

ESI (Electronic Supplementary Information)

Title:

Electric field-assisted NSR process for lean NO_x reduction at low temperatures

Authors

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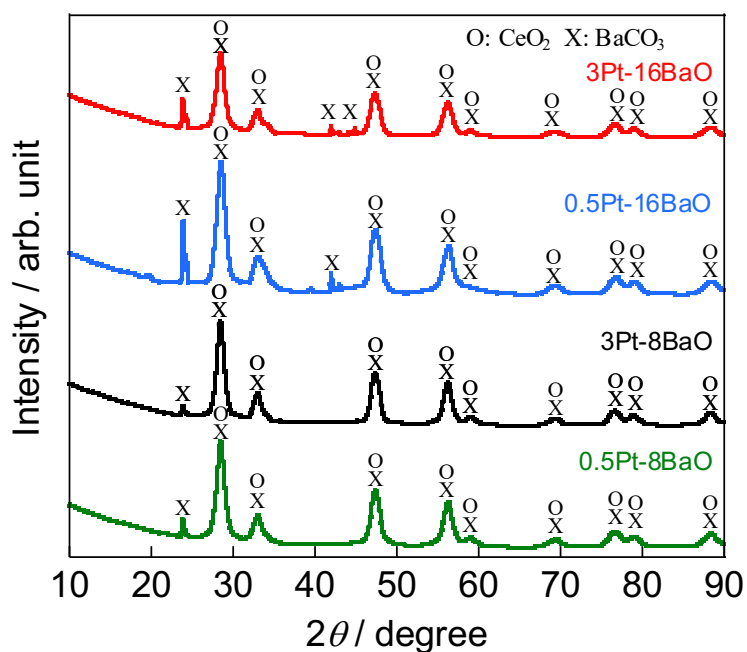
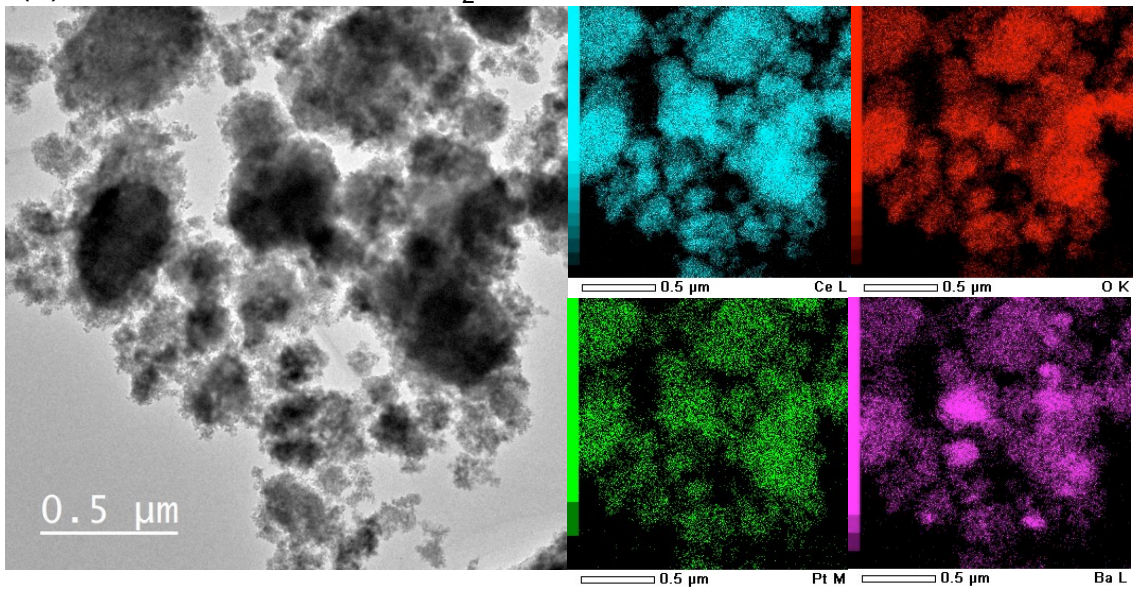
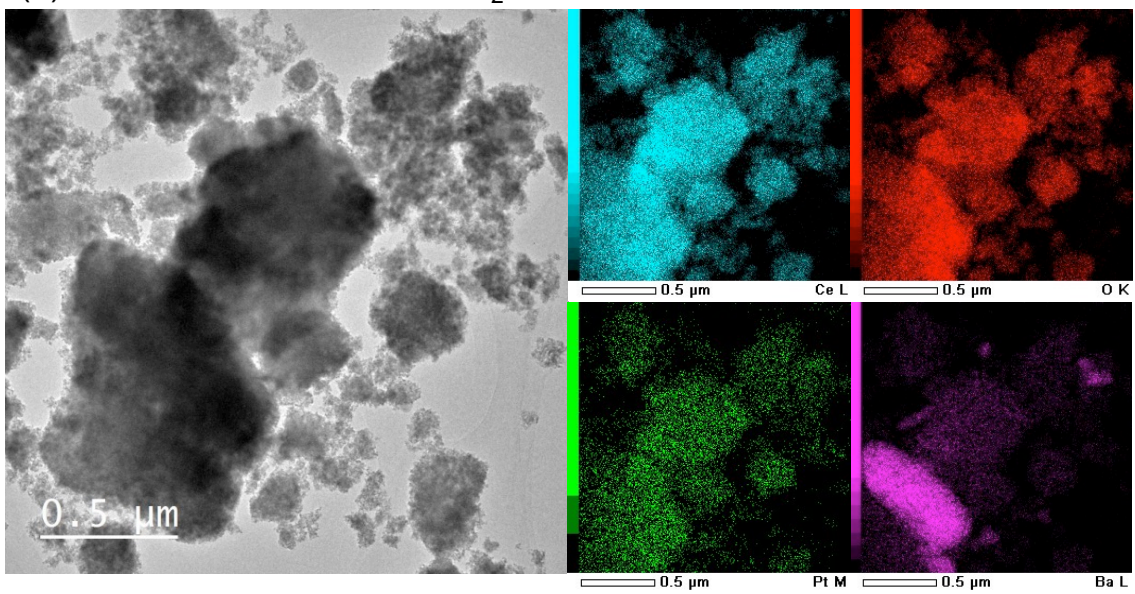


