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Nickel–praseodymium catalysts supported on $LaFeO_3/SiO_2$ for ethanol steam reforming reaction

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Synthesis

Silica precursor gels were synthesized by the sol-gel method. The following substances were used as starting materials: tetraethoxysilane (TEOS) (pre-distilled at a temperature of 166 °C and a pressure of 753 mmHg), concentrated nitric acid (purity 99.9%), lanthanum(III) nitrate hexahydrate (purity 99%), iron(III) nitrate nonahydrate (purity 99%), praseodymium(III) nitrate hexahydrate (purity 99.9%), nickel(II) nitrate hexahydrate (purity 99%), β-cyclodextrin (purity >98%), urea (purity > 99%), distilled water.

The synthesis scheme is shown in Figure S1. The preliminary hydrolysis of TEOS was carried out in 0.1 M nitric acid (3.7 ml TEOS and 1.3 ml HNO_3 0.1 M were taken per 1 g of SiO_2) with stirring at 25 °C (2 h). Then, an aqueous solution of β-cyclodextrin (β-CD) and urea (U) was added drop by drop with stirring [m(β-CD) : m(U) = 1:3, the mass fraction of the template ($\omega = \frac{m_{\beta-CD}+m_U}{m_{\beta-CD}+m_U+m_{SiO_2}} \cdot 100\% = 60\%$)] and stirred at 25 °C (1 h). The ratio of the mass of water used in the synthesis of silica to the mass of SiO_2 (X) was equal to either 5 or 20. Then the sols were left for 2 weeks under a perforated film at room temperature for gelation and aging of the gels. After 2 weeks, the obtained gels were dried at 120 °C (24 h). A solution of lanthanum(III) nitrate was loaded to the dried gels, kept for 1 day and dried at 120 °C (24 h). After that, decomposition was carried out at 350–600 °C (3.5 h) followed by annealing in air at 600 °C (5 h). After annealing, iron was loaded in the form of aqueous solution of iron(III) nitrate by wet impregnation with drying at 100 °C (40–60 min) and annealing in air at 600 °C (2 h). After iron loading, praseodymium was loaded using praseodymium(III) nitrate and nickel in the form of an aqueous solution of nickel(II) nitrate by wet impregnation with drying at 100 °C (40–60 min) to prevent carburization of the samples. After loading, annealing in air was carried out at 600 °C (2 h), after which a fraction with a particle diameter of 0.25–0.5 mm was made. Each sample was designated as X-NP, where X is the ratio of the mass of water used in the synthesis of silica to the mass of SiO_2. Thus, the samples obtained were named 5-NP and 20-NP.

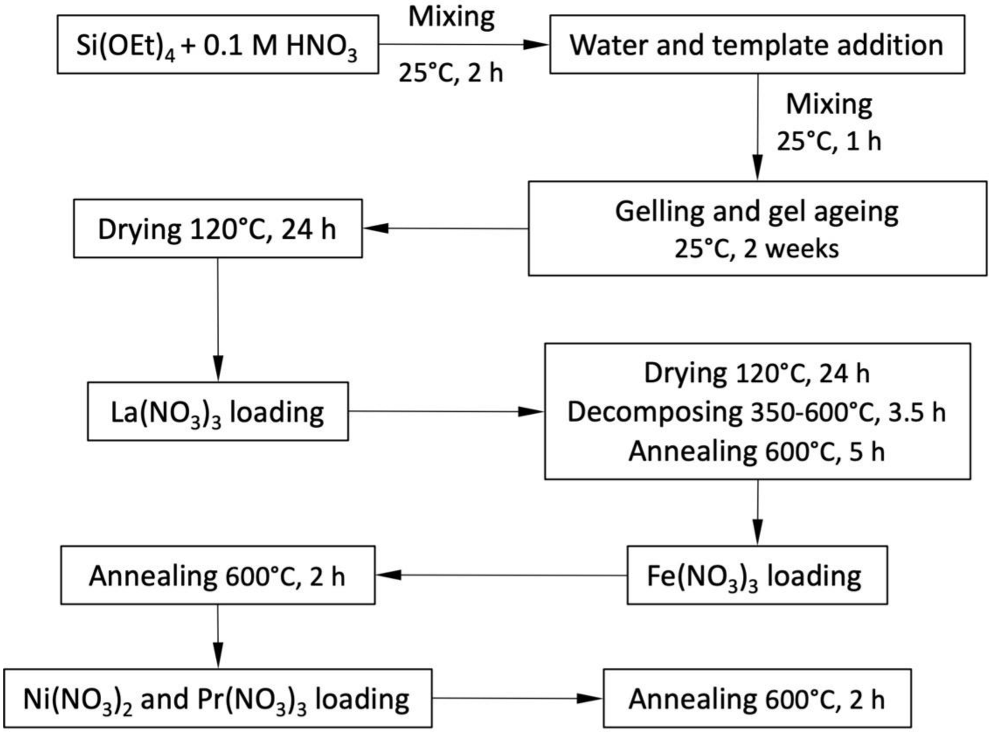

Figure S1 Sample synthesis scheme.

Characterization methods

XRD was performed on a Rigaku D/MAX 2500 diffractometer with a rotating anode (CuKα radiation; graphite monochromator). The XRD profiles were recorded in the 2θ range from 10° to 80°. The experimental data were processed using the STOE software package.

EDX analysis was carried out on a Supra 50 VP LEO high-resolution scanning electron microscope with an INCA Energy+Oxford microanalysis system at 500x magnification with a resolution of 129 eV on the Kα(Mn) line in a low vacuum with nitrogen to remove the charge. The nitrogen pressure was 40 Pa.

