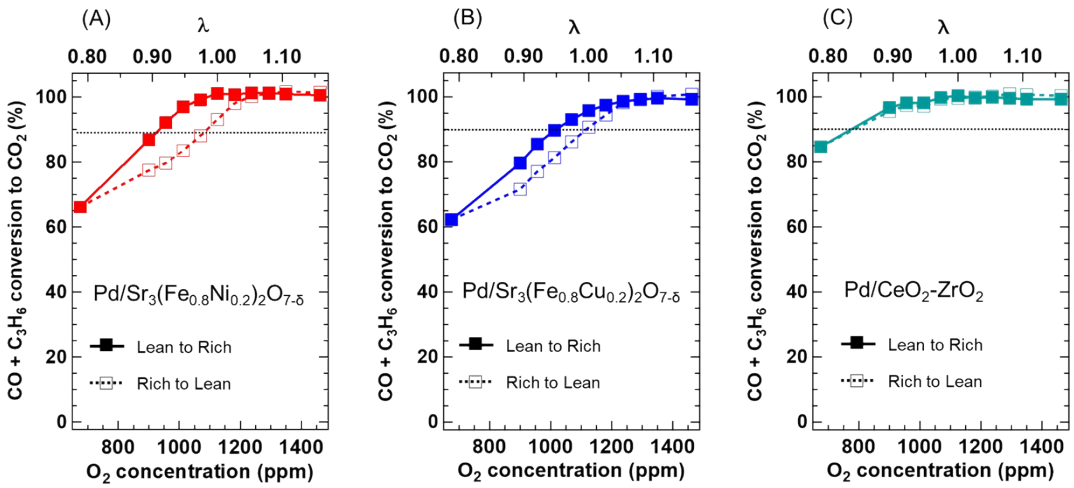

Figure S2 CO and C_3H_6 conversion to CO_2 during lean/rich/lean transition test over (A) $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$, (B) $Pd/Sr_3(Fe_{0.8}Cu_{0.2})_2O_{7-\delta}$ and (C) Pd/CeO_2-ZrO_2. The λ value was defined as follows: the number of oxygen atoms in the reaction system ([NO] + [CO] + $[O_2] \times 2$) was divided by the number of oxygen atoms under stoichiometric conditions ([NO] + [CO] + $[O_2] \times 2$ = 4250 ppm).

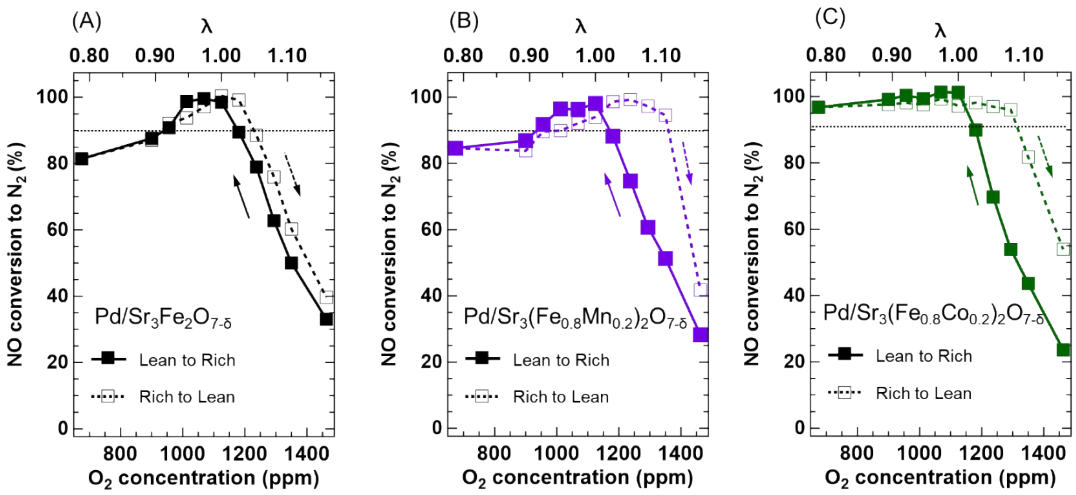

Figure S3 (A-C) NO conversion to N_2 during lean/rich/lean transition test over $Pd/Sr_3Fe_2O_{7-\delta}$ in which 20 mol% of Fe atoms was replaced by Mn or Co.

