

## ESI (Electronic Supplementary Information)

Title:

### Elucidation of catalytic NO<sub>x</sub> reduction mechanism in an electric field at low temperatures

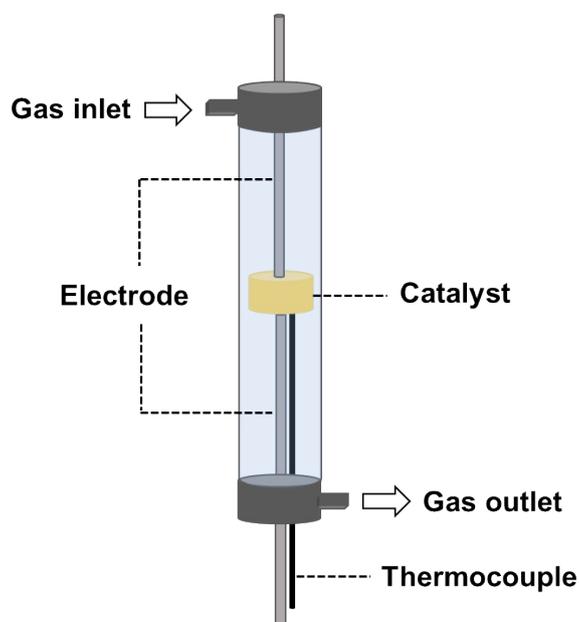
Authors

Ayaka Shigemoto <sup>a</sup>, Takuma Higo <sup>a</sup>, Yuki Narita <sup>a</sup>, Seiji Yamazoe <sup>b</sup>, Toru Uenishi <sup>c</sup> and Yasushi Sekine <sup>\*a</sup>

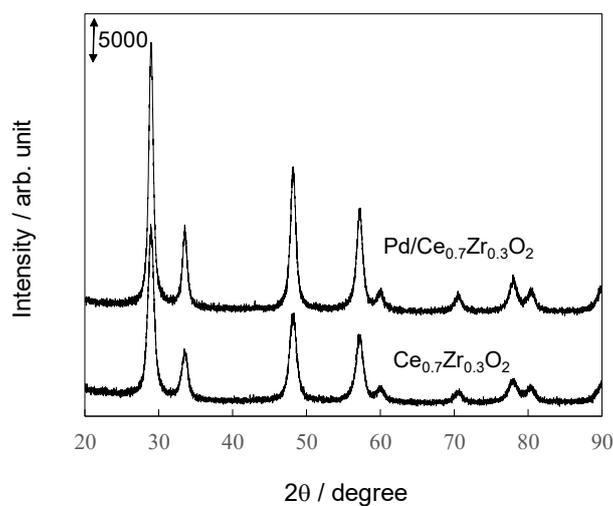
<sup>a</sup> Department of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, 169-8555, Japan, E-mail ysekine@waseda.jp

<sup>b</sup> Department of Chemistry, Tokyo Metropolitan University, 1-1, Minamiosawa, Hachioji, Tokyo, 192-0397, Japan

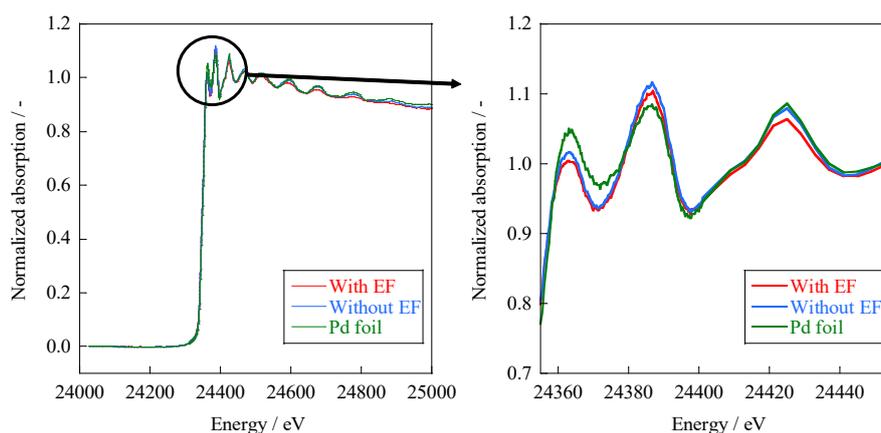
<sup>c</sup> Toyota Motors, 1200, Mishuku, Susono, Shizuoka 410-1193, Japan