Textural parameters of the samples were measured on a Quantachrome Nova 4200e sorption analyzer. The specific surface area was calculated by the BET method, and the BJH method was used to plot pore size distributions.

Material reactivity was characterized by the temperature-programmed reduction with H_2 (TPR-H_2) (10% H_2 in Ar, feed rate 40 ml/min and temperature ramp from 25 to 900 °C at 10 °C/min) in a flow kinetic setup with a quartz U-shaped reactor equipped with a Tsvet-500 chromatograph and a thermal conductivity detector.

Mössbauer spectra were measured with a conventional electrodynamic spectrometer in the constant acceleration mode with an 1850 MBq ^{57}Co(Rh) γ-ray source equipped with Cryogen-free closed cycle cryostat for Mössbauer spectroscopy CFPR-221-MESS. The values of the isomer shift were given relative to α-Fe (298 K). The experimental spectra were processed using the program package 'SpectrRelax'.[S1]

XPS spectra were acquired on an Axis Ultra DLD spectrometer (Kratos Analytical, UK) with monochromatic AlKα radiation. Tablets of 3 mm in diameter were analyzed before and after *in situ* reduction in the gas reaction cell of the spectrometer in a mixture of 5% H_2 in Ar (flow rate of 20 ml/min) at temperatures of 500 and 850 °C for 30 min (heating rate of 10 °C/min). The pass energies of the analyzer were 160 eV for survey spectra and 40 eV for high-resolution scans. The Kratos charge neutralizer system was used, and the spectra were charge-referenced to the position of the La $3d_{5/2}$ peak (835.0 eV).

The oxygen isotope exchange of the samples was studied in a straight flow reactor in a temperature-programmed mode. A mixture of 0.9 vol% $C^{18}O_2$, 1.0 vol% Ar and helium were supplied to the reactor inlet. Gradual heating was carried out from 50 °C to 600 °C at a rate of 5 °C/min. The gas mixture for the study of isotope exchange was formed from He (purity >99.9%), Ar (purity >99.9%) and $C^{18}O_2$ (purity >99.9%). The sample weight was 50 ± 0.5 mg. The total flow rate was 25 ml/min. A custom flow-mass controller from Quarta LTD was used to regulate gas flows. The composition of the mixture was determined using a Stanford Research Systems UGA200 mass spectrometer. The magnetic mass analyzer was controlled and ion currents were recorded automatically using a computer program. The treatment was carried out using the software developed by the senior researcher of the Institute of Catalysis, Dr. E. M. Sadovskaya.

The catalysts were tested in ethanol steam reforming (ESR) in a continuous flow fixed-bed quartz reactor under atmospheric pressure in the temperature range of 550–650 °C. A total amount of catalyst (0.25–0.5 mm fraction), which was calculated according to the formula $m_{\mathrm{cat}}(\mathrm{mg}) = 1000u\tau\rho$, where u is the flow rate (100 ml/min), τ – contact time (10 ms), ρ – bulk density, was loaded and sandwiched between two quartz wool layers. The catalyst was pre-reduced with 10 vol% H_2/He at 600 °C for 1 h. Reaction feed was prepared by mixing He (purity >99.99%) with H_2O (distilled) and EtOH (95% water solution, purity >99.9%), yielding a gas composition C(EtOH) = 2 vol%, $C(H_2O)$ = 8 vol%. The outlet products were analyzed with a Chromos GCh-1000 gas chromatograph with flame ionization and thermal conductivity detectors. Ethanol conversion $X_{\mathrm{C_2H_5OH}}$, hydrogen yield $Y_{\mathrm{H_2}}$ and product selectivities S_{i} were calculated according to the formulas:

$$X_{\mathrm{C_2H_5OH}}(\%) = \frac{C^0_{\mathrm{C_2H_5OH}} - C_{\mathrm{C_2H_5OH}}}{C^0_{\mathrm{C_2H_5OH}}} \times 100,$$

$$Y_{\mathrm{H_2}}(\%) = \frac{C_{\mathrm{H_2}}}{6C^0_{\mathrm{C_2H_5OH}}} \times 100,$$

$$S_{\mathrm{i}}(\%) = \frac{\nu_{\mathrm{i}} C_{\mathrm{i}}}{2\left(C^0_{\mathrm{C_2H_5OH}} - C_{\mathrm{C_2H_5OH}}\right)} \times 100,$$

where $C^0_{\mathrm{C_2H_5OH}}$ is the initial ethanol concentration, ν_{i} – number of carbon atoms in a molecule and i = CO, CO_2, CH_4. Not only methane but also other by-products were detected: acetone and acetaldehyde for both the catalysts and even ethylene for 20-NP and ethane for 5-NP. However, their concentrations were not presented in Figure S12 due to difficulties in the exact estimation of their content by accessible techniques. This problem will be solved in further studies, since at ethanol conversion for the 20-NP catalyst exceeding 90% at 600 °C (Figure S12) the sum of CO and CO_2 selectivities is only around 40%, which demonstrates a strong contribution of by-products that, nevertheless, did not affect catalyst stability.