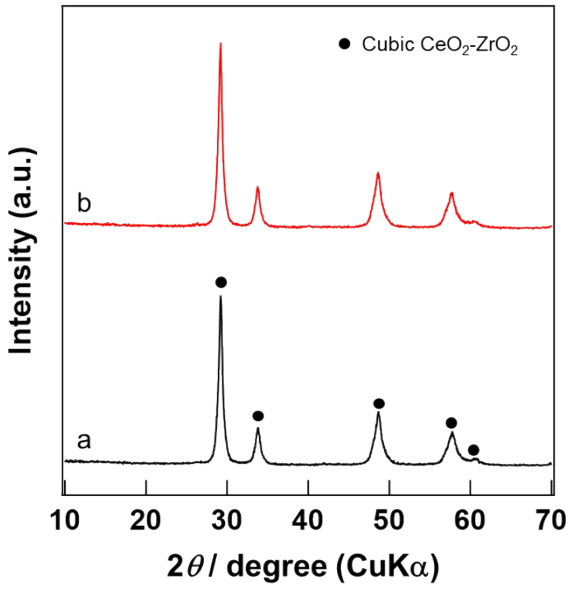

Figure S4 XRD patterns of Pd/CeO_2-ZrO_2 solid solution. a; as-synthesized catalyst and b; catalyst after reaction.

There was no difference among these XRD patterns, indicating that Pd/CeO_2-ZrO_2 had high structural stability without phase segregation as the formation of CeO_2 and ZrO_2.

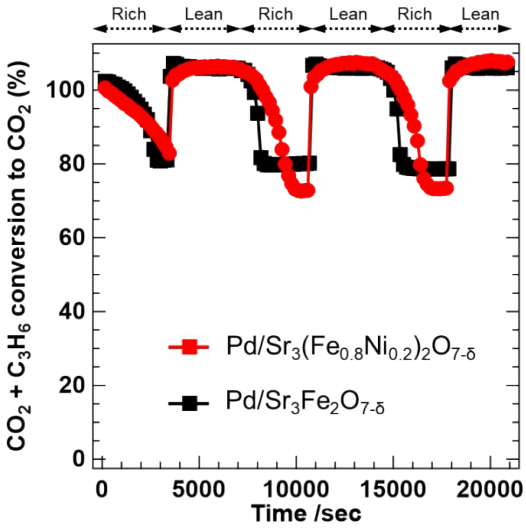

Figure S5 Time courses for the CO and C_3H_6 conversion to CO_2 during lean-rich cycle test over $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ and $Pd/Sr_3Fe_2O_{7-\delta}$. The lean-rich cycle test was carried out by instantaneously alternating the atmospheric conditions between lean ($\lambda = 1.15$; NO, 1000 ppm; CO, 1000 ppm; C_3H_6, 250 ppm; O_2, 1444 ppm) and rich ($\lambda = 0.85$; NO, 1000 ppm; CO, 1000 ppm; C_3H_6, 250 ppm; O_2, 806 ppm).