**Figure S1.** A schematic image of the activity test reactor.



**Figure S2.** XRD spectra for the prepared catalysts.

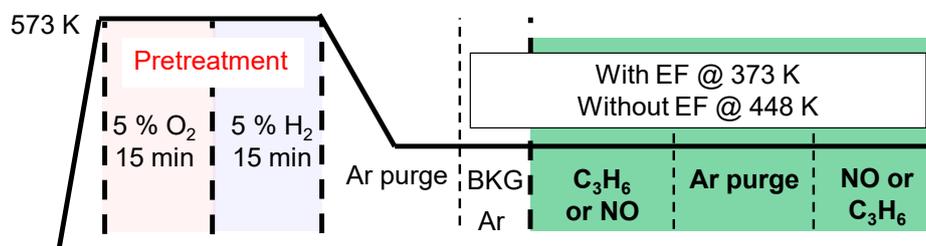


**Figure S3.** *In situ* Pd K-edge XANES spectra of  $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$  under  $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$  reaction (NO: 2500 ppm, CO: 3000 ppm,  $\text{C}_3\text{H}_6$ : 500 ppm,  $\text{O}_2$  2500 ppm, Ar balance, total flow:  $200 \text{ cc min}^{-1}$ ) with/without the electric field (3 mA) at 373 K.

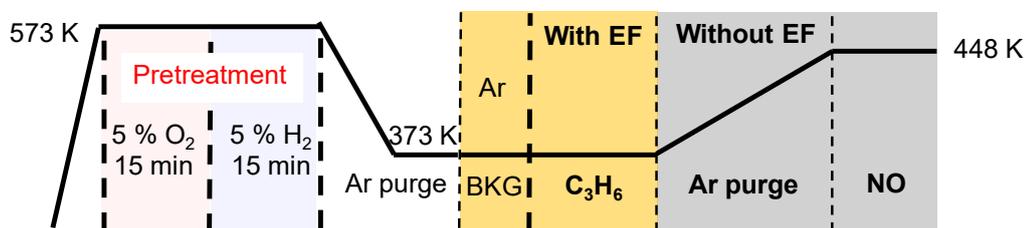
We conducted *in-situ* XAFS measurement in a reaction gas atmosphere ( $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ ) at 373 K after  $\text{H}_2$  reduction to evaluate the electronic state of Pd supported by  $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ . Fig. S3 depicts spectra for the Pd K-edge of  $\text{Pd/Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$  with and without the electric field. As Fig. S3 shows, Pd loaded on  $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$  was in the metallic state with or without the application of the electric field.

No change in the electronic state of Pd attributable to application of the electric field was observed.