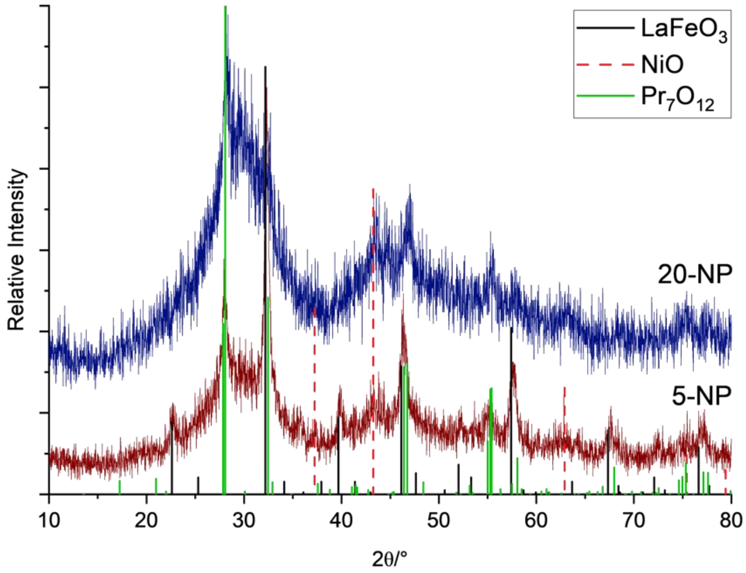

Figure S2 XRD patterns of samples. Vertical bars show reflections of $LaFeO_3$ (75-541), NiO (47-1049) and Pr_7O_{12} (6-329) phases from the powder database.[S2]

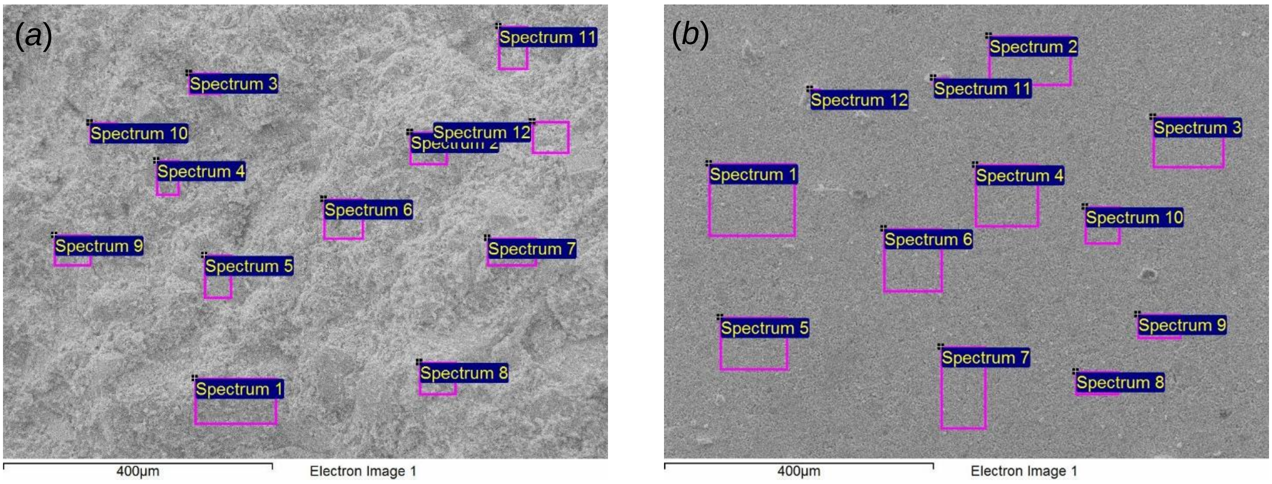

Figure S3 SEM photographs of (*a*) 5-NP and (*b*) 20-NP samples with marked regions of spectra for EDX analysis.

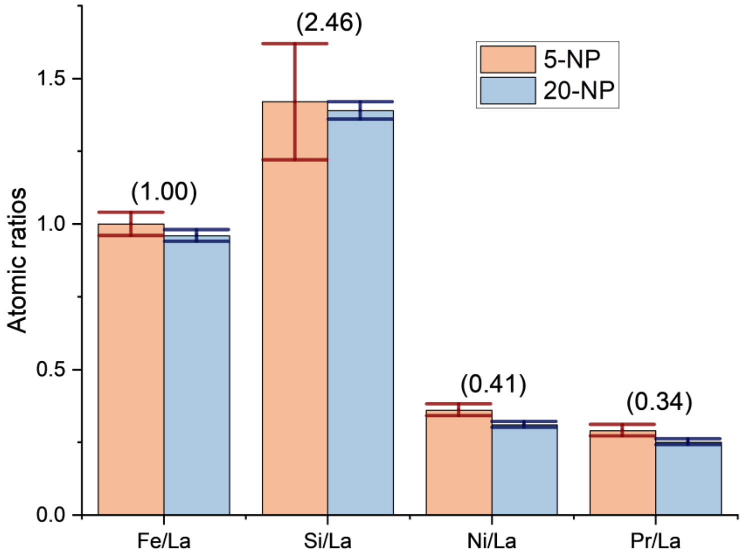

Figure S4 Atomic ratios of elements in samples. The theoretical values are shown in parentheses.

Table S1 Atomic ratios of elements in samples annealed at 600 °C.

Sample	Fe/La		Si/La		Ni/La		Pr/La	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
5-NP	1.00±0.04	1.00	1.42±0.20	2.46	0.36±0.02	0.41	0.29±0.02	0.34
20-NP	0.96±0.02		1.39±0.03		0.31±0.01		0.25±0.01	

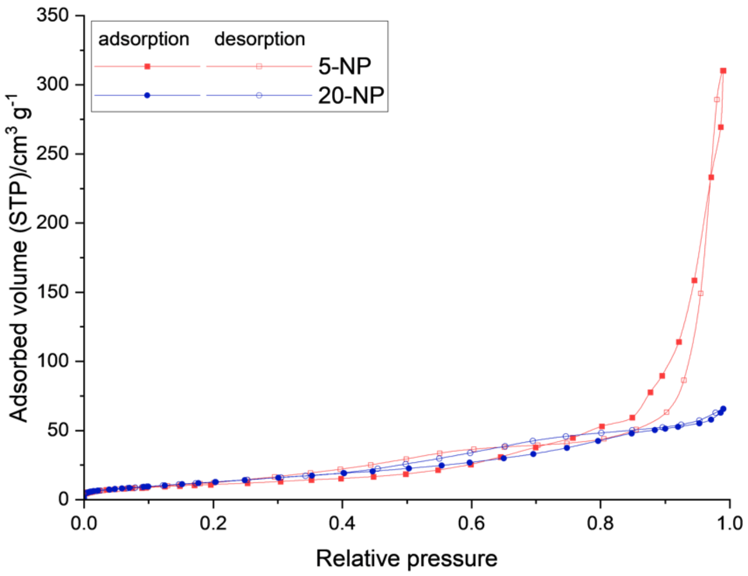

Figure S5 Low-temperature nitrogen physisorption isotherms of samples.