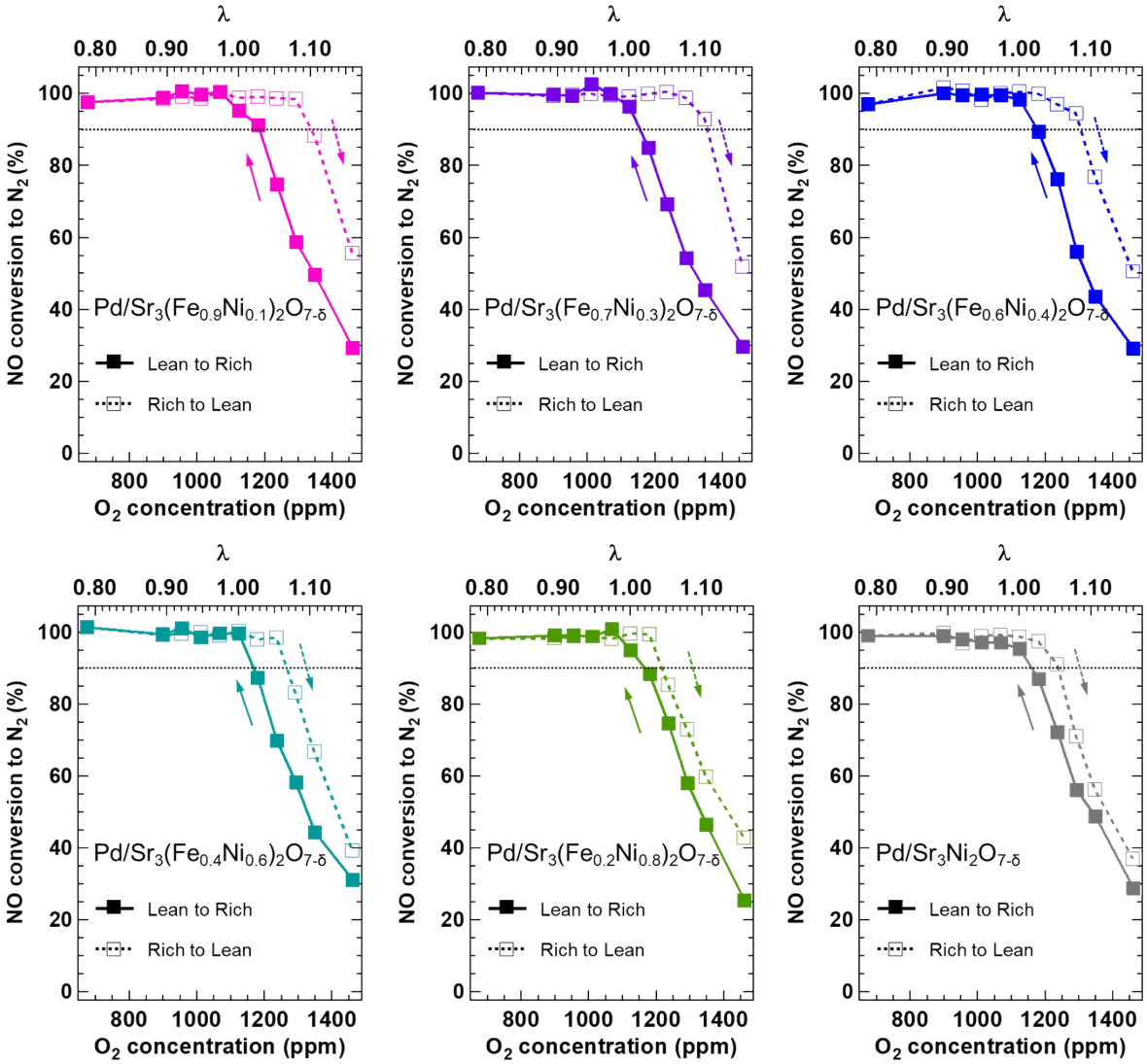

Figure S6 NO conversion to N_2 during lean/rich/lean transition test over $Pd/Sr_3(Fe_{1-x}Ni_x)_2O_{7-\delta}$ catalysts.

