

ESI (Electronic Supplementary Information)

Title:

Catalytic N₂O decomposition in an electric field at low temperatures

Authors

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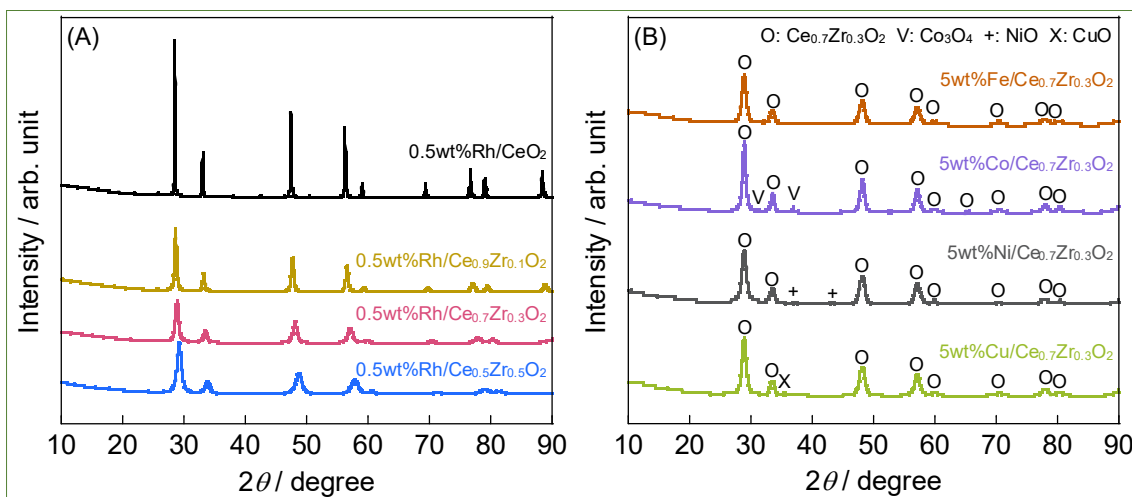


Figure S1. XRD patterns of (A) 0.5wt%Rh/Ce_{1-x}Zr_xO₂ (x = 0, 0.1, 0.3 and 0.5) and (B) 5wt%Fe, Co, Ni, Cu/Ce_{0.7}Zr_{0.3}O₂.

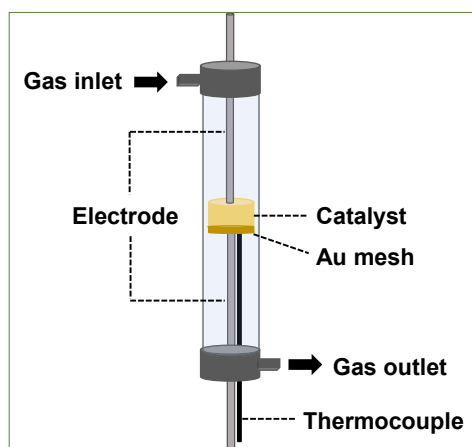


Figure S2. A schematic image of the activity test reactor.