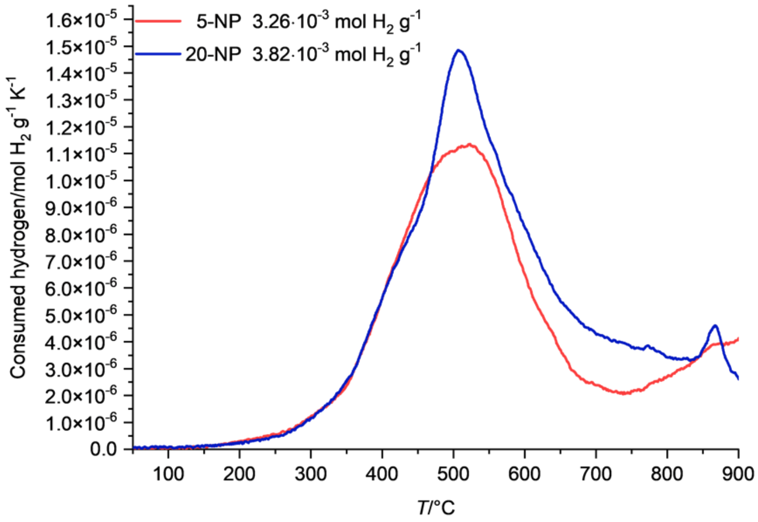

Figure S6 TPR profiles of samples.

Table S2 XPS surface compositions of samples (at%) calculated from high-resolution XPS spectra.

5-NP

Sample	**Pr**	**La**	**Ni**	**Fe**	**O**	**C**	**Si**
Initial	6.4	5.2	5.9	4.9	53.4	19.2	5.0
500°C	9.3	7.3	3.7	7.5	52.3	12.7	7.2
850°C	7.2	11.1	2.9	8.9	55.0	6.8	8.1

20-NP

Sample	**Pr**	**La**	**Ni**	**Fe**	**O**	**C**	**Si**
Initial	6.3	4.6	5.3	6.6	50.9	21.6	4.7
500°C	11.2	8.1	3.1	11.1	52.8	7.1	6.6
850°C	7.5	9.8	2.2	10.2	57.1	3.3	9.9

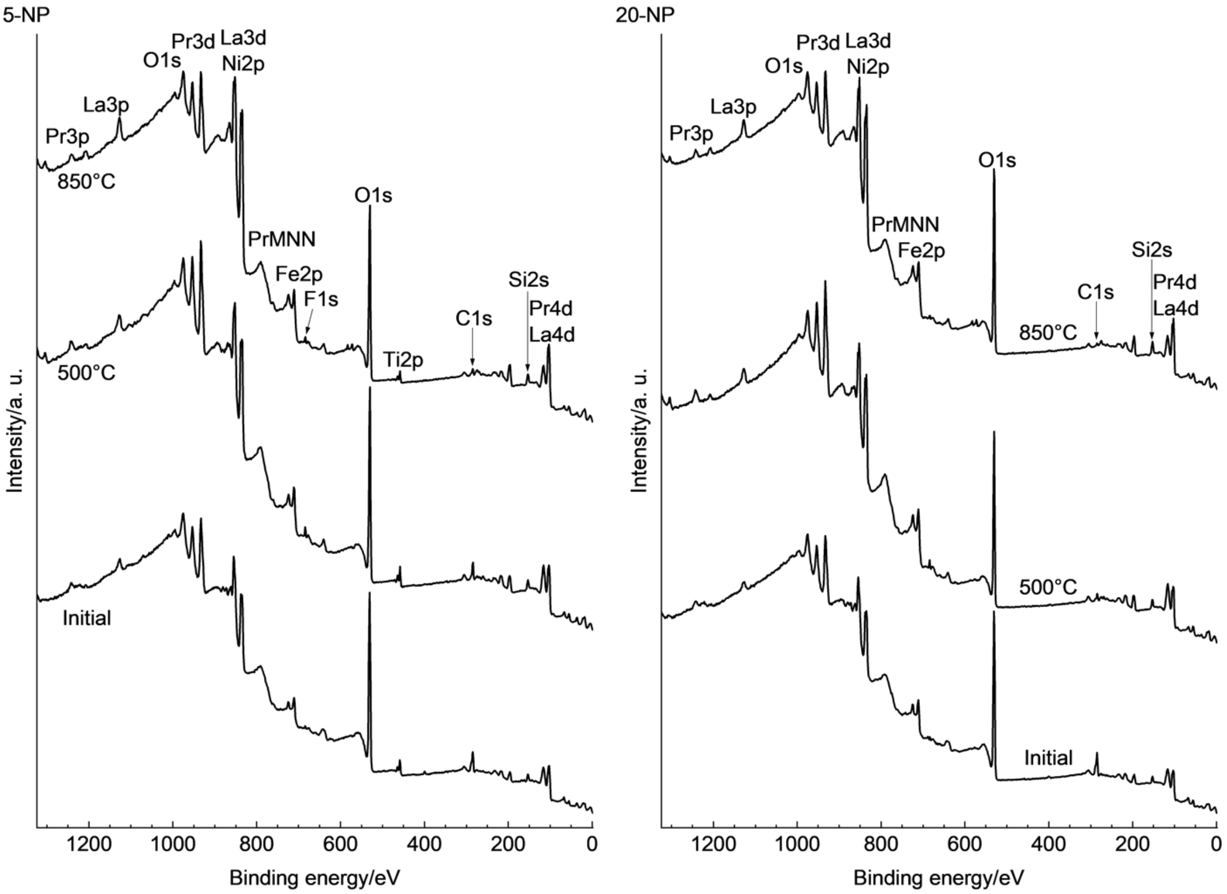

Figure S7 Survey XPS spectra of unreduced and *in situ* H_2-reduced samples.

