SUPPORTING INFORMATION

Oxygen vacancies on nanosized ceria govern the NO_x storage capacity of NSR catalysts

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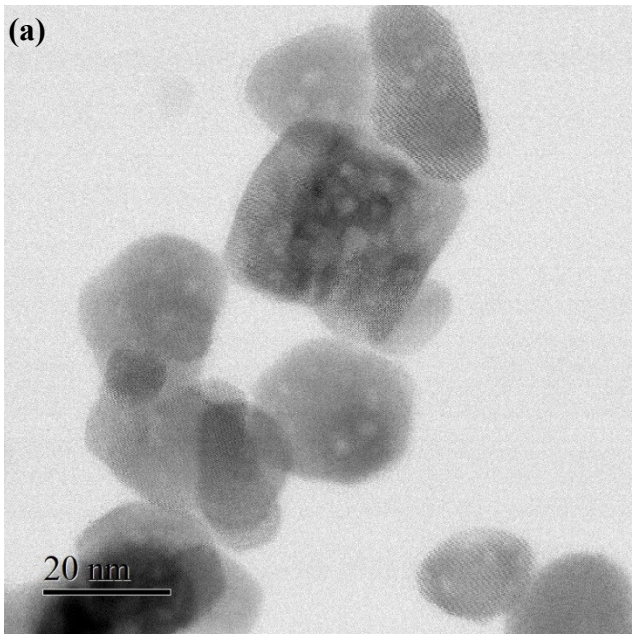
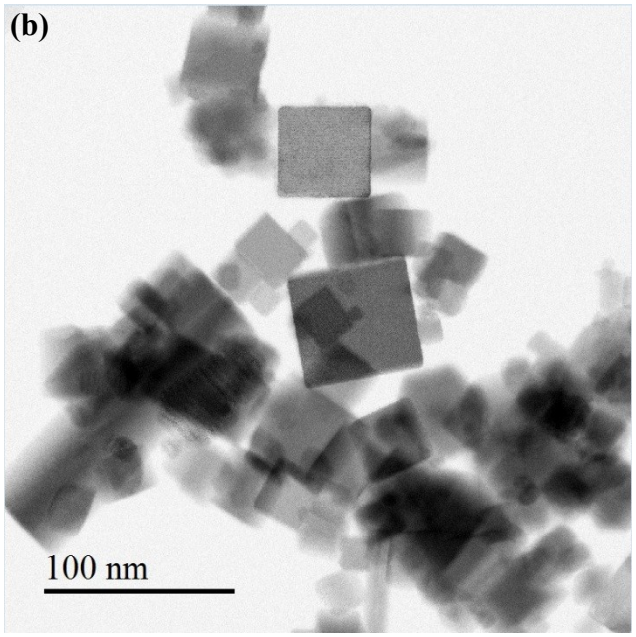
1. Experimental.

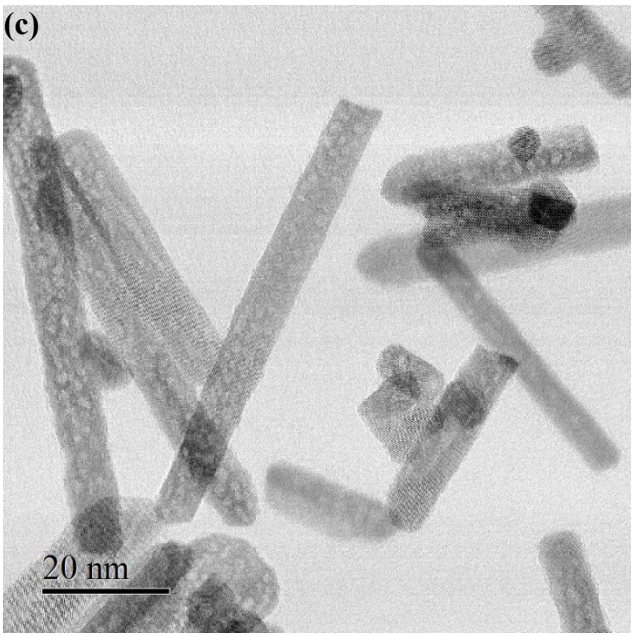
Methanol adsorption: The Pt/BaO/CeO_2 samples were pretreated in the DRIFTS cell in flowing 10% H_2/He (25 mL/min) at 450 ^oC for 1h and then cooled to room temperature before switching to He. During the process, the reduced samples do not expose to the oxygen. Methanol (Sigma-Aldrich, >99.9%) was bubbled with 25 mL/min He at room temperature, which was fed to the in situ DRIFTS cell. Then, IR measurement was carried out until the spectrum was stable.

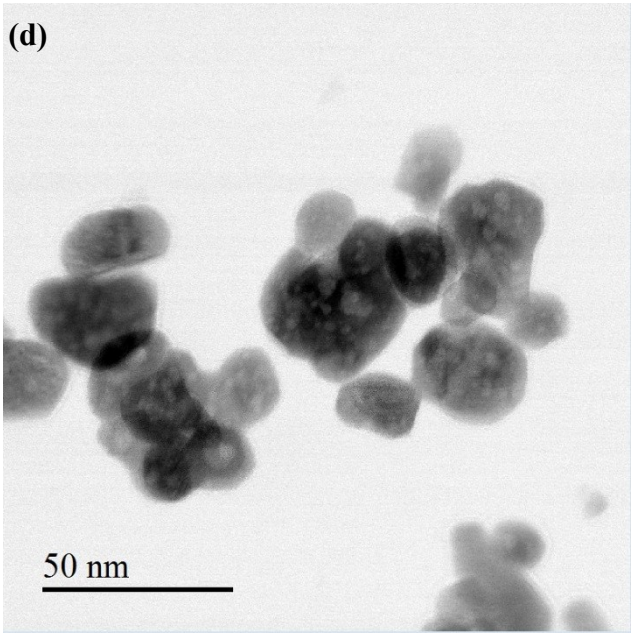
2. Results.

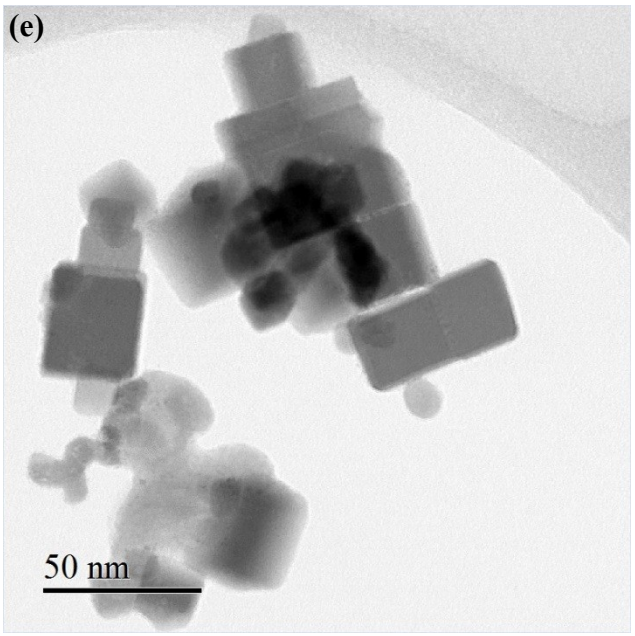
2.1 TEM and HRTEM images of NSR catalysts.