Figure S1. XRD spectra for $x\text{wt}\%\text{Pt}-y\text{wt}\%\text{BaO}/\text{CeO}_2$ ($x:y=3:16, 0.5:16, 3:8, 0.5:8$) after H_2 pre-treatment.

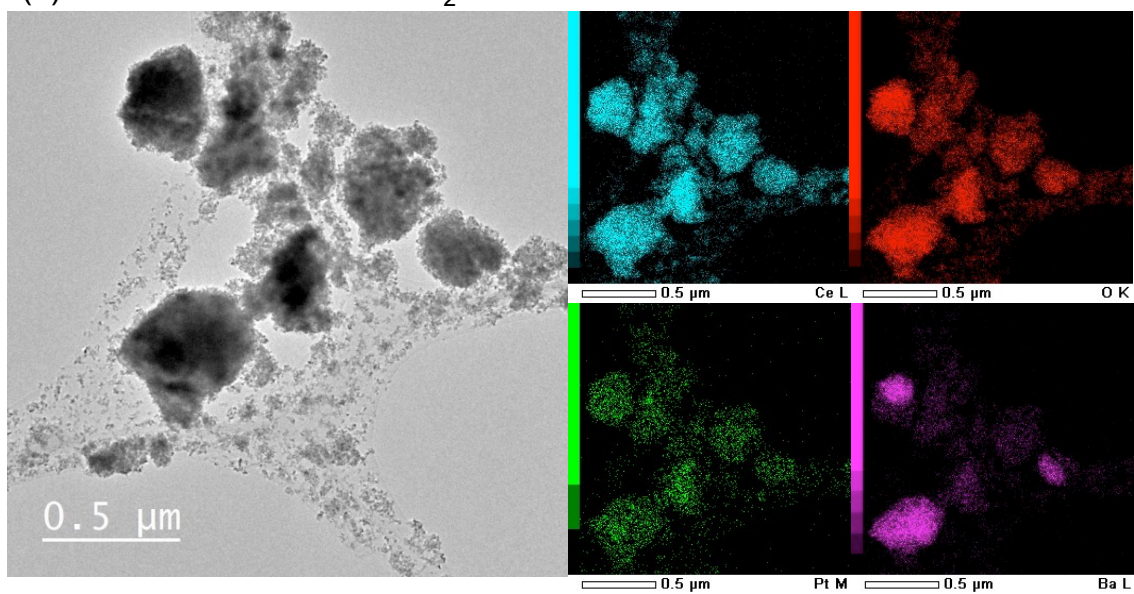
(a) 3wt%Pt–16wt%BaO/CeO₂



(b) 0.5wt%Pt–16wt%BaO/CeO₂



(c) 3wt%Pt–8wt%BaO/CeO₂



(d) 0.5wt%Pt–8wt%BaO/CeO₂

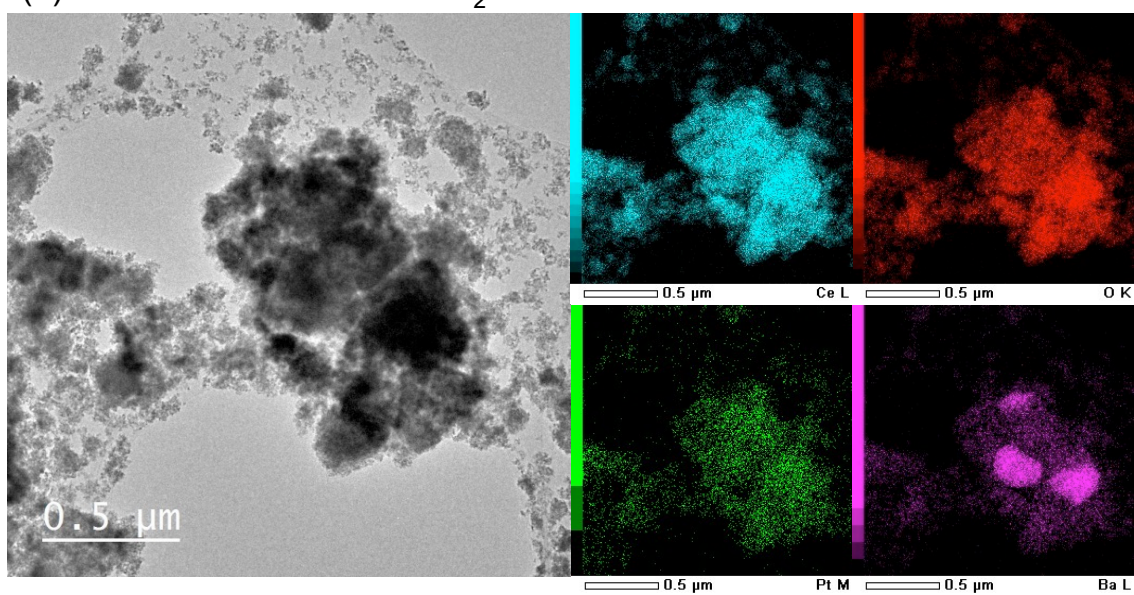