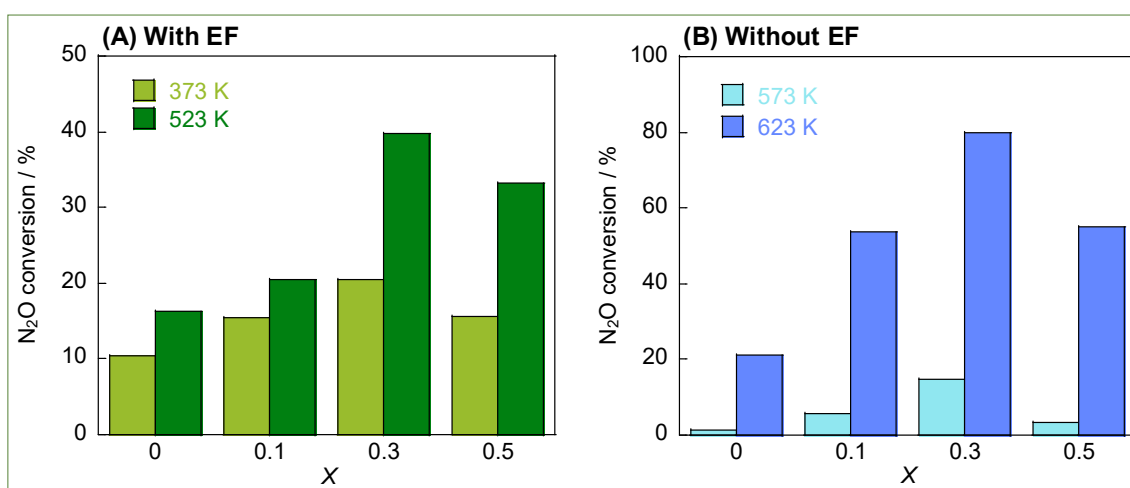


Figure S3. Catalytic decomposition of N₂O over 0.5wt%Rh/Ce_{1-x}Zr_xO₂ (x = 0, 0.1, 0.3 and 0.5) catalysts (A) with and (B) without the electric field. Conditions: 1000 ppm N₂O + 10%O₂, weight of catalyst: 100 mg, total flow rate: 100 mL min⁻¹, SV: 100,000 h⁻¹, current: 0 or 6 mA.

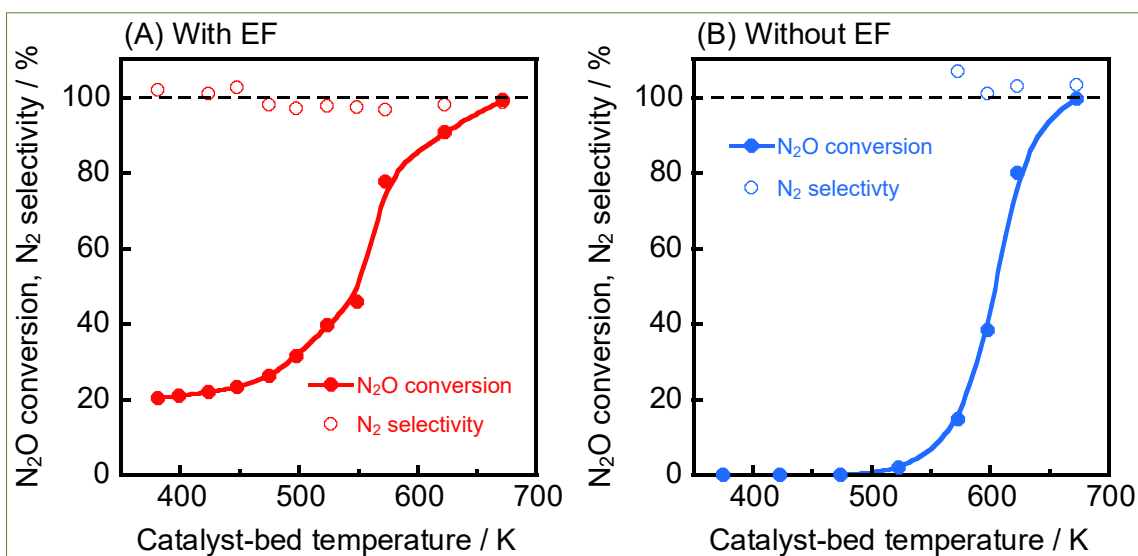


Figure S4. N₂O conversion and N₂ selectivity over 0.5wt%Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst (A) with and (B) without the electric field under 1000 ppm N₂O + 10%O₂. Weight of catalyst: 100 mg, total flow rate: 100 mL min⁻¹, SV: 100,000 h⁻¹, current: 0 or 6 mA.

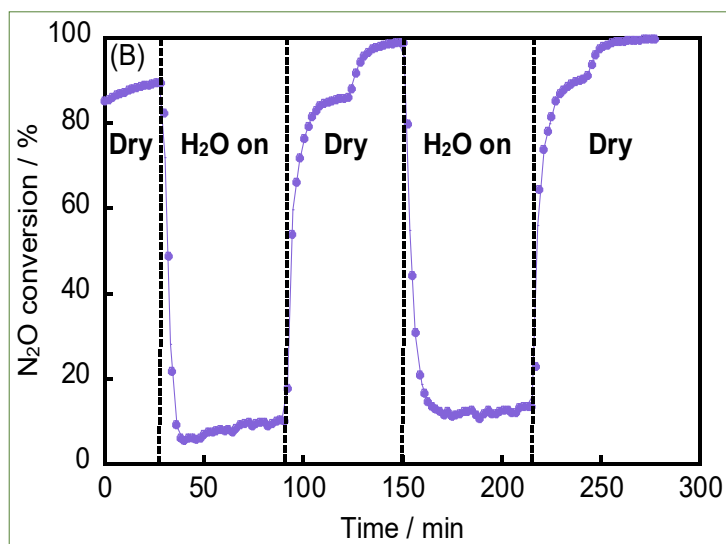


Figure S5. Effect of H₂O on N₂O conversion over 0.5wt%Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst without the electric field. Conditions: 1000 ppm N₂O + 10%O₂ + 0 or 10%H₂O, weight of catalyst: 200 mg, total flow rate: 100 mL min⁻¹, SV: 50,000 h⁻¹, catalyst bed temperature: 623 K.