(c)
20 nm


(d)
50 nm



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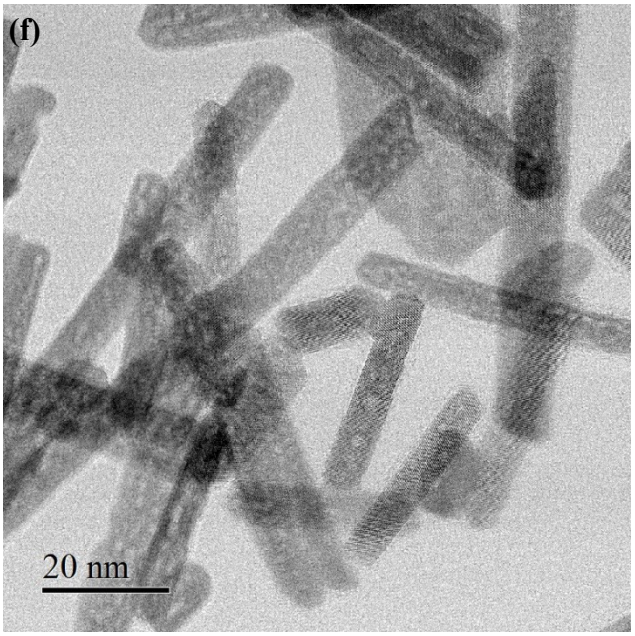

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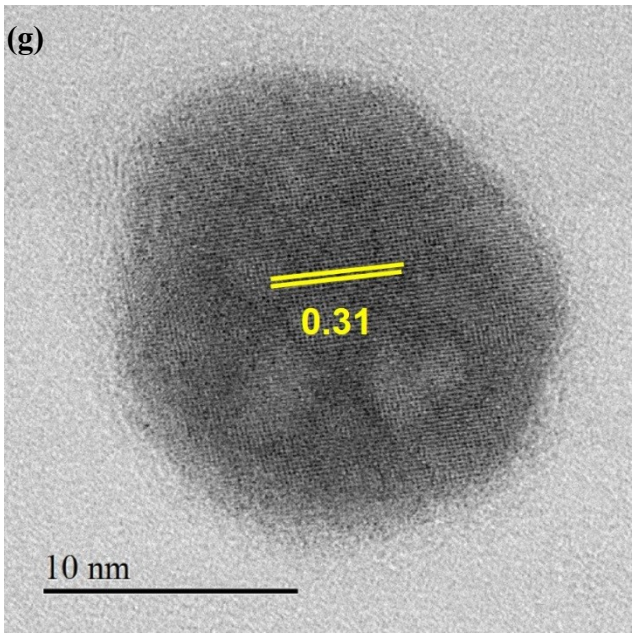

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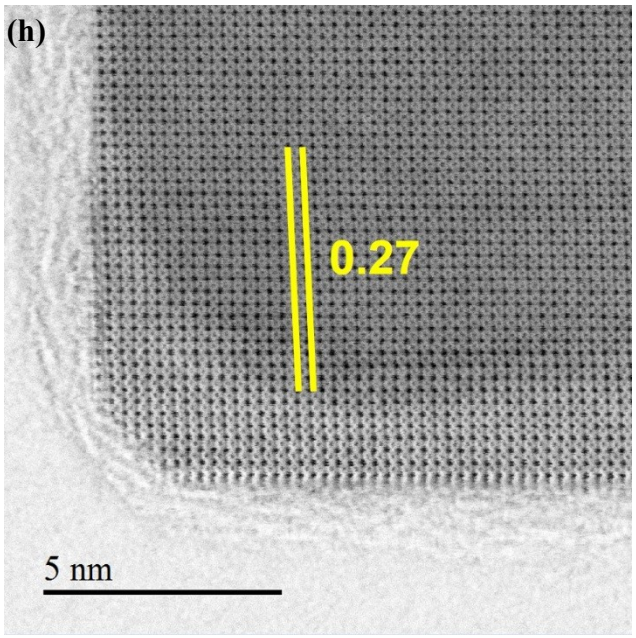