Figure S2. TEM and HAADF images and EDX mapping of (a) 3wt%Pt–16wt%BaO/CeO₂, (b) 0.5wt%Pt–16wt%BaO/CeO₂, (c) 3wt%Pt–8wt%BaO/CeO₂ and (d) 0.5wt%Pt–8wt%BaO/CeO₂.

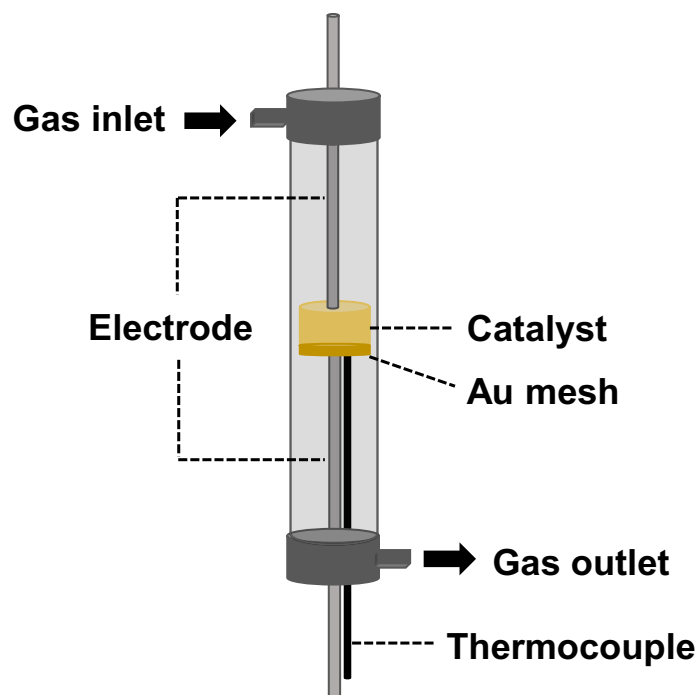
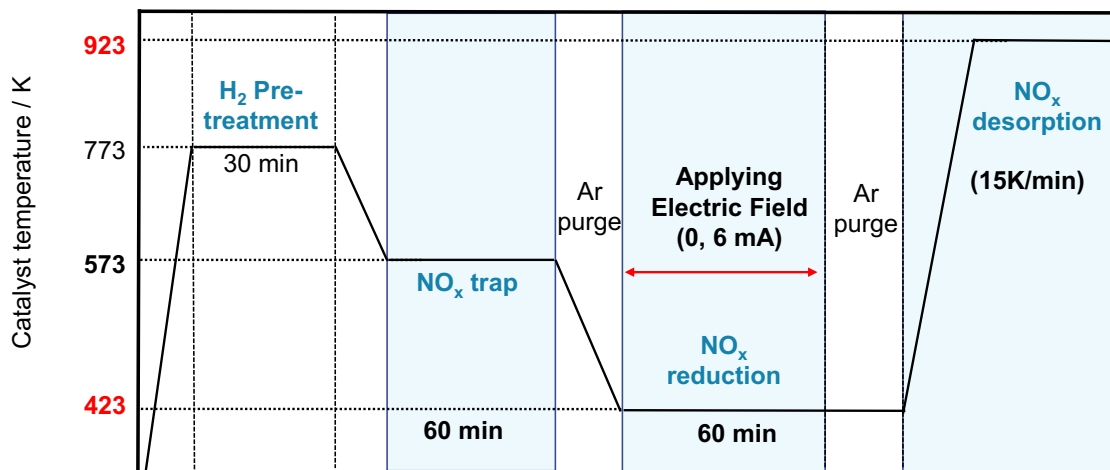


Figure S3. A schematic image of the activity test reactor.