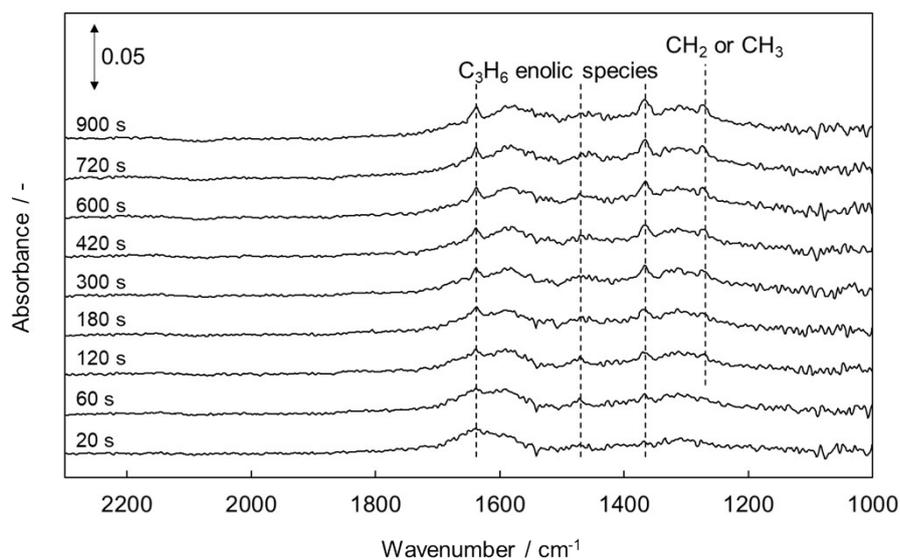
**A) With/without the electric field**



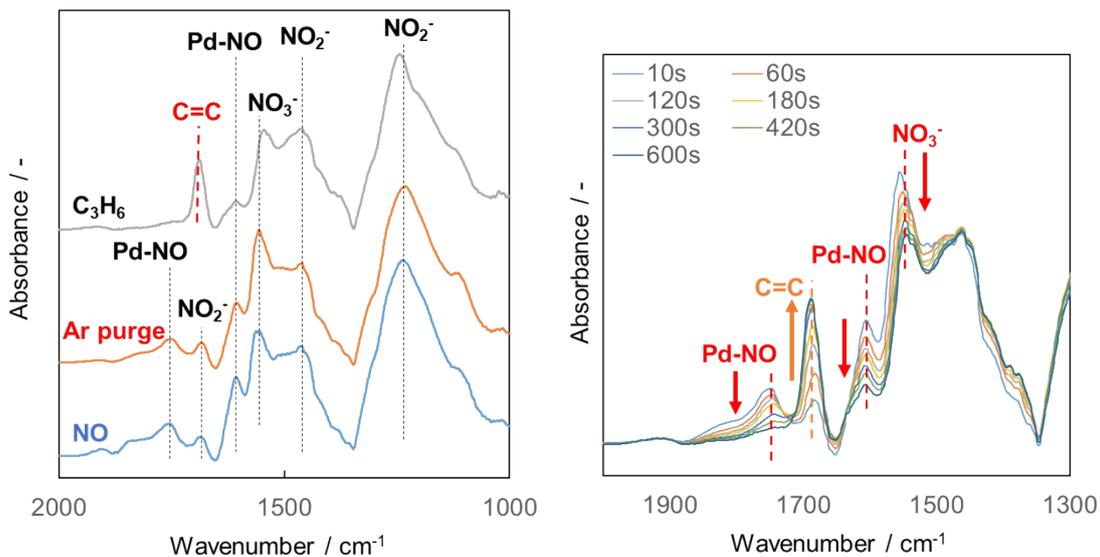
**B) With the electric field → Without the electric field**



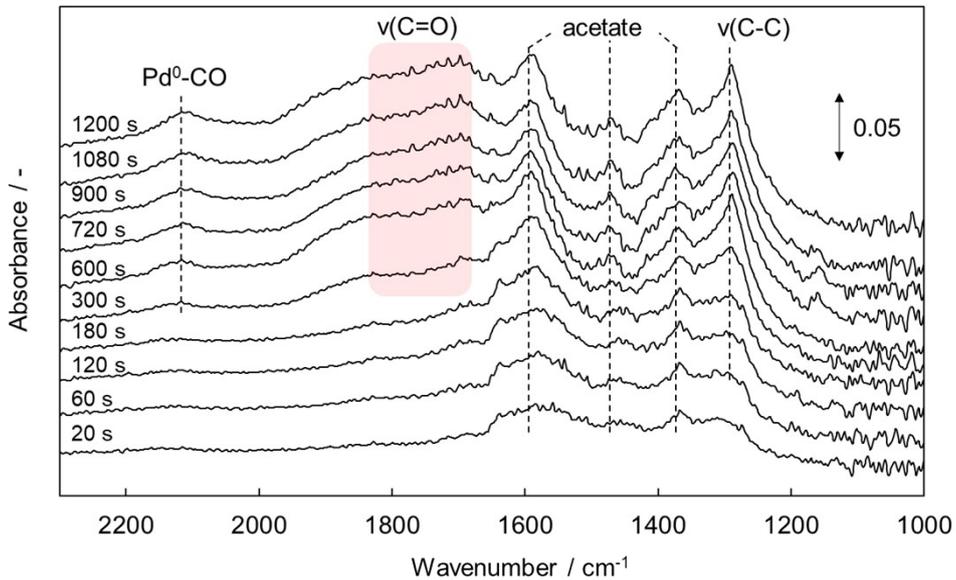
**Figure S4.** Protocol for *in-situ* DRIFTS measurement (A) with/without the electric field (3 mA) at each temperature (with: 373 K, without: 448 K) (B) with the electric field (3 mA) when dosing C<sub>3</sub>H<sub>6</sub> at 373 K → without the electric field when dosing NO at 448 K