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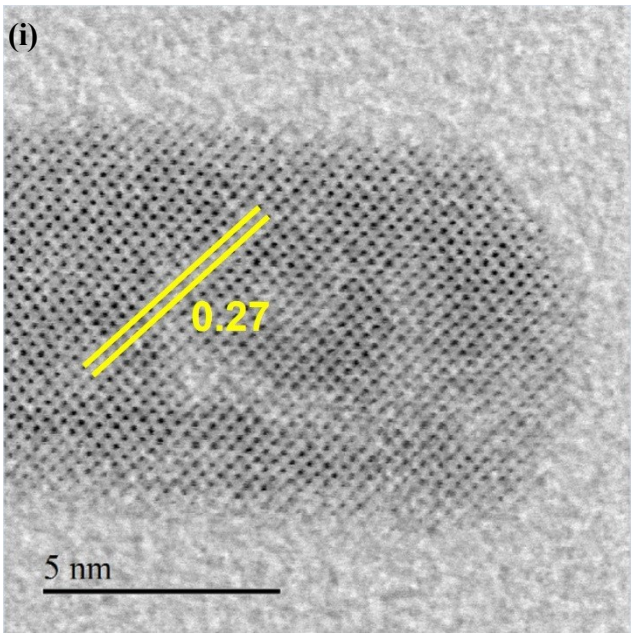
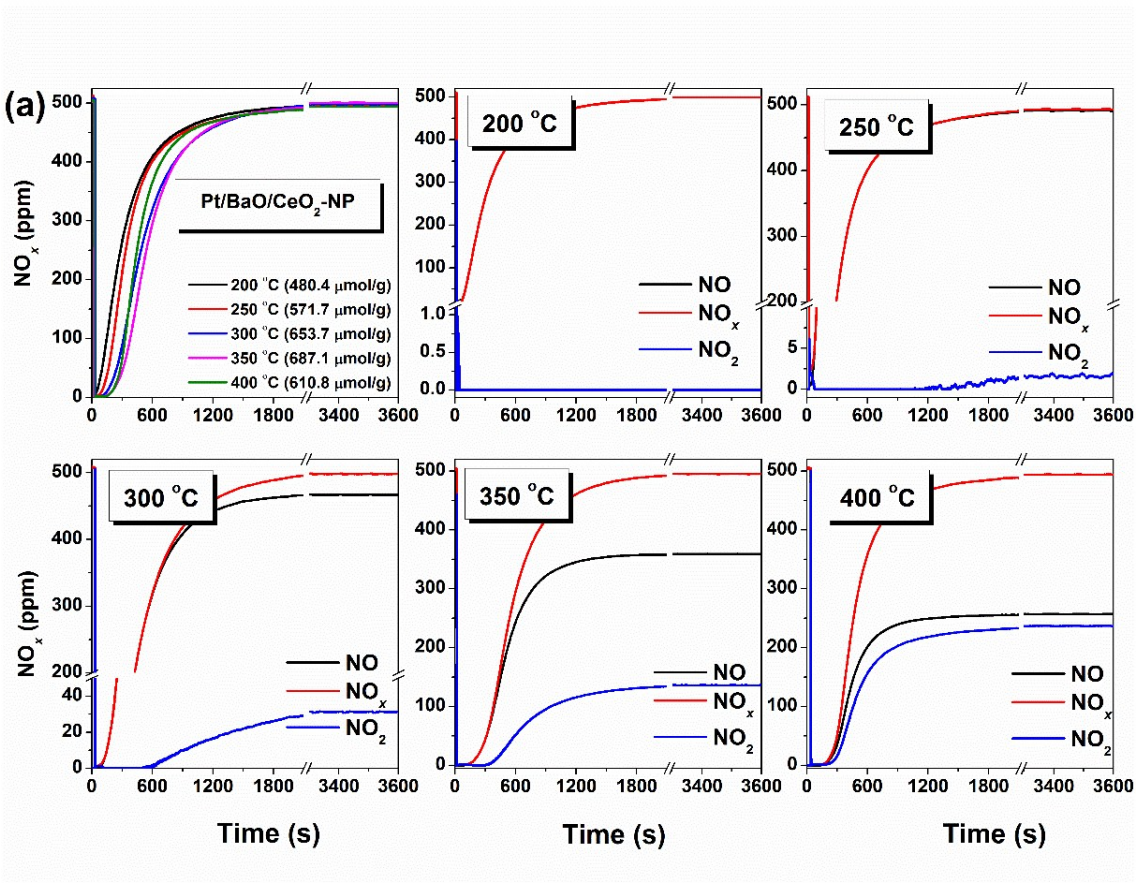
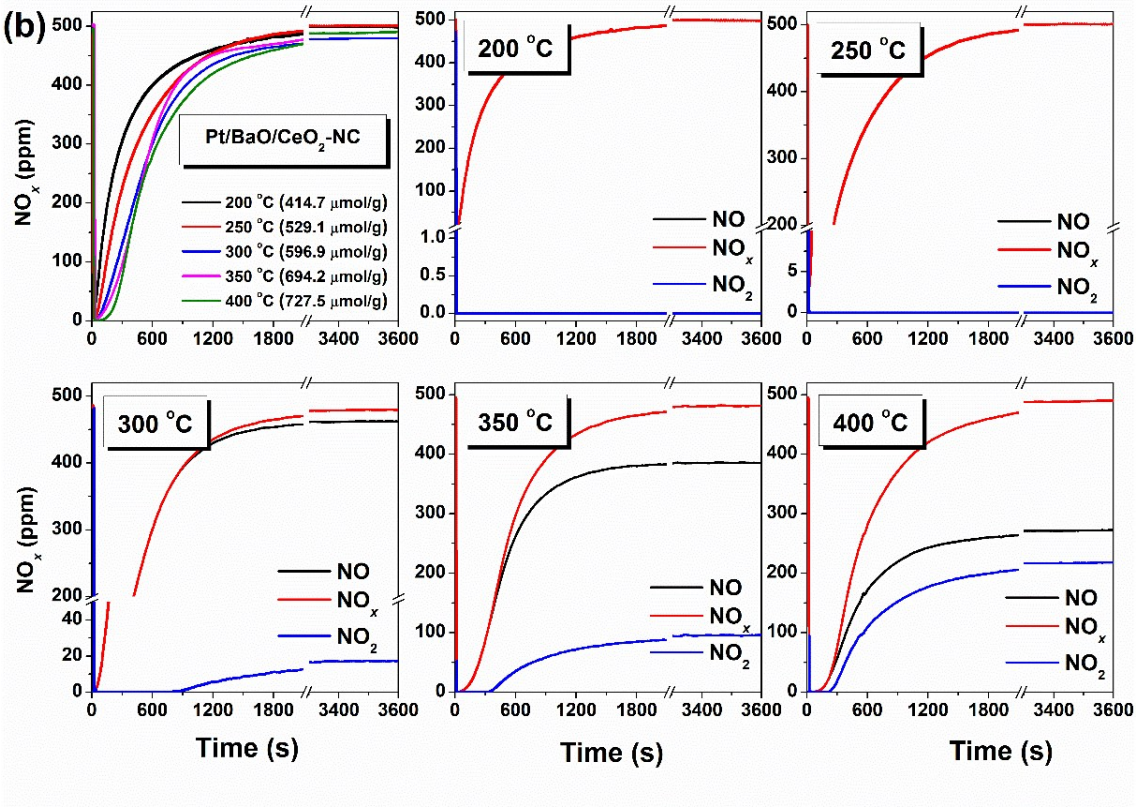


Figure S1. TEM and HRTEM images of CeO_2-NP (a), CeO_2-NC (b), CeO_2-NR (c), and Pt/BaO/CeO_2-NP (d and g), Pt/BaO/CeO_2-NC (e and h), Pt/BaO/CeO_2-NR (f and i).