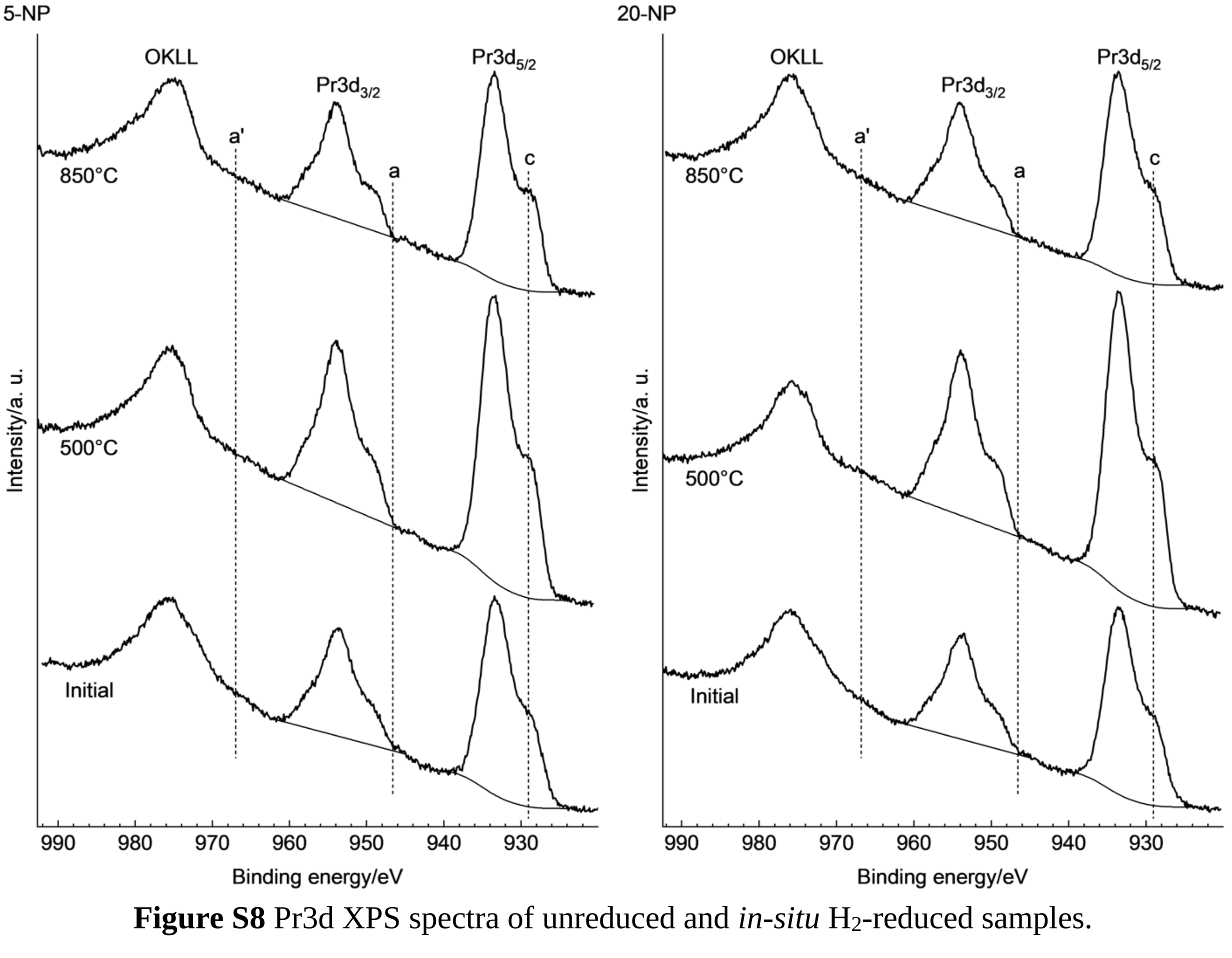

Figure S8 Pr3d XPS spectra of unreduced and *in-situ* H_2-reduced samples.