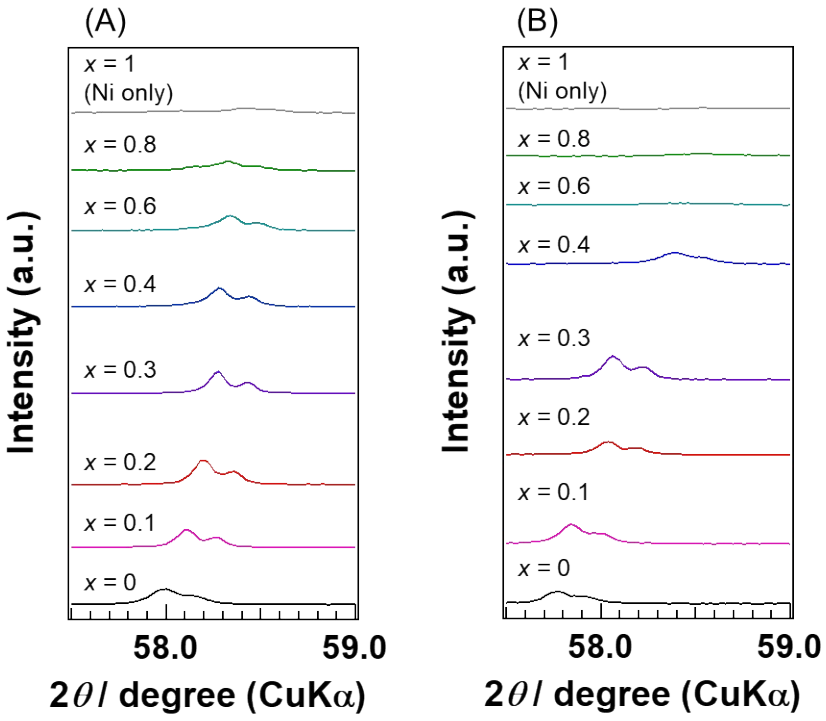

Figure S7 Magnified view of the XRD patterns of $Pd/Sr_3(Fe_{1-x}Ni_x)_2O_{7-\delta}$. (A) As-synthesized samples and (B) samples after reaction.

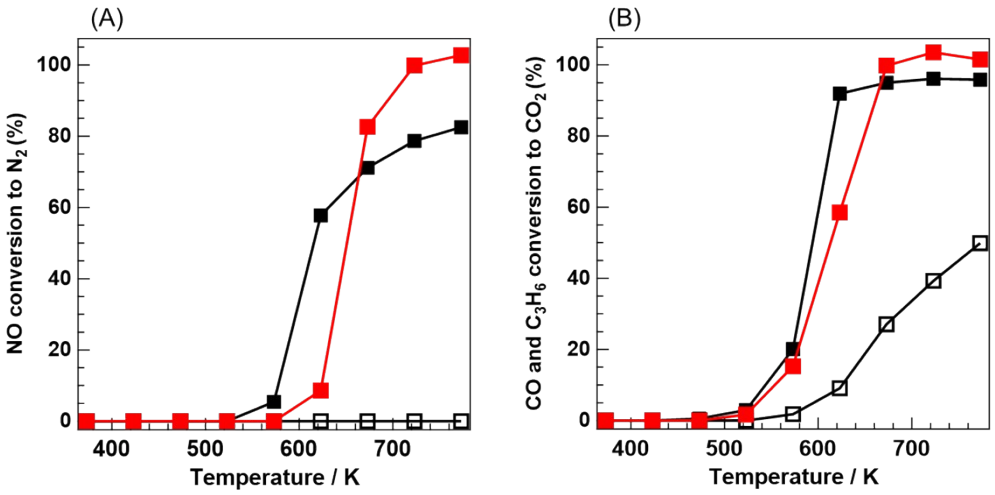

Figure S8 (A) NO conversion to N_2 and (B) CO and C_3H_6 conversion to CO_2 in the temperature programmed reaction ($\lambda = 1$) over (open square) $Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$, (closed black square) $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ and (closed red square) $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ calcined at 1273 K.