2.2 NSC measurements and theoretical NO_x storage capacity.





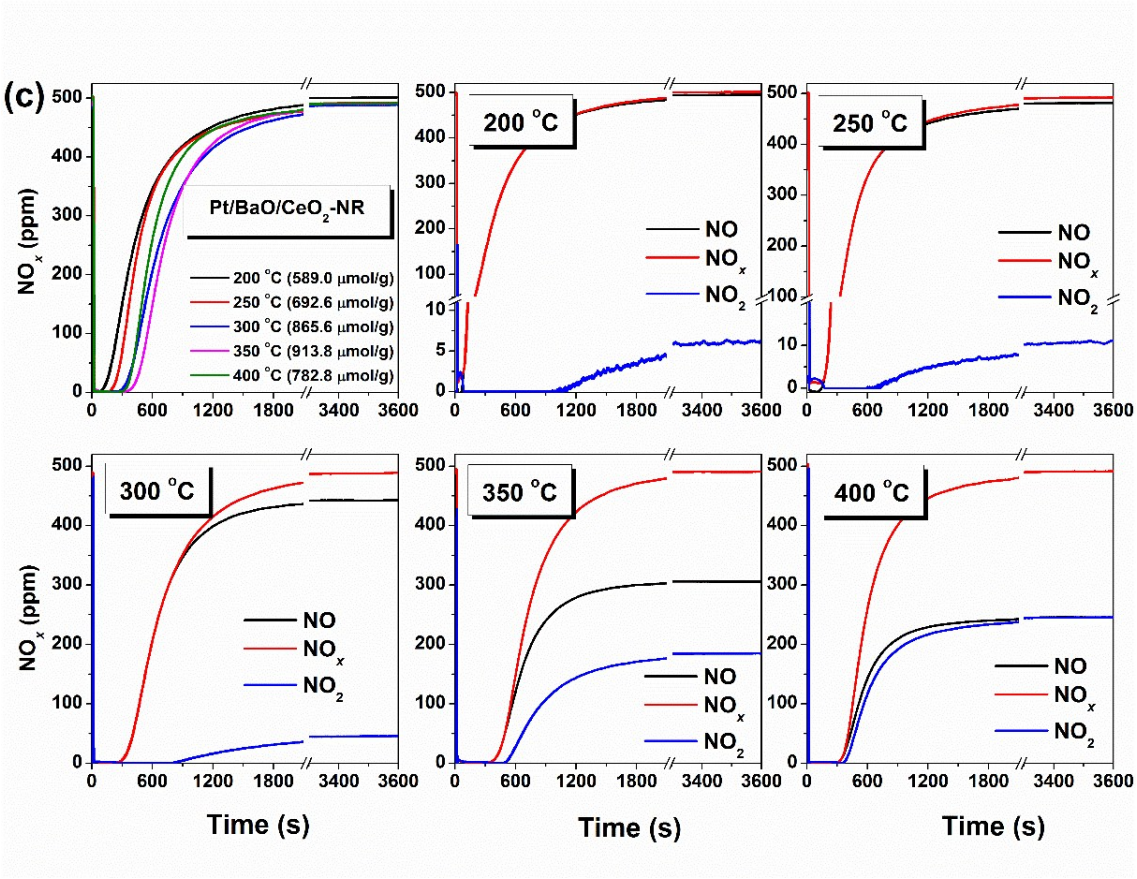


Figure S2. Evolutions of NO, NO_2 and NO_x as a function of time and temperature under lean condition over Pt/BaO/CeO_2-NP (a), Pt/BaO/CeO_2-NC (b), and Pt/BaO/CeO_2-NR (c).

Theoretical NO_x storage capacity. We also measured the NO_x storage capacity on the Ba-free samples. Taking Pt/CeO_2-NR as an example (Figure S4), the maximium NSC value of 93.2 μmol/g-cat was obtianed at 350 °C, which is 10% of the NSC value of Pt/BaO/CeO_2-NR at the same temperature. At whole temperature range, the NO_x storage capacity of Pt/CeO_2-NR is much lower than that Ba-containing one (Pt/BaO/CeO_2-NR). As a result, the theoretical NSC is calculated in accordance with the actual amount of BaO obtained from ICP-OES, considering all the NO_x storaged on the BaO sites.

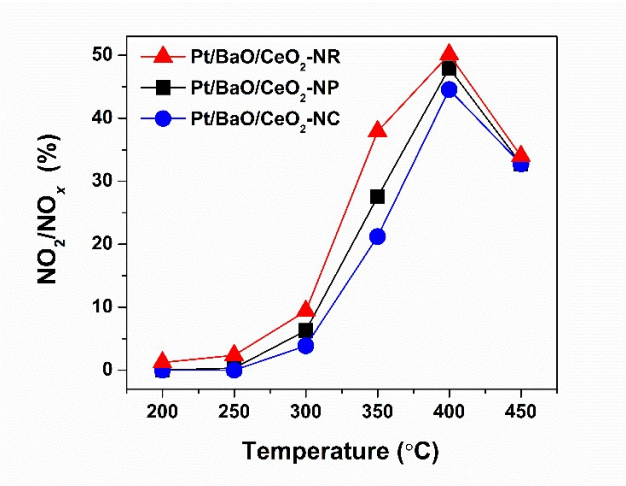
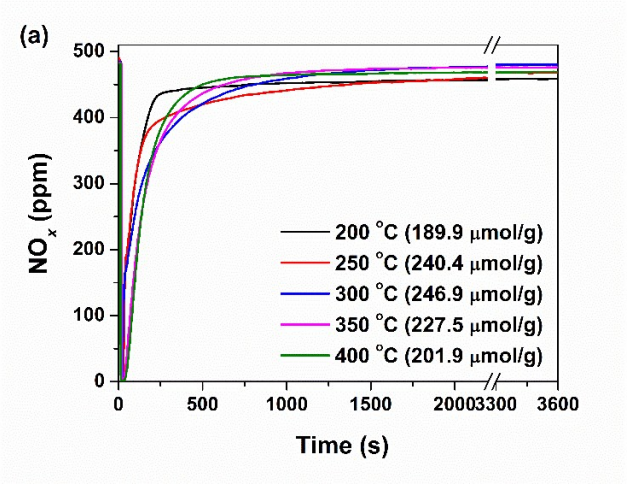
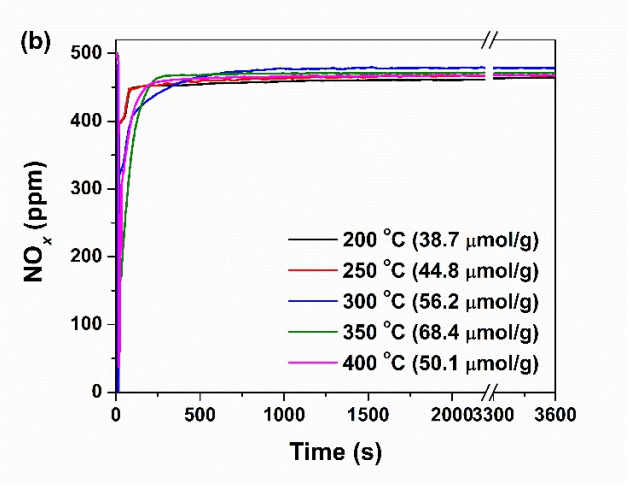
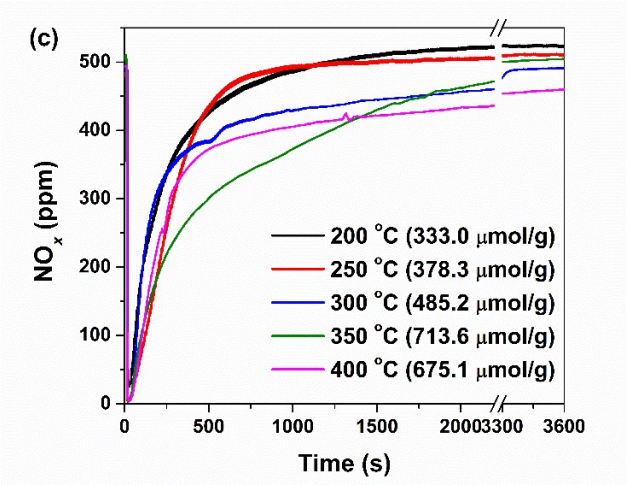


Figure S3. The outlet $NO_2/(NO+NO_2)$ ratio at the end of 3600 s for NO_x adsorption over Pt/BaO/CeO_2-NP, Pt/BaO/CeO_2-NC, and Pt/BaO/CeO_2-NR.