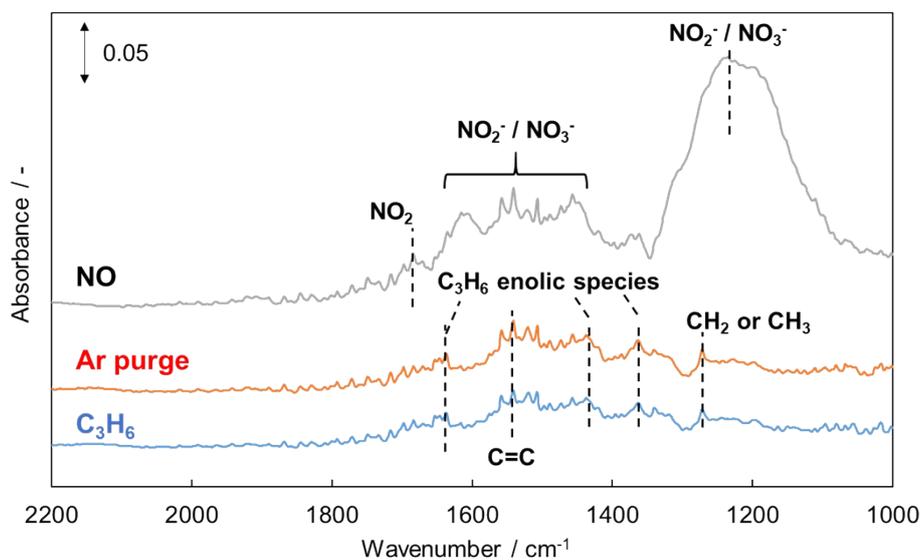
**Figure S5.** 2D graph for the DRIFT spectra of Pd/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> during the transient test (switching from C<sub>3</sub>H<sub>6</sub> to NO flow) without the electric field at 448 K.



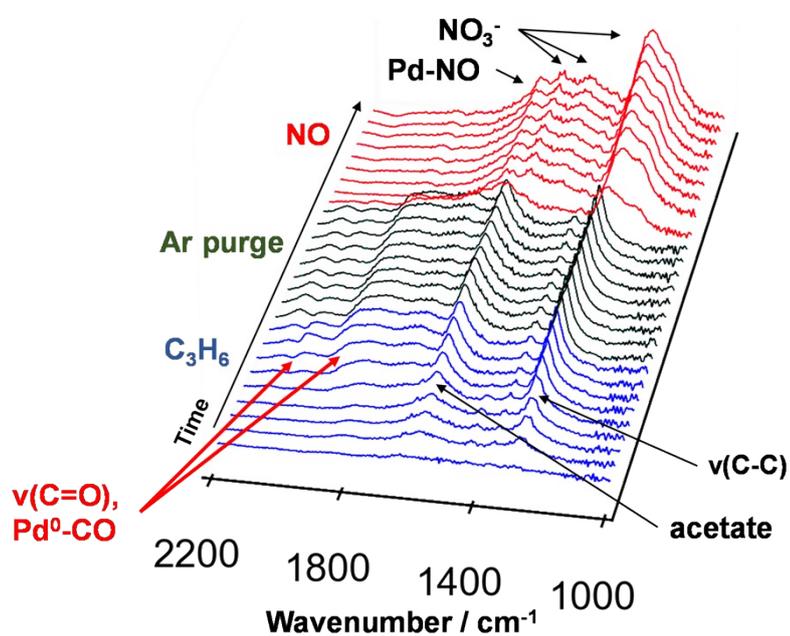
**Figure S6.** DRIFT spectra of Pd/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> during transient test (switching from NO to C<sub>3</sub>H<sub>6</sub> flow) without the electric field at 448 K.



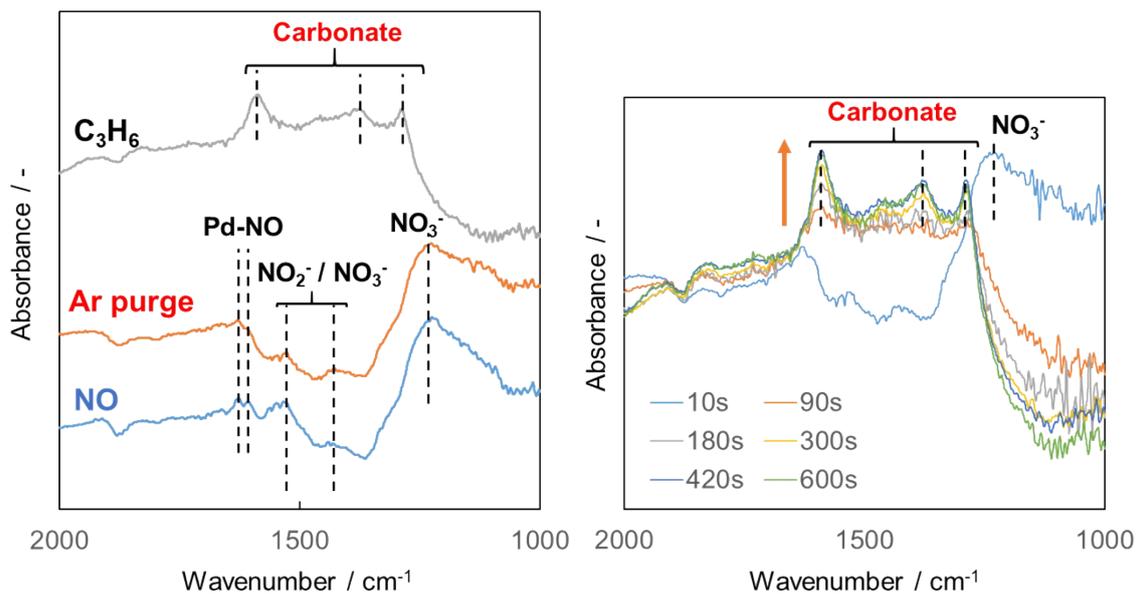
**Figure S7.** 2D graph for the DRIFT spectra of Pd/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> during the transient test (switching from C<sub>3</sub>H<sub>6</sub> to NO flow) with the electric field (3 mA) at 373 K.