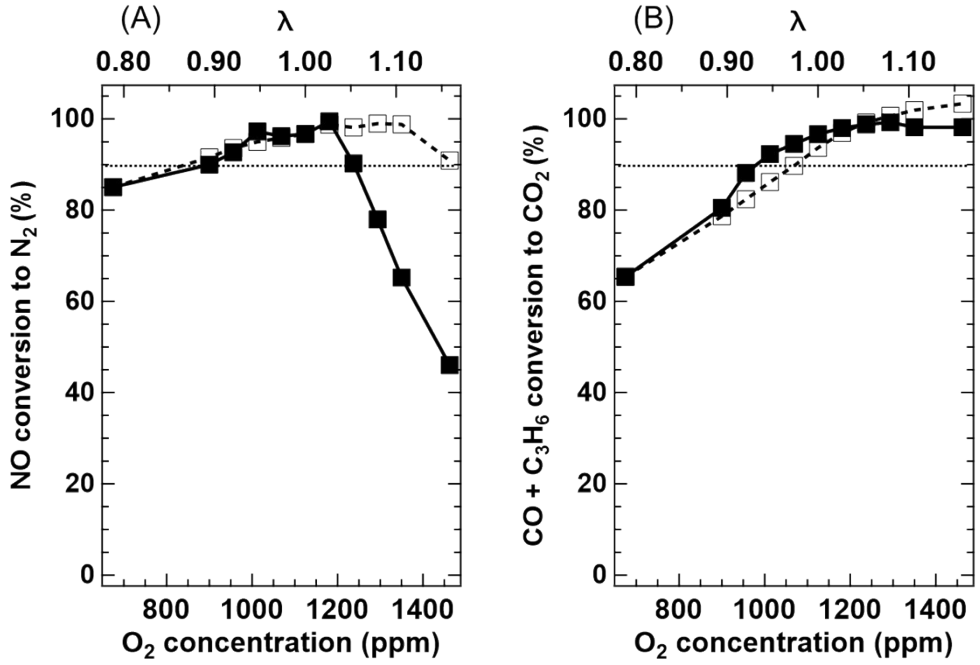

Figure S9 (A) NO conversion to N_2 and (B) CO and C_3H_6 conversion to CO_2 during lean/rich/lean transition test over 5 wt% Pd/Sr($Fe_{0.8}Ni_{0.2}$)$_2O_{7-\delta}$.

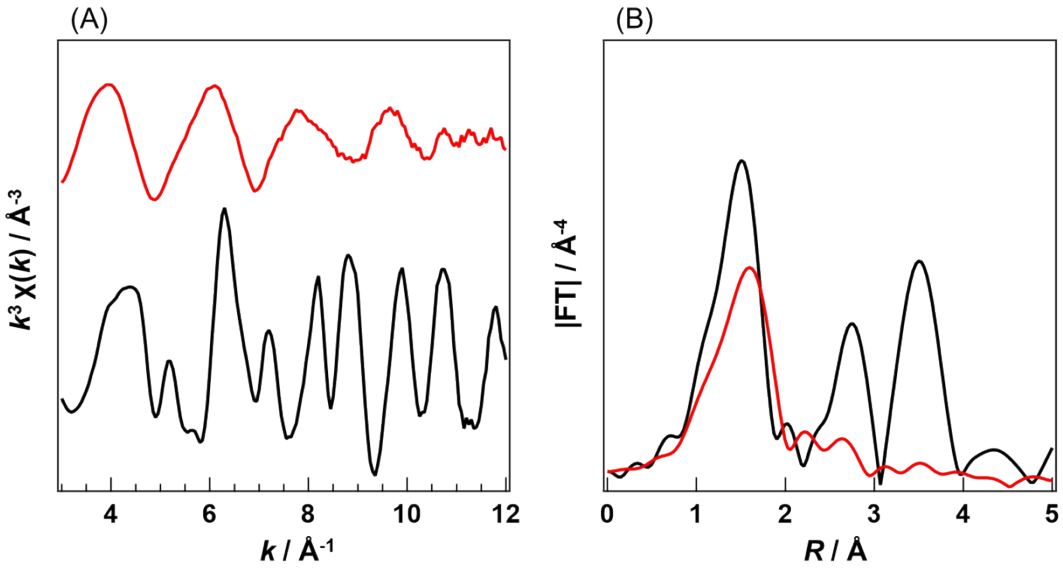

Figure S10 (A) EXAFS oscillations and (B) Fourier transformed Ni K-edge EXAFS spectra. (black line), as-synthesized $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ and (red line), $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ reduced under 5% H_2/Ar flow (100 mL min^{-1}) at 773 K for 1 h.

Table S2 Results of EXAFS curve fitting.

Catalyst	Shell	CN[1)]	R[2)] (Å)	D.W.[3)] (Å^2)	dE[4)] (eV)	R-factor
$Pd/Sr(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$	Pd-O	5.0(0.9)	2.02(0.01)	0.003(0.001)	-1.8(2.7)	0.030