2.3 The effect of CO_2 and H_2O on the catalytic performance and NH_3 selectivity.







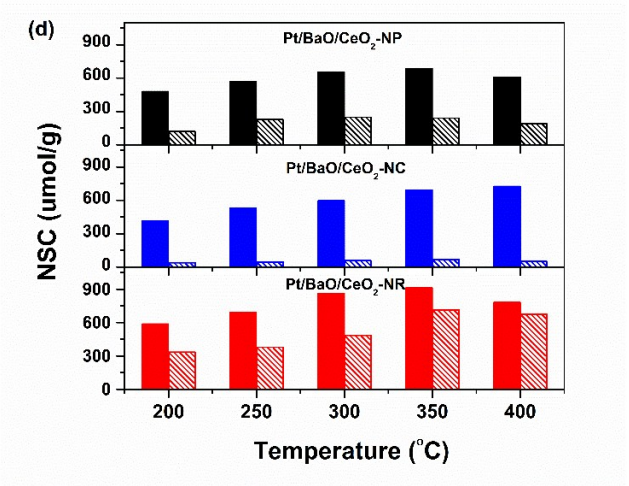


Figure S4. Evolutions of NO_x as a function of time and temperature under lean conditions over Pt/BaO/CeO_2-NP (a), Pt/BaO/CeO_2-NC (b), and Pt/BaO/CeO_2-NR (c); NO_x storage capacities (NSC) tested at different temperatures over Pt/BaO/CeO_2 catalysts without CO_2 and H_2O (solid), or with 1% CO_2, 2% H_2O (hatchfaces) (d).

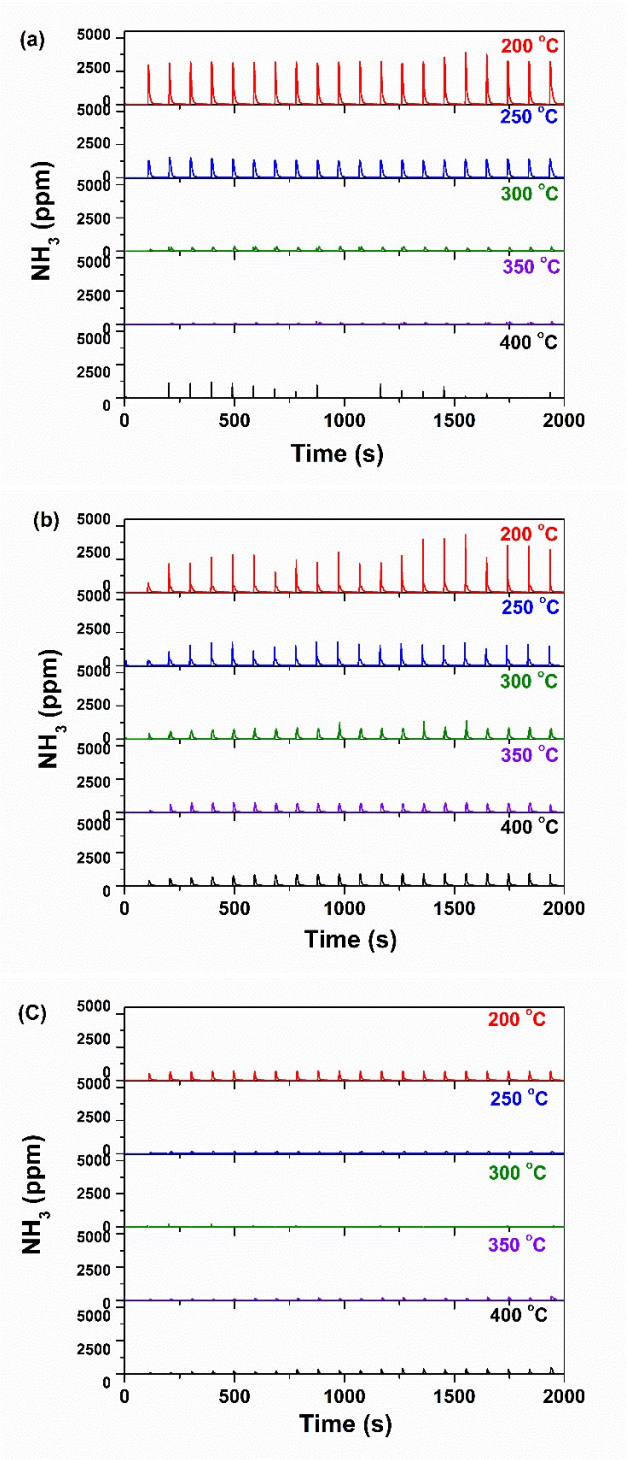
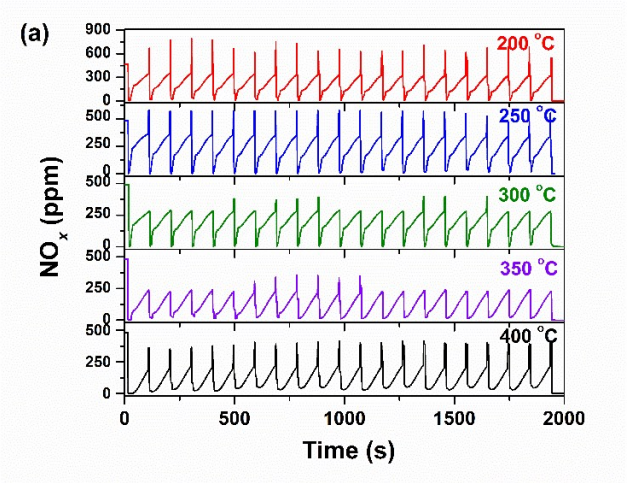
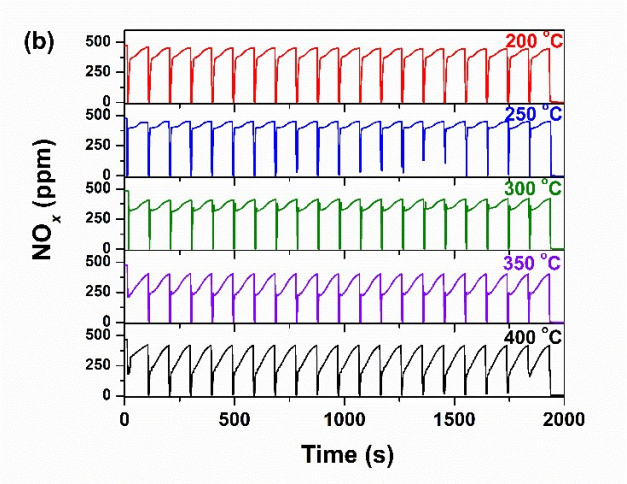


Figure S5. Evolutions of NH_3 concentrations under cyclic lean-rich conditions at different temperatures on Pt/BaO/CeO_2-NP (a), Pt/BaO/CeO_2-NC (b), and Pt/BaO/CeO_2-NR (c).