■ **Gas composition**

- Pre-treatment : 5 vol% H₂ (100mL/min)
- NO_x trap : 700 ppm NO, 8 vol% O₂ (total 200mL/min)
- NO_x reduction : 0.2 vol% H₂, 8 vol% O₂, 10 vol% H₂O (total 200mL/min)
- NO_x desorption : Ar (total 200mL/min)

Figure S4. Protocol for activity tests.

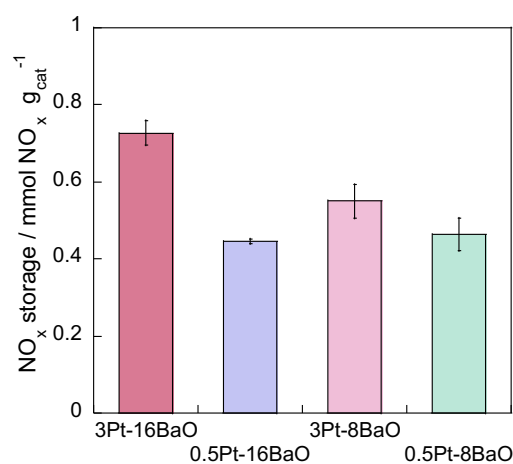


Figure S5. NO_x storage capacity for xwt%Pt–ywt%BaO/CeO₂ (x: y= 3: 16, 0.5: 16, 3: 8, 0.5: 8).

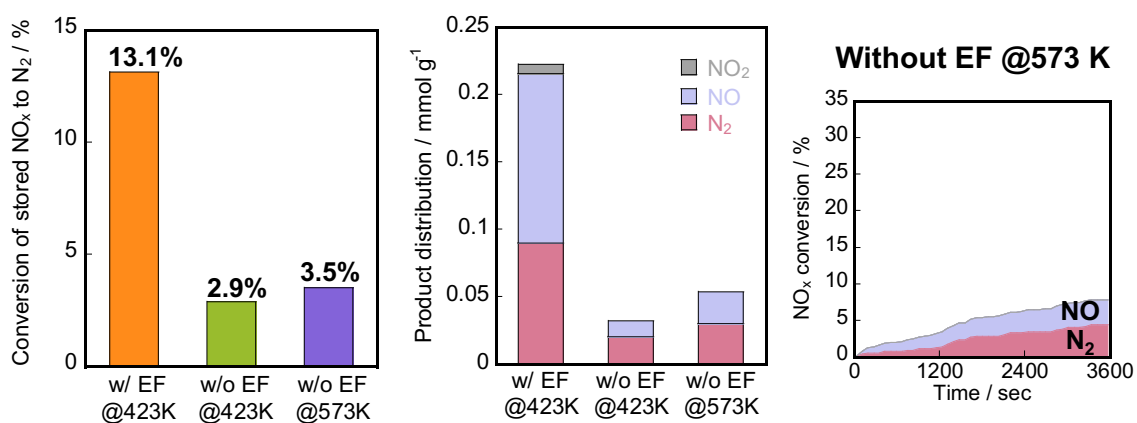


Figure S6. Lean NO_x reduction (0.2 vol% H₂, 8 vol% O₂, 10 vol% H₂O) over 3wt%Pt–16wt%BaO/CeO₂ without the electric field at 573 K.