	Pd-O-Sr	4.0[5)]	3.27(0.03)	0.006(0.001)	-9.8(6.7)	
	Pd-O-Fe	4.0[5)]	3.76(0.05)	0.007(0.002)	3.8(-7.5)	
$Pd/Sr(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ reduced at 773 K	Pd-O	1.6(1.3)	2.04(0.03)	0.005[6)]	0.2	0.010
	Pd-Fe	1.6(1.7)	2.63(0.06)	0.005(0.004)	-14.7(8.8)	
	Pd-Pd	3.5(3.0)	2.69(0.03)	0.005[7)]	-14.7	
$Pd/Sr_3Fe_2O_{7-\delta}$	Pd-O	4.0(0.7)	2.02(0.01)	0.002(0.001)	-2.7(2.5)	0.020
	Pd-O-Sr	4.0[5)]	3.27(0.02)	0.005(0.001)	-11.8(4.8)	
	Pd-O-Fe	4.0[5)]	3.79(0.04)	0.006(0.002)	3.9(5.9)	
$Pd/Sr_3Fe_2O_{7-\delta}$ reduced at 773 K	Pd-O	1.4(0.8)	2.06(0.03)	0.005(0.003)	0.2(5.1)	0.001
	Pd-Fe	0.8(0.9)	2.69(0.05)	0.006(0.002)	-11.2(4.4)	
	Pd-Pd	3.7(1.5)	2.72(0.02)	0.006[7)]	-11.2	
$Pd/Sr(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ (for Ni K-edge)[8)]	Ni-O	5.1(0.7)	1.94(0.01)	0.005(0.001)	-1.0(1.9)	0.006