Table S1 NH_3 selectivity of all NSR catalysts under lean-rich conditions at different temperatures.

Samples	NH_3 selectivity (%)				
	200 °C	250 °C	300 °C	350 °C	400 °C
Pt/BaO/CeO_2-NP	52.83	35.54	10.07	5.24	0.88
Pt/BaO/CeO_2-NC	58.70	46.52	41.43	33.97	37.41
Pt/BaO/CeO_2-NR	11.54	4.39	0.74	4.07	5.37





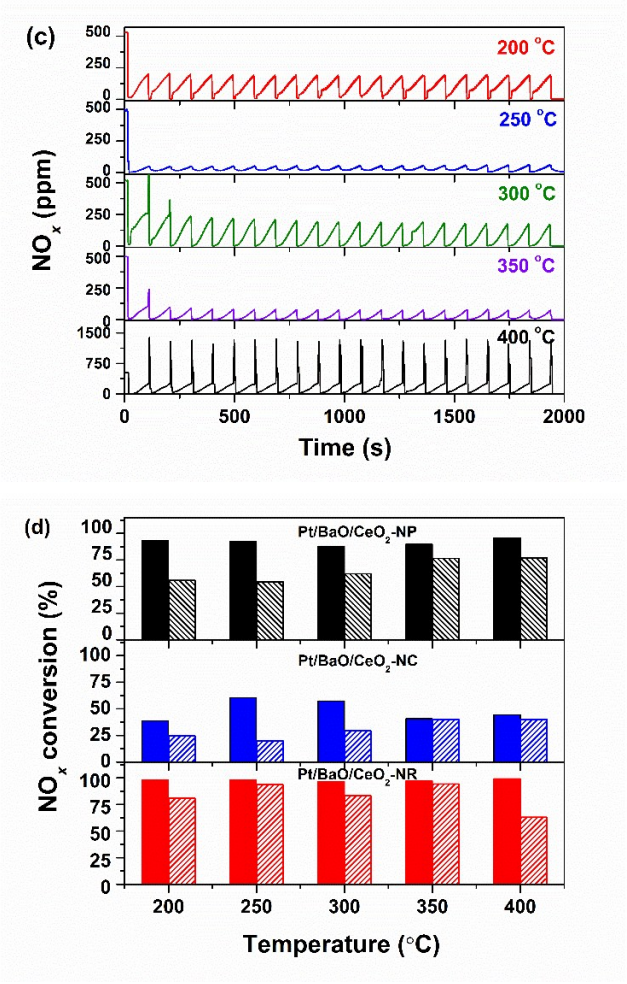
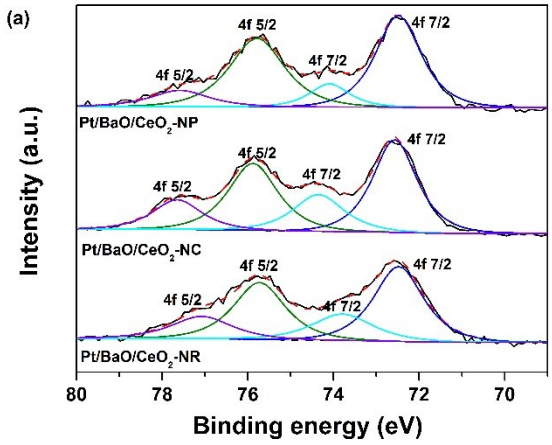


Figure S6. Evolutions of NO_x concentrations under cyclic lean-rich conditions at different temperatures on Pt/BaO/CeO_2-NP (a), Pt/BaO/CeO_2-NC (b), and Pt/BaO/CeO_2-NR (c); average NO_x conversion over all NSR catalysts under cyclic lean-rich conditions at different temperatures without CO_2 and H_2O (solid), or with 1% CO_2, 2% H_2O (hatchfaces) (d).

2.4 Pt XPS, Pt-L_{III} EXAFS spectra, and Ce XPS.



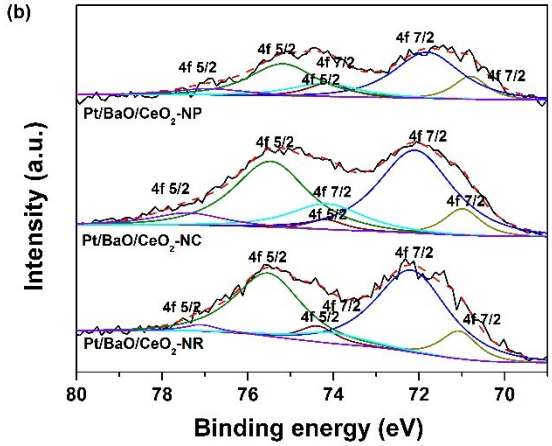


Figure S7. Pt 3d XPS spectra of $Pt/BaO/CeO_2$ (a), and the NSR catalysts reduced by 3 % H_2 ($Pt/BaO/CeO_2$-R) (b).

Table S2. XPS binding energies of individual peaks of the Pt 4f spectra for NSR catalysts and corresponding H_2-treated catalysts.

Samples	Pt $4f_{7/2}$	Pt $4f_{5/2}$	Pt $4f_{7/2}$	Pt $4f_{5/2}$	Pt $4f_{7/2}$	Pt $4f_{5/2}$
Pt/BaO/CeO_2-NP	72.5	75.8	74.1	77.6	-	-
Pt/BaO/CeO_2-NP-R	71.8	75.2	74.2	77.0	70.8	74.1
Pt/BaO/CeO_2-NC	72.5	75.8	74.3	77.6	-	-
Pt/BaO/CeO_2-NC-R	72.1	75.5	74.2	77.4	70.9	74.1
Pt/BaO/CeO_2-NR	72.4	75.7	73.8	77.1	-	-
Pt/BaO/CeO_2-NR-R	72.2	75.5	74.0	77.1	71.0	74.3