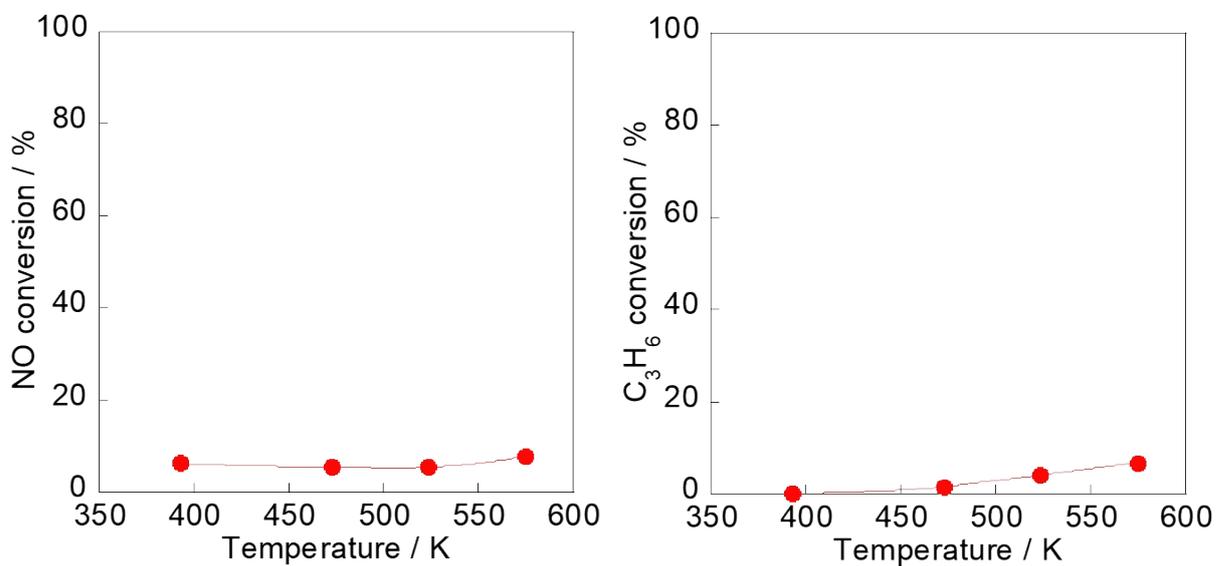
**Figure S8.** DRIFT spectra of Pd/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> during the transient test (switching from C<sub>3</sub>H<sub>6</sub> to NO flow) without the electric field at 373 K.



**Figure S9.** DRIFT spectra of Pd/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> during transient test (switching from C<sub>3</sub>H<sub>6</sub> to NO flow) with the electric field (3 mA) when dosing C<sub>3</sub>H<sub>6</sub> at 373 K → without the electric field when dosing NO at 448 K.



**Figure S10.** DRIFT spectra of Pd/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> during transient test (switching from NO to C<sub>3</sub>H<sub>6</sub> flow) with the electric field at 373 K.



**Figure S11.** NO and C<sub>3</sub>H<sub>6</sub> conversion over Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> under NO–C<sub>3</sub>H<sub>6</sub> reaction (NO: 2700 ppm, C<sub>3</sub>H<sub>6</sub>: 300 ppm, Ar balance, SV: 108 800 h<sup>-1</sup>) applying 3.0 mA direct current.

**Table S1** BET specific surface area

	Surface area /m <sup>2</sup> g <sup>-1</sup>
Pd/Ce <sub>0.7</sub> Zr <sub>0.3</sub> O <sub>2</sub>	14
Ce <sub>0.7</sub> Zr <sub>0.3</sub> O <sub>2</sub>	16