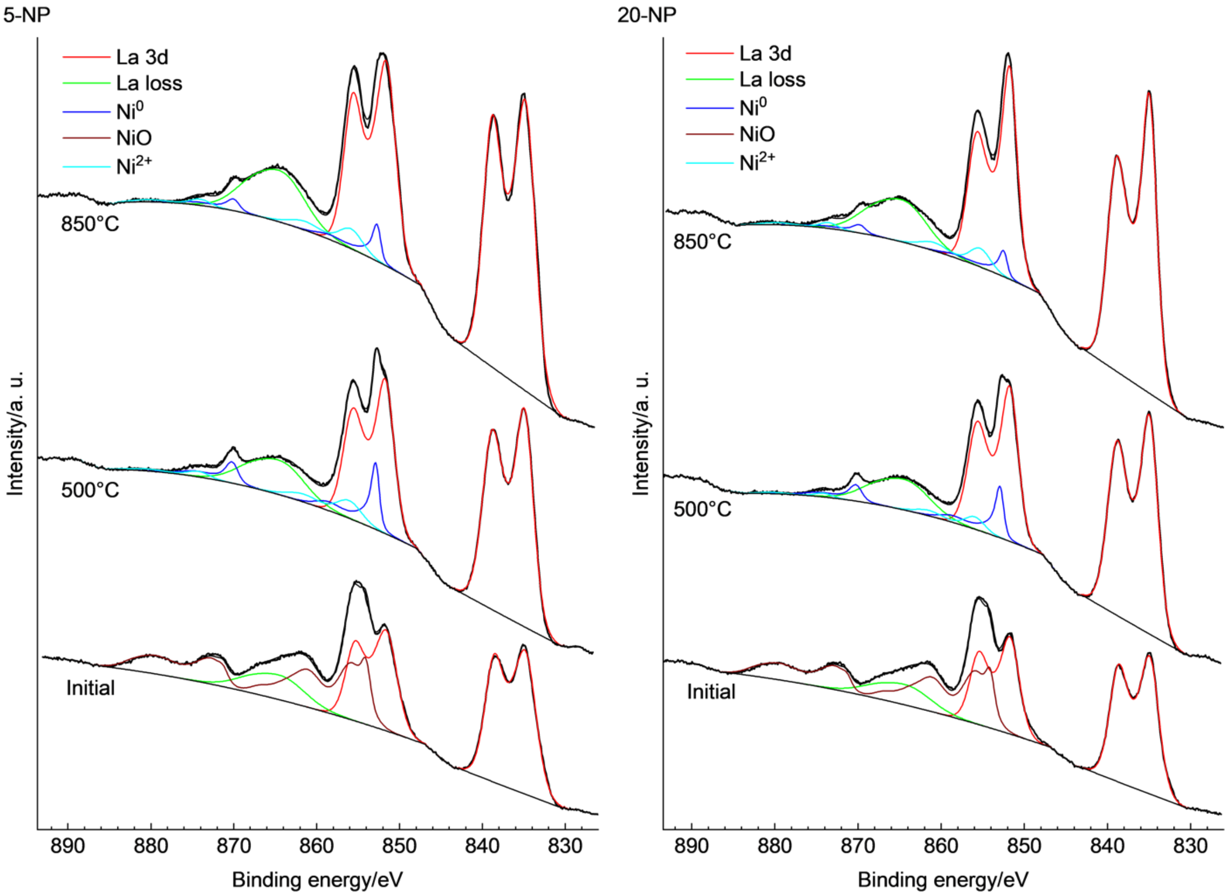

Figure S9 La3d and Ni2p XPS spectra of unreduced and *in situ* H_2-reduced samples.

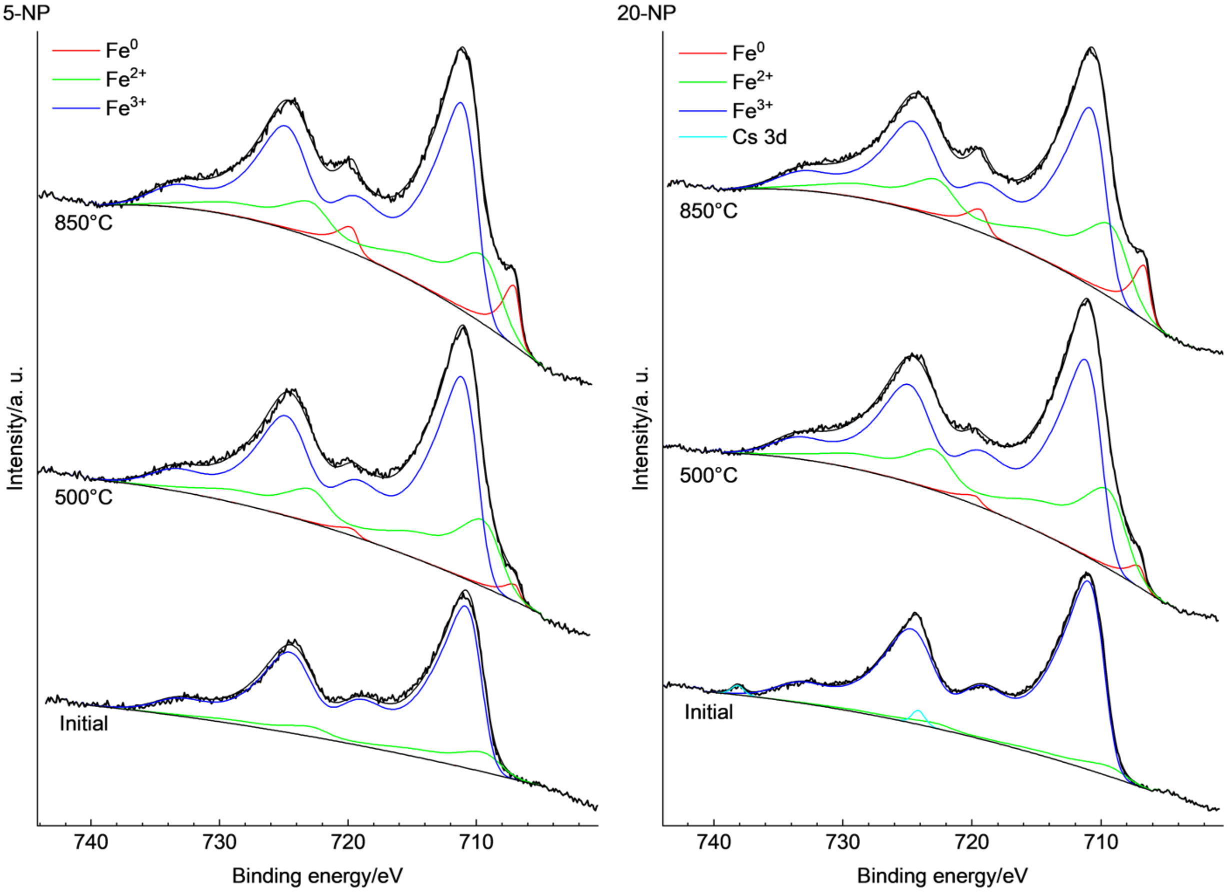

Figure S10 Fe2p XPS spectra of unreduced and *in situ* H_2-reduced samples.