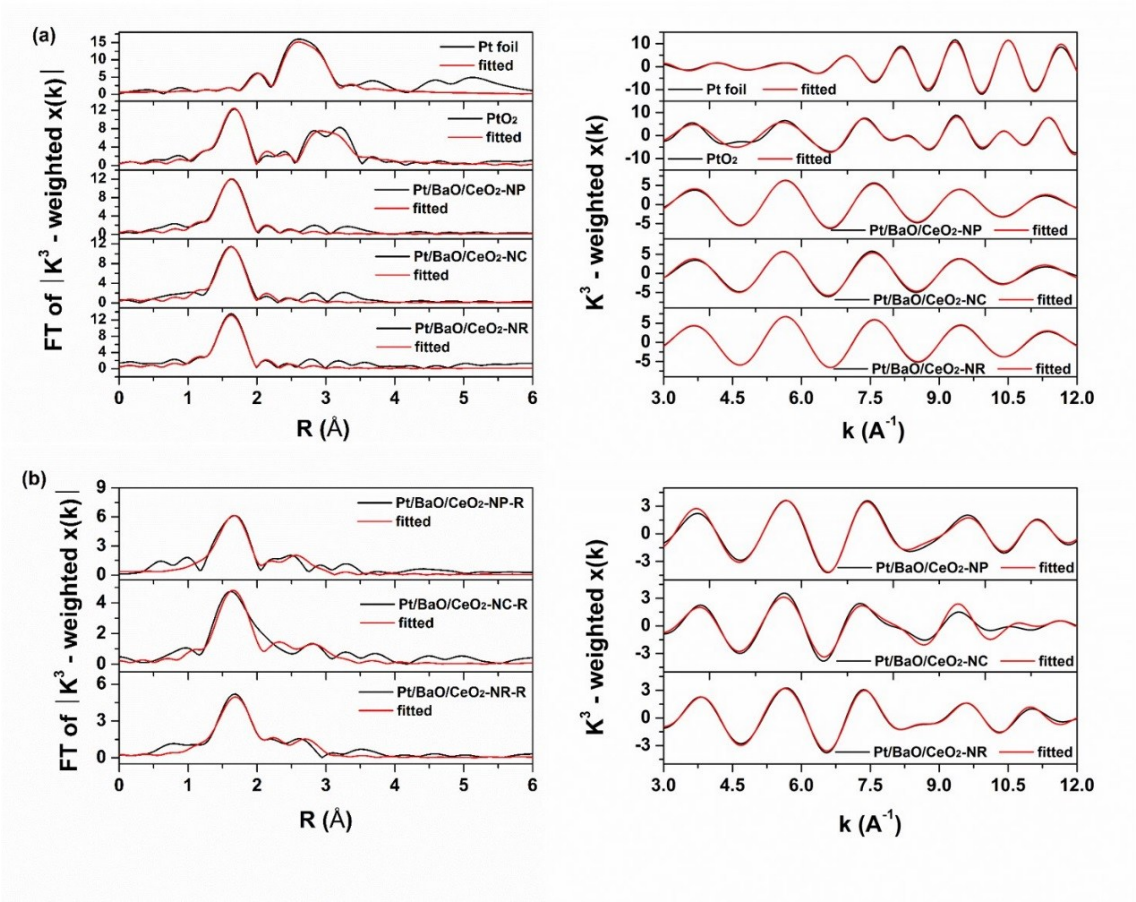


Figure S8. Pt-L_{III} EXAFS results of Fourier transformation of filtered $k^3 \cdot \chi$ (k); and filtered $k^3 \cdot \chi$ (k) in the k range of 3-12 $Å^{-1}$. (a) samples before H_2 reduction; (b) samples exposed to air after H_2 reduction.

Table S3. Fitting parameters of the curve fitted k^3-weighted EXAFS analysis of all samples[a].

Samples	Shell	CN	R/Å (±0.001)	DW/Å	R factor
Pt foil	Pt-Pt	12.0	2.77	0.073	1.5
PtO_2	Pt-O	6.0	2.02	0.069	4.2
	Pt-O-Pt	4.0	3.10	0.048	
Pt/BaO/CeO_2-NP	Pt-O	5.7 ± 0.7	2.00	0.065	0.37
Pt/BaO/CeO_2-NC	Pt-O	5.4 ± 0.7	2.00	0.066	0.97
Pt/BaO/CeO_2-NR	Pt-O	5.9 ± 0.7	2.00	0.062	0.12
Pt/BaO/CeO_2-NP-R[b]	Pt-O	3.9 ± 0.3	2.01	0.084	1.79
	Pt-Pt	1.7 ± 0.3	2.67	0.083	
Pt/BaO/CeO_2-NC-R[b]	Pt-O	3.1 ± 0.3	2.02	0.078	5.41
	Pt-Pt	1.5 ± 0.4	2.78	0.078	
Pt/BaO/CeO_2-NR-R[b]	Pt-O	3.7 ± 0.4	2.02	0.091	0.62
	Pt-Pt	2.1 ± 0.5	2.67	0.092	

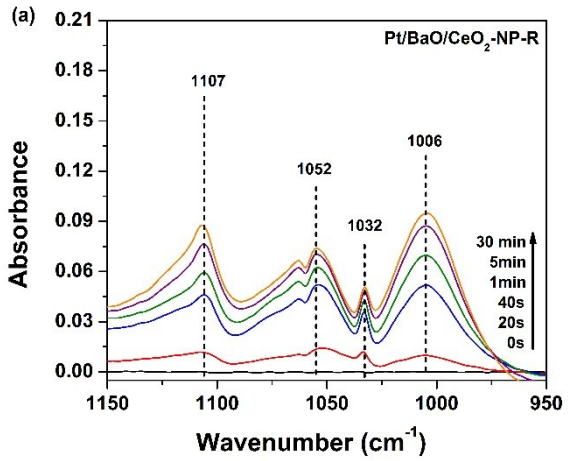
[a] CN = coordination number, R = bond length, DW = Debye-Waller factor, Pt-Pt is the coordination shell in Pt metal, Pt-O is the first coordination shell in PtO_2, Pt-O-Pt is the second coordination shell in PtO_2.

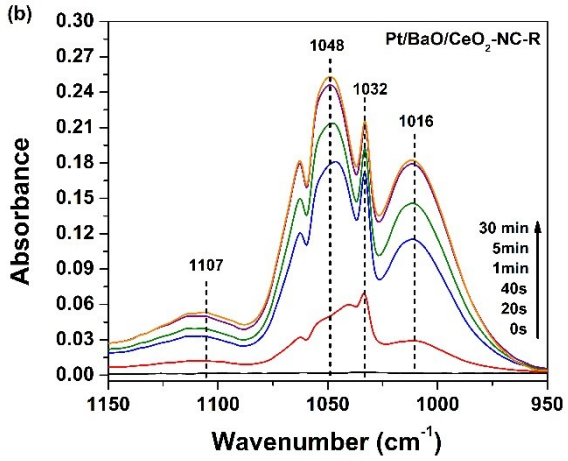
[b] Samples exposed to ambient air after H_2 reduction at 450 °C for 60 min.

Table S4. XPS binding energies of individual peaks of the Ce 3d spectra for CeO_2 nanomaterials calcined at 550 °C and corresponding NSR catalysts.

Sample	Ce^{4+}						Ce^{3+}	
	v	v''	v''	u	u''	u''' (relative peak area/%)	v'	u'
CeO_2-NP	881.9	888.4	897.8	900.4	907.1	916.2 (14.8)	884.6	903.0
Pt/BaO/CeO_2-NP	881.9	888.5	897.8	900.5	907.1	916.2 (14.4)	884.8	902.7
Pt/BaO/CeO_2-NP-R[b]	882.0	888.6	897.9	900.5	907.2	916.3 (13.5)	884.8	902.6
CeO_2-NC	881.9	888.5	897.8	900.5	907.2	916.2 (15.1)	884.5	902.3
Pt/BaO/CeO_2-NC	881.9	888.5	897.8	900.5	907.1	916.2 (15.2)	884.8	902.0
Pt/BaO/CeO_2-NC-R[b]	882.0	888.6	897.8	900.4	907.0	916.2 (14.3)	884.7	901.7
CeO_2-NR	881.8	888.3	897.7	900.4	907.2	916.1 (14.7)	884.3	903.0
Pt/BaO/CeO_2-NR	882.0	888.6	897.9	900.5	907.2	916.3 (13.9)	884.8	902.8
Pt/BaO/CeO_2-NR-R[b]	881.6	888.2	897.5	900.2	906.9	915.9 (12.7)	884.2	903.3

R[b]: the NSR catalysts reduced by 3% H_2.