Data reduction was performed with Athena and Artemis ver. 0.9.25. Curve fitting analysis were done with scattering paths generated with FEFF 6L. k-range: 3 – 12 Å^{-1}, R-range: 1.0 – 3.8 Å for as-synthesized samples and 1.0 – 2.8 Å for reduced samples.

1) Coordination number, 2) Interatomic distance, 3) Debye-Waller factor, and 4) Energy shift,

5) Coordination number for Pd-O-Sr and Pd-O-Fe shells in as-synthesized samples were fixed.

6) Debye-Waller factor and energy shift values in reduced $Pd/Sr_3Fe_2O_{7-\delta}$ were used. 7) Debye-Waller factor and energy shift of Pd-Fe shell were assumed to be the same as that of Pd-Pd shell. S_0^2 value of 0.93 was determined from Pd foil, and used for the fitting.

8) Fitting for Ni K-edge EXAFS spectrum. S_0^2 value of 0.90 was determined from Ni foil, and used for the fitting. k-range: 3 – 12 Å^{-1}, R-range: 1.0 – 2.0 Å.

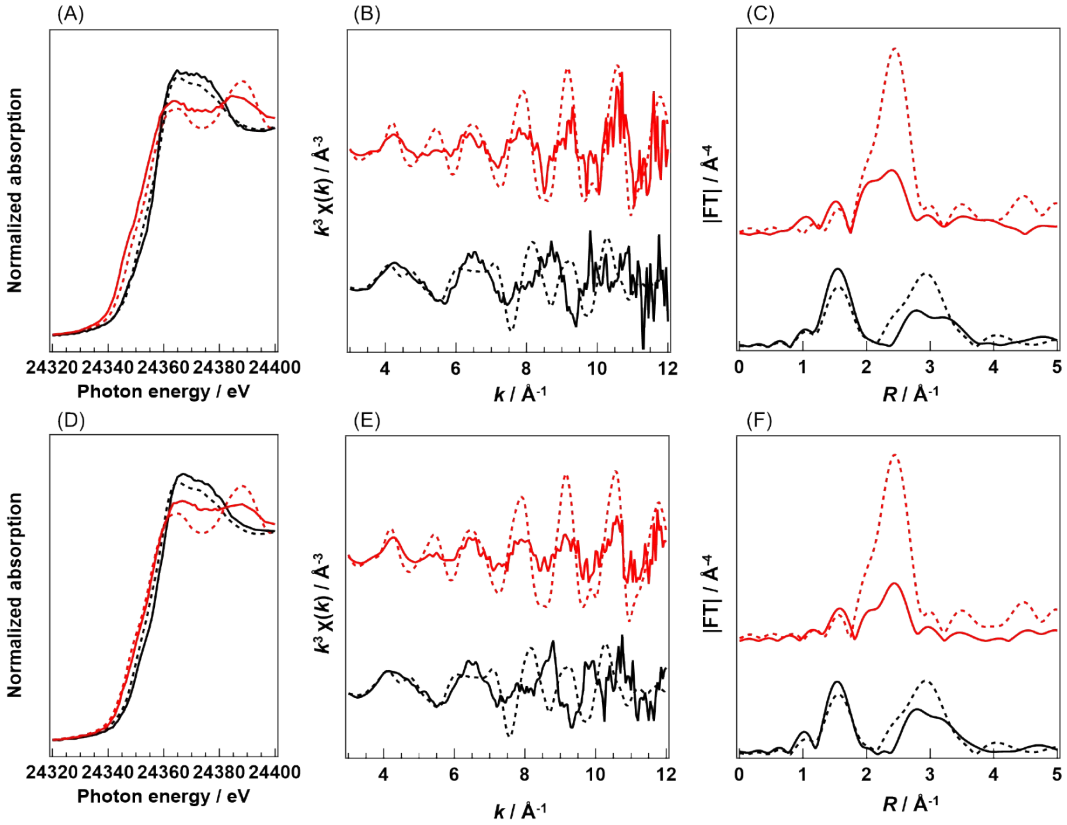

Figure S11 (A, D) Pd K-edge XANES spectra, (B, E) EXAFS oscillations and (C, F) Fourier transformed EXAFS spectra of (A-C) $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ and (D-F) $Pd/Sr_3Fe_2O_{7-\delta}$. Black solid line, as-synthesized sample; red solid line, sample reduced under 5% H_2/Ar flow (100 mL min^{-1}) at 773 K for 1 h: black dotted line, PdO and red dotted line, Pd foil.

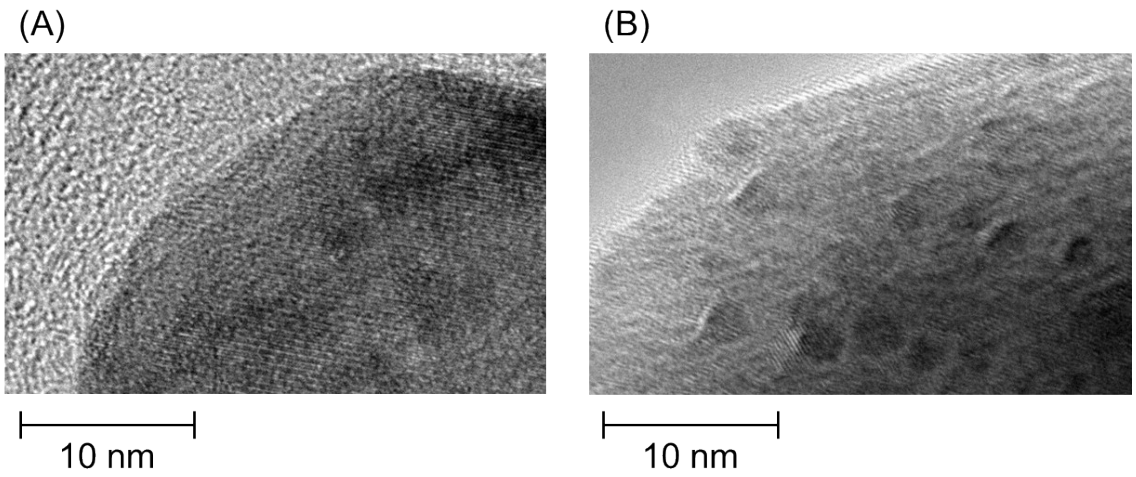

Figure S12 TEM images of $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$. (A) As-synthesized sample and (B) sample reduced under 5% H_2/Ar flow (100 mL min^{-1}) at 773 K for 1 h.