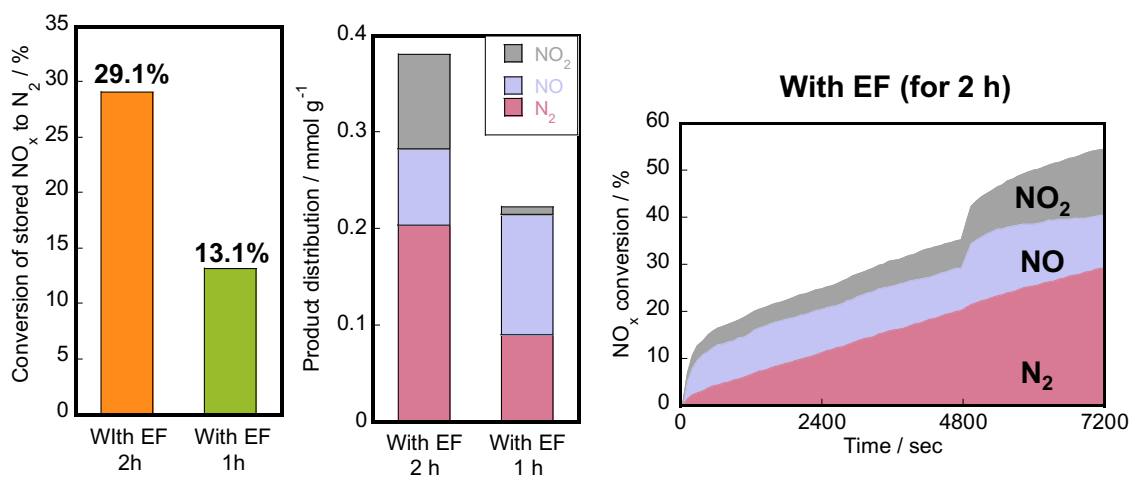


Figure S7. Lean NO_x reduction (0.2 vol% H₂, 8 vol% O₂, 10 vol% H₂O) for 2 hours over 3wt%Pt–16wt%BaO/CeO₂ with the electric field at 423 K.

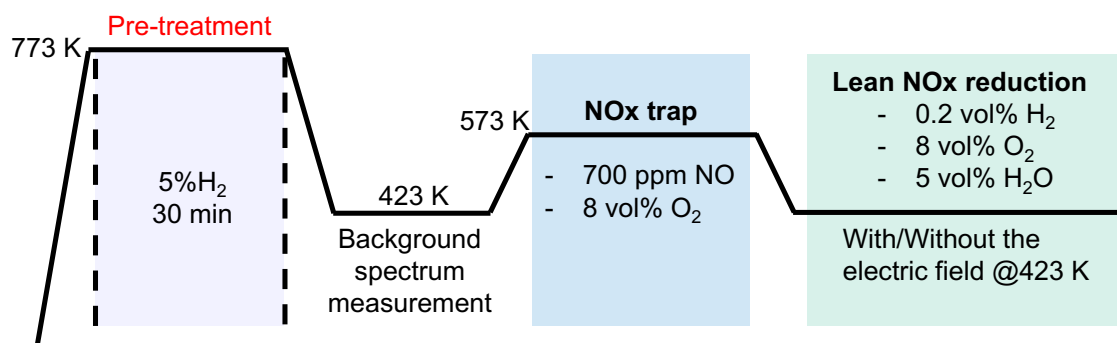


Figure S8. Protocol for *in-situ* TIRS measurement without and with the electric field (6-mA) at 423 K.

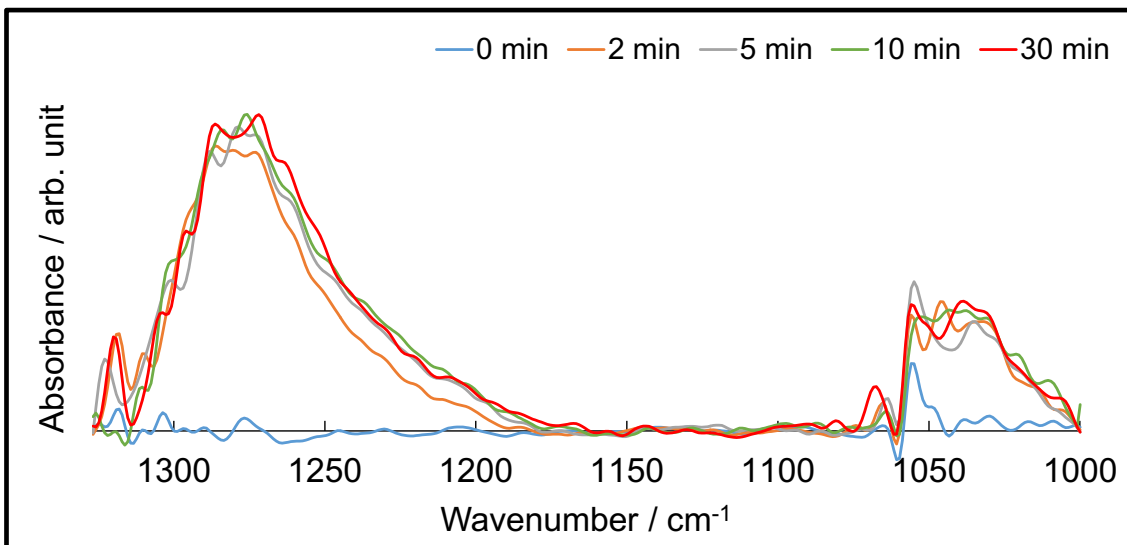


Figure S9. Transmission infrared spectroscopy spectra during NO_x storage over 3wt%Pt-16wt%BaO/CeO₂.