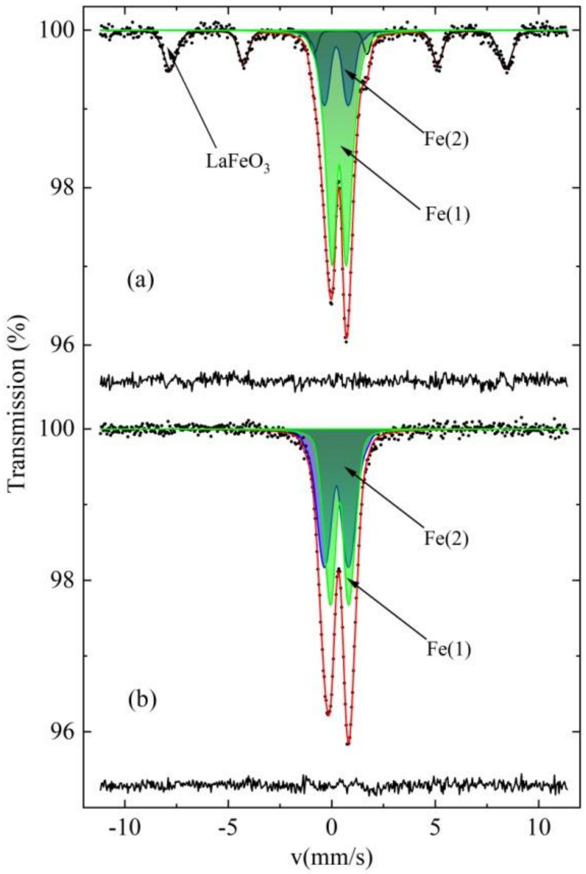

Figure S11 ^{57}Fe Mössbauer spectra of (a) 5-NP and (b) 20-NP samples measured over a wide velocity range at room temperature.

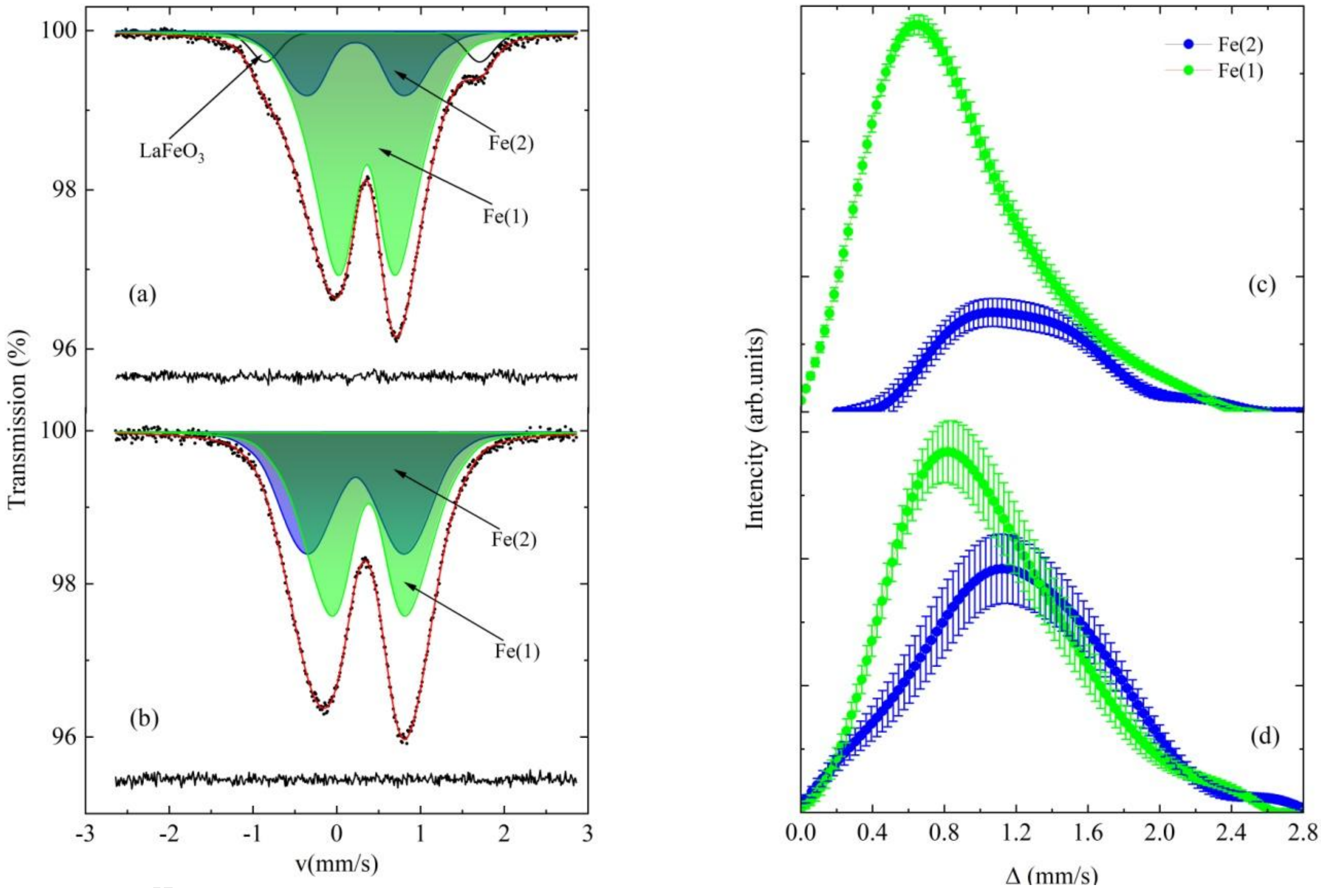

Figure S12 ^{57}Fe Mössbauer spectra of (a) 5-NP and (b) 20-NP samples measured over a narrow velocity range at room temperature and (c),(d) the reconstructed distributions of the quadrupole splitting.