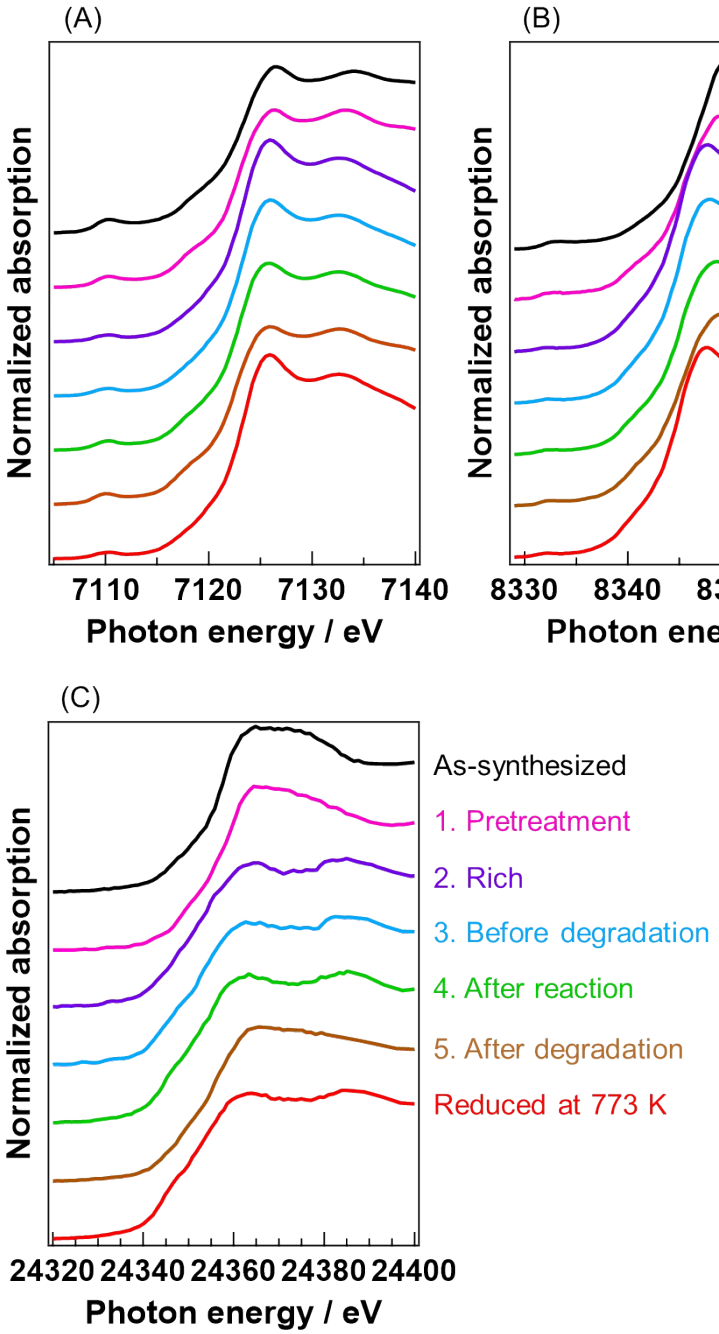

Figure S13 (A) Fe K-edge, (B) Ni K-edge, and (C) Pd K-edge XANES spectra of $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$ at each analysis point.

Table S3 Lattice parameters of $Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$.

		Lattice parameter (Å)	
		a	*c*
$Pd/Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$	as-synthesized	3.856	20.136
	reduced	3.877	20.213

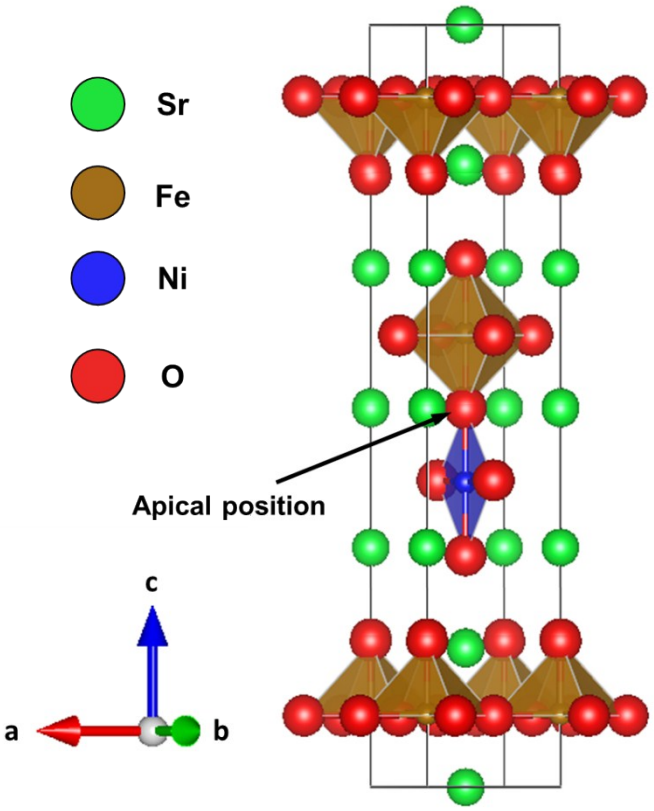

Figure S14 Proposed crystal structure of reduced Pd/$Sr_3(Fe_{0.8}Ni_{0.2})_2O_{7-\delta}$.