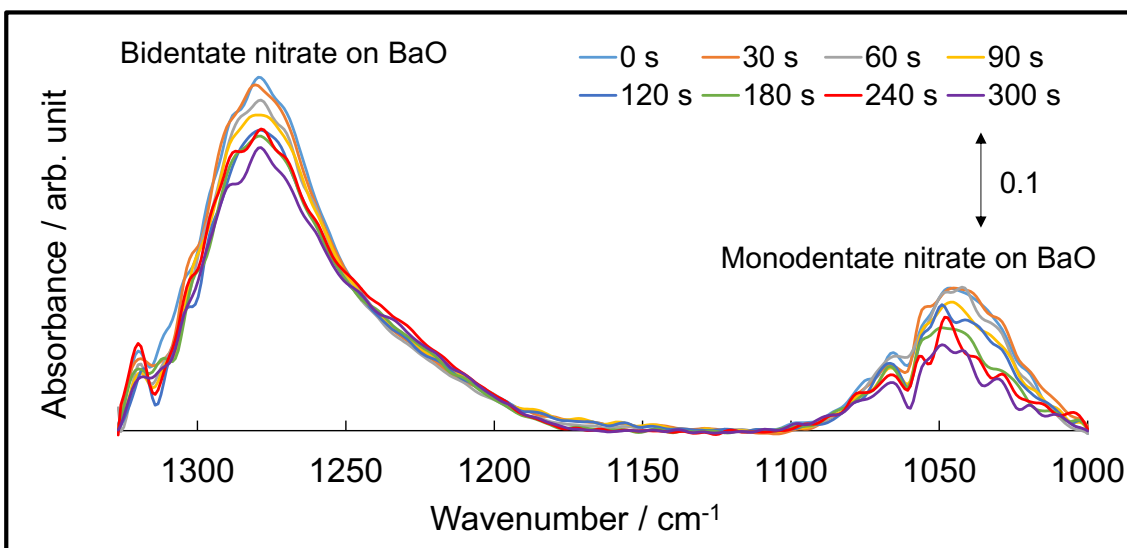


Figure S10. Transmission infrared spectroscopy spectra during lean NO_x reduction over 3wt%Pt-16wt%BaO/CeO₂ without the electric field.

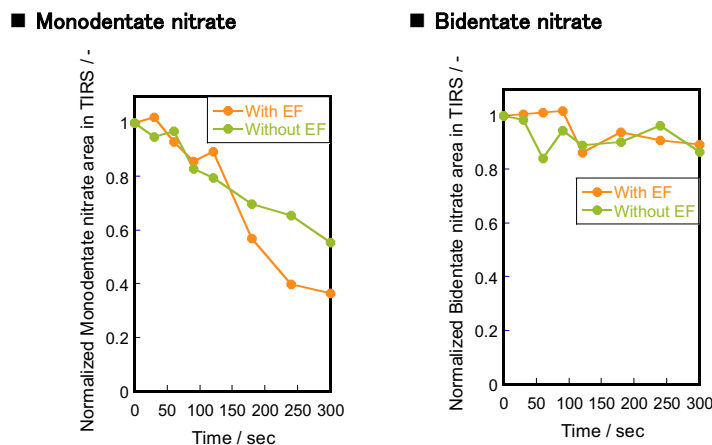


Figure S11. Normalized area of monodentate and bidentate nitrates in TIRS (Normalized based on 0 sec).

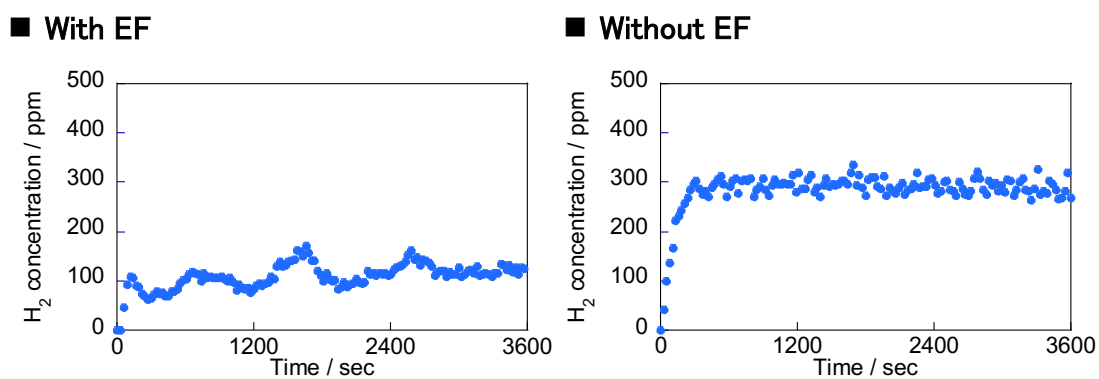


Figure S12. Outlet H₂ concentration during NO_x reduction over 3wt%Pt-16wt%BaO/CeO₂.