Table S3 ^{57}Fe hyperfine parameters at room temperature.^{a}

Sample	Component	$\bar{\delta}$/mm s^{-1}	$\bar{\Delta}$/mm s^{-1}	B_{hf}/T	A (%)
5-NP	Fe(1)	0.36(1)	0.86(2)	–	57(3)
	Fe(2)	0.22(1)	1.26(4)	–	19(3)
	$LaFeO_3$	0.36(1)	−0.13(1)*	50.2(1)	24(1)
20-NP	Fe(1)	0.38(1)	1.04(1)	–	58(7)
	Fe(2)	0.23(1)	1.20(1)	–	42(7)

^{a} $\bar{\delta}$ and $\bar{\Delta}$ are the mean values of the isomer shift and quadrupole splitting, respectively; B_{hf} is the hyperfine magnetic field; A is the partial area; * denotes the value of the doubled quadrupole shift ε for Zeeman sextet: $\Delta = 2\varepsilon$.

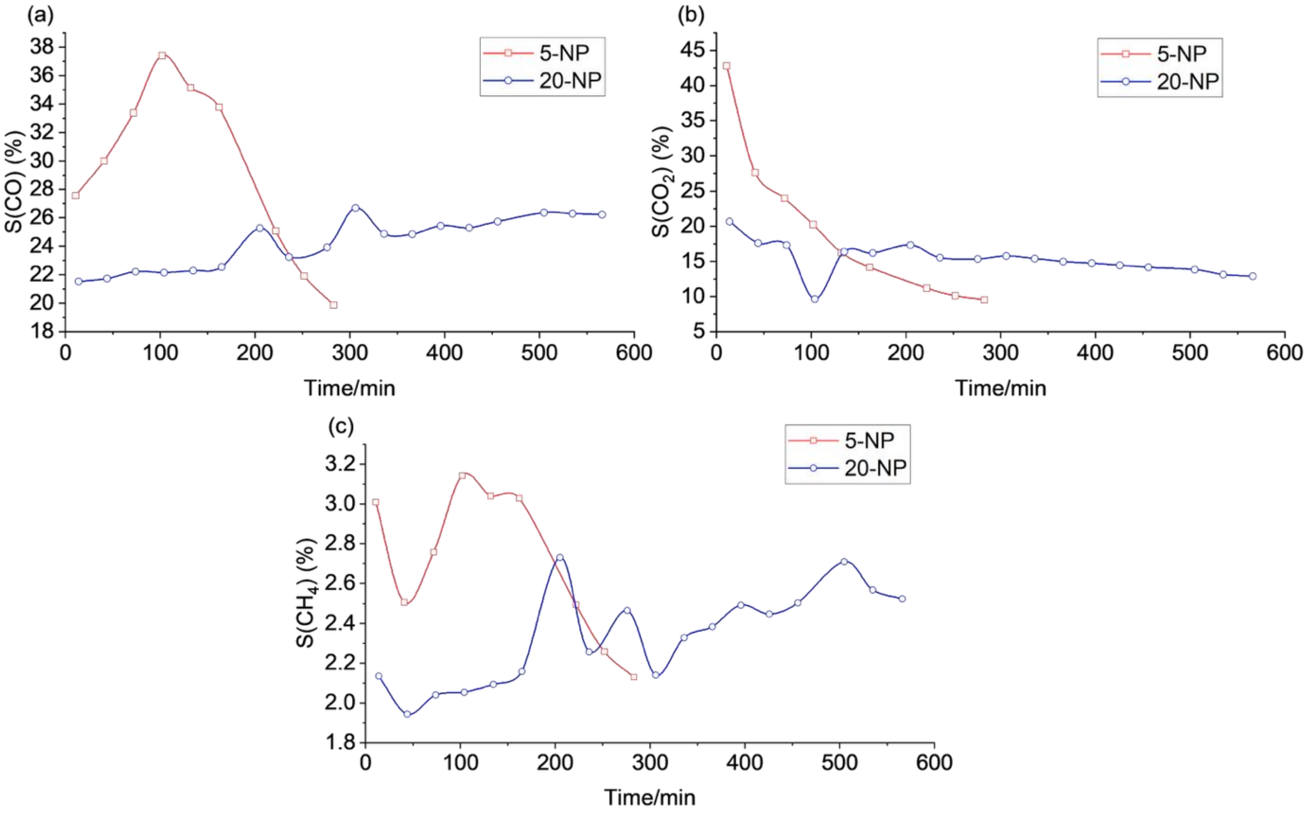

Figure S13 (a) CO, (b) CO_2 and (c) CH_4 selectivities *versus* time on stream for 5-NP and 20-NP catalysts tested in ethanol steam reforming at 600 °C.

References

S1 M. E. Matsnev and V. S. Rusakov, *AIP Conf. Proc.*, 2014, **1622**, 40; https://doi.org/10.1063/1.4898609.

S2 [dataset] JCPDS-ICDD, *PCPDFWIN, Version 2.2*, 2001.