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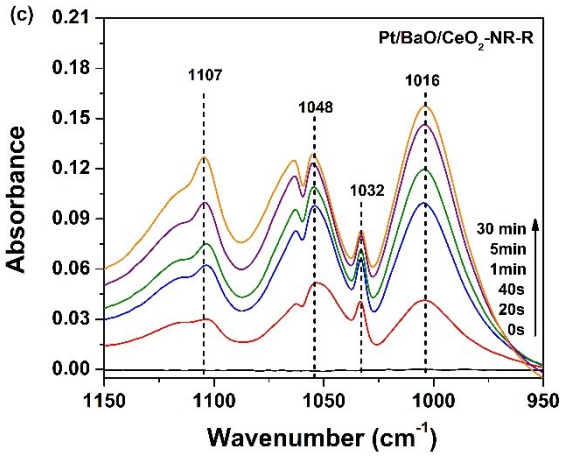

2

3 **Figure S9**. *in situ* DRIFTS spectra of adsorbed species in flowing methanol at room
4 temperature on Pt/BaO/CeO_2-NP-R (a), Pt/BaO/CeO_2-NC-R (b), and Pt/BaO/CeO_2-
5 NR-R (c).

6 Before the measurement, the samples were pretreated by 10% H_2/He (25 mL/min) at
7 450 ^oC for 1h, and then cooled to room temperature. Conditions: 16.6 % CH_3OH, He
8 balance.

9 **Table S5**. The integral area of band at 970-1085 cm^{-1} on the reduced NSR catalysts.

Samples	**Integral Area of 970-1085 cm^{-1} (g^{-1})**		
	NP	**NC**	**NR**
Pt/BaO/CeO_2-R	0.185	0.104	0.240

2.5 Reducibility of NSR catalysts

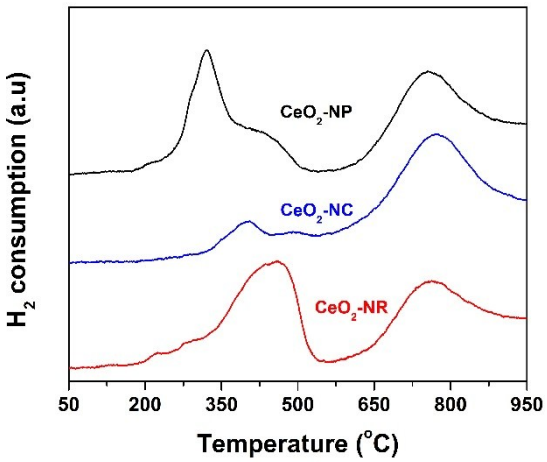

Figure S10. H_2-TPR profiles of the different shaped CeO_2.

Table S6. The ratios of different species estimated by the area of corresponding peak during H_2-TPR on Pt/BaO/CeO_2-NP, Pt/BaO/CeO_2-NC, and Pt/BaO/CeO_2-NR.

Samples	Total H_2 consumption (μmol)	Peak	Peak max (°C)	Peak area	Peak area ratio (%)	H_2 consumption (μmol)
Pt/BaO/CeO_2-NP	110.8	Platinum oxide	213.1	0.53	13.7	31.8
		Promoted surface CeO_2	226.9	0.50	13.0	
		Surface CeO_2	598.1	0.61	15.7	
		Total surface CeO_2[a]	–	1.11	28.7	
		Bulk CeO_2	747.3	2.23	57.6	
Pt/BaO/CeO_2-NC	123.6	Platinum oxide	201.0	0.34	8.2	18.3
		Promoted surface CeO_2	225.4	0.14	3.3	
		Surface CeO_2	556.5	0.47	11.5	
		Total surface CeO_2[a]	–	0.61	14.8	
		Bulk CeO_2	760.3	3.17	77.0	
Pt/BaO/CeO_2-NR	158.8	Platinum oxide	137.2	1.08	20.0	67.6
		Promoted surface CeO_2	182.3	0.78	14.5	
		Surface CeO_2	553.7	1.52	28.1	
		Total surface CeO_2[a]	–	2.30	42.6	
		Bulk CeO_2	746.9	2.03	37.4	

[a] the total amounts of H_2 consumption related to promoted surface CeO_2 and surface CeO_2 far away from Pt.

2.6 Relationship between properties of the catalysts and catalytic performance

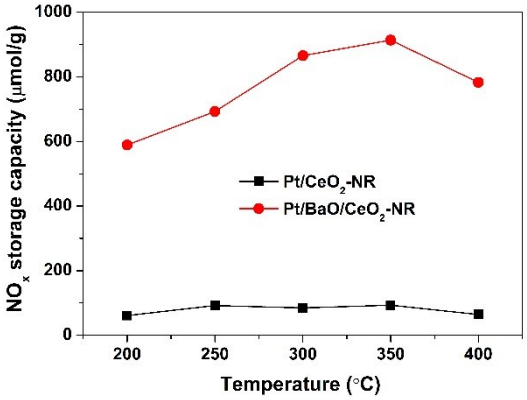

Figure S11. NO_x storage capacities (NSC) tested at different temperatures for Pt/CeO_2-NR, and Pt/BaO/CeO_2-NR.

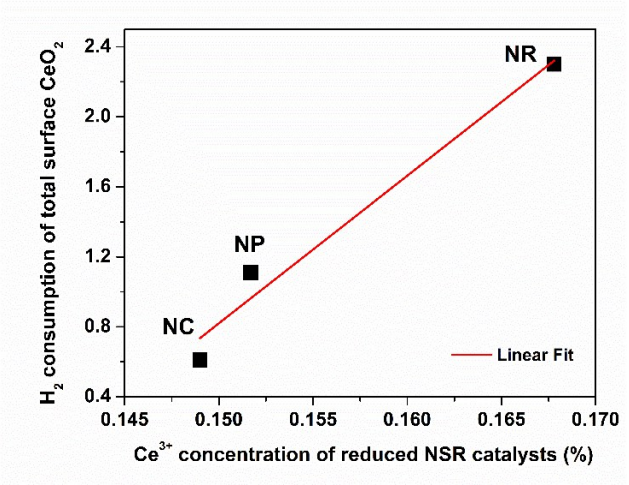

Figure S12. The relationship between the Ce^{3+} concentration on reduced NSR catalysts and the H_2 consumption of total surface CeO_2.