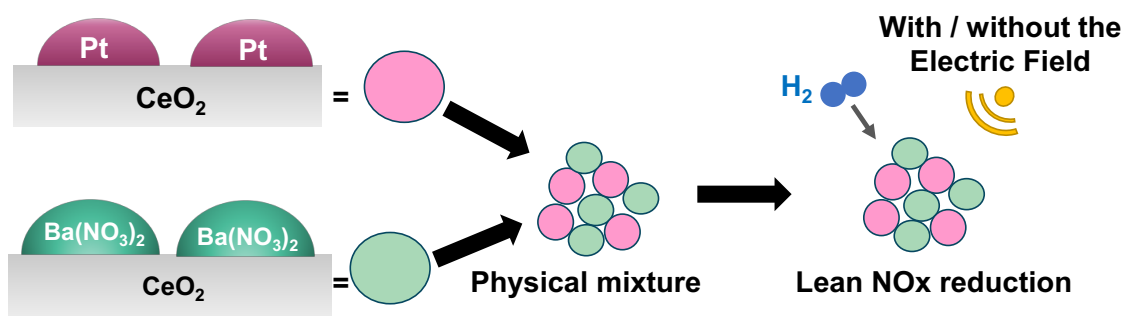


Figure S13. A schematic image of a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst.

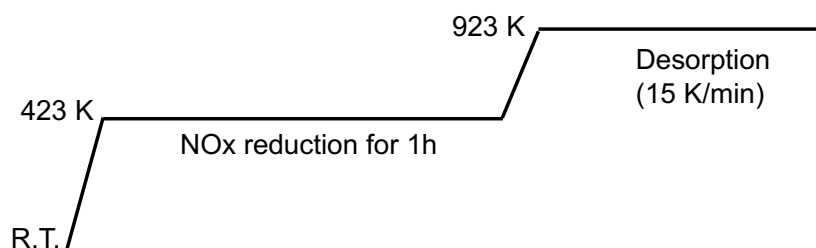


Figure S14. Protocol for activity tests with a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst.

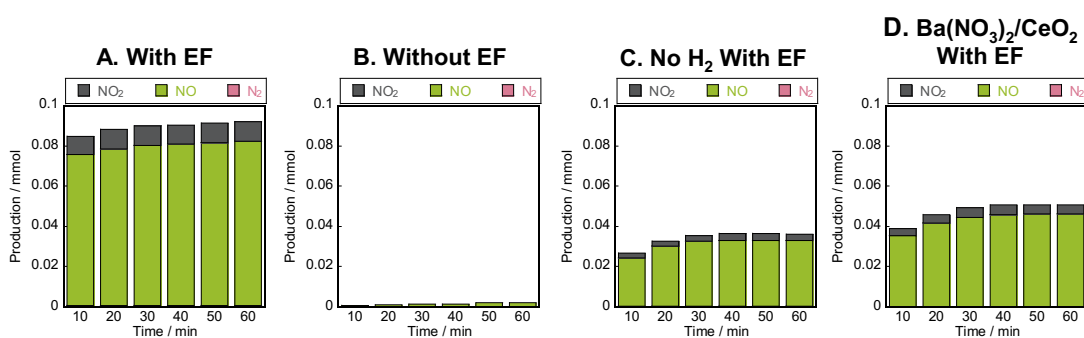


Figure S15. The distribution of nitrogen-containing species in the outlet gas (calculated on nitrogen-base) during (A) lean NO_x reduction (0.2 vol% H₂, 8 vol% O₂, 10 vol% H₂O) over a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ with the electric field at 423 K, (B) lean NO_x reduction over a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ without the electric field at 423 K, (C) lean NO_x reduction without H₂ (8 vol% O₂, 10 vol% H₂O) over a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ with the electric field at 423 K, and (D) lean NO_x reduction (0.2 vol% H₂, 8 vol% O₂, 10 vol% H₂O) over 16wt%Ba(NO₃)₂/CeO₂ with the electric field at 423 K.

In order to verify the promotion of hydrogen spillover/migration by the electric field, we performed the following four reduction tests.

1. Lean NO_x reduction over a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst with the electric field
2. Lean NO_x reduction over a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst without the electric field

3. Lean NO_x reduction without supplying H₂ over a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst with the electric field
4. Lean NO_x reduction over 16wt%Ba(NO₃)₂/CeO₂ catalyst with the electric field

First, we prepared 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂. With CeO₂ (JRC-CEO-1) selected as the catalyst support, Pt(C₅H₇O₂)₂ or Ba(NO₃)₂ was used as a precursor, where 3 wt% of Pt or 16 wt% Ba was loaded onto the support using the impregnation method. They were dried at 393 K for 20 h, and only Pt/CeO₂ was calcined in air at 823 K for 3 h. Then, we physically mixed 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂. Finally, the physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst was obtained. An image of this catalyst is shown in Figure. S13.

Tests 1&2: Lean NO_x reduction over a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst with and without the electric field.

Figure S14 shows the measurement flow. The lean NO_x reduction tests were performed with and without the 6-mA electric field; 0.2 vol % H₂, 8 vol % O₂, and 10 vol% H₂O were supplied. Subsequently, a temperature-programmed desorption was performed. The results are shown in Figure S15 (A), (B). Table S4 shows the production of NO_x during reduction tests. The amount of NO and NO₂ at the outlet gas during reduction was higher when the electric field was applied than when it was not applied. The reason why the NO comes out in the electric field mainly as NO rather than N₂ is because Pt is further away from the Ba(NO₃)₂, and this result is consistent with earlier studies ¹⁾. These results clearly show that the nitrate decomposition occurs not only in close proximity to the Pt, but also further away from the Pt in the electric field.

Test 3: Lean NO_x reduction without supplying H₂ over a physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst with the electric field.

The purpose of this test is to verify the hydrogen functions as a reductant. Using the physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst, only the electric field was applied without supplying H₂ in the reduction step; 8 vol % O₂, and 10 vol% H₂O were supplied. The results are shown

in Figure S15 (C) and Table S4. Even in the absence of H₂, nitrate decomposition occurred in the electric field. However, this phenomenon is thought to be due to the instantaneous energy input from the application of the electric field. In addition, the amount of NO was less than half that when H₂ was supplied (Fig. S15 (A)). Therefore, hydrogen spillover/migration is promoted by applying the electric field, and hydrogen reaches Ba(NO₃)₂ which is further away from Pt.

Test 4: Lean NO_x reduction over 16wt%Ba(NO₃)₂/CeO₂ catalyst with the electric field.

In order to discuss the role of Pt for hydrogen spillover/migration, lean NO_x reduction test was performed in the electric field using only 16wt%Ba(NO₃)₂/CeO₂ catalyst without Pt. The results are shown in Figure S15 (D) and Table S4. The amount of reduced NO_x was decreased compared to the physical mixture of 3wt%Pt/CeO₂ and 16wt%Ba(NO₃)₂/CeO₂ catalyst,. This result indicates that Pt is essential for hydrogen spillover/migration in the electric field.

The total NO_x desorption (= the total NO_x desorption during lean reduction + the total NO_x desorption during temperature-programmed desorption) were in agreement in all tests, shown in Table S4. In other words, the amount of NO_x accumulated on the catalyst was the same in all tests.

Table S1. BET surface area and Pt particle size of xwt%Pt–ywt%BaO/CeO₂ (x: y= 3: 16, 0.5: 16, 3: 8, 0,5: 8).

	S _{BET} [m ² /g]	Pt particle size* ¹ [nm]
3wt%Pt-16wt%BaO/CeO ₂	100.7	5.06
0.5wt%Pt-16wt%BaO/CeO ₂	99.7	4.07
3wt%Pt-8wt%BaO/CeO ₂	110.7	3.00
0.5wt%Pt-8wt%BaO/CeO ₂	104.5	3.38

*1: estimated by CO pulse chemisorption

Table S2. NO_x storage capacity for xwt%Pt–ywt%BaO/CeO₂ (x: y= 3: 16, 0.5: 16, 3: 8, 0.5: 8).

	NO _x storage [mmol NO _x /g _{cat}]	Storage efficiency ^{*2} [%]
3wt%Pt-16wt%BaO/CeO ₂	0.727	52.1
0.5wt%Pt-16wt%BaO/CeO ₂	0.446	32.0
3wt%Pt-8wt%BaO/CeO ₂	0.550	39.4
0.5wt%Pt-8wt%BaO/CeO ₂	0.464	33.2

*2: (NO_x storage/NO supplied to catalyst in 60min) × 100

Table S3. Relationship between the NO_x stored and the released nitrogen-containing species.

	Nitrogen balance / % ³⁾
With EF	100.97
Without EF	101.84

*3: Balance = $\frac{\text{the released nitrogen-containing species}}{\text{the accumulated NO}_x} \times 100$

In order to quantify the amount of accumulated NO_x remaining on the catalyst after the NO_x reduction measurement, a temperature-programmed desorption was performed, heating every catalyst up to 973 K in inert atmosphere. The nitrogen-balance calculated based on the accumulated NO_x (during NO_x storage) and the released nitrogen-containing species (the reduction and desorption step) is almost 100% shown in Table S3, suggesting that no byproducts such as N₂O and NH₃ other than N₂, NO and NO₂ are formed.

Table S4. Production of NO_x during reduction tests and NO_x storage in Figure S15.

	NO [mmol/g]	NO ₂ [mmol/g]	N ₂ [mmol/g]	NO _x storage [mmol/g]
A. With EF	0.082	0.010	0.000	0.8954
B. Without EF	0.002	0.000	0.000	0.9068
C. No H ₂ With EF	0.033	0.003	0.000	0.8956
D. Ba(NO ₃) ₂ /CeO ₂ With EF	0.046	0.005	0.000	0.8802

The unit [mmol/g] means the amount of NO_x attached per amount of Ba(NO₃)₂ in the preparation.

[Reference]

1. J. Coronado and J. Anderson, *J. Mol. Catal. A: Chem.*, 1999, **138**, 83-96.