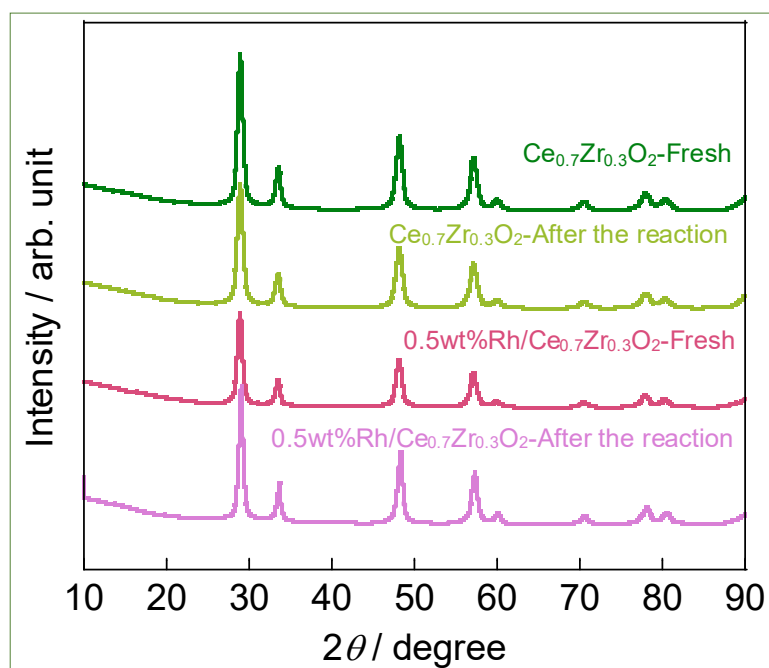


Figure S6. XRD patterns of $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ and 0.5wt%Rh/ $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalysts before and after the reaction with the electric field.

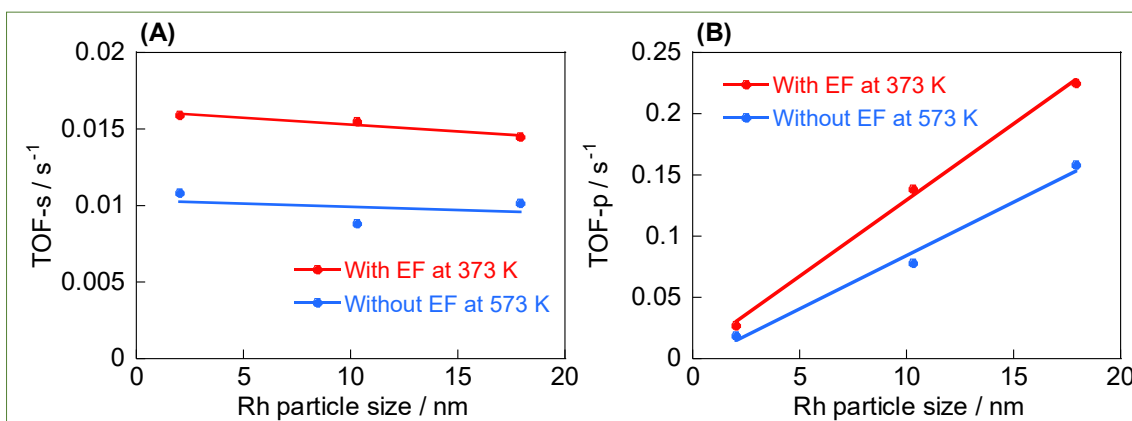


Figure S7. Number of moles of decomposed N_2O per number of (A) Rh atoms present on the surface (TOF-s) and (B) per number of Rh atoms at the Rh- $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ interface (TOF-p). Conditions: 1000 ppm N_2O + 10% O_2 , weight of catalyst: 100 mg, total flow rate: 100 mL min⁻¹, SV: 100,000 h⁻¹, current: 0 or 6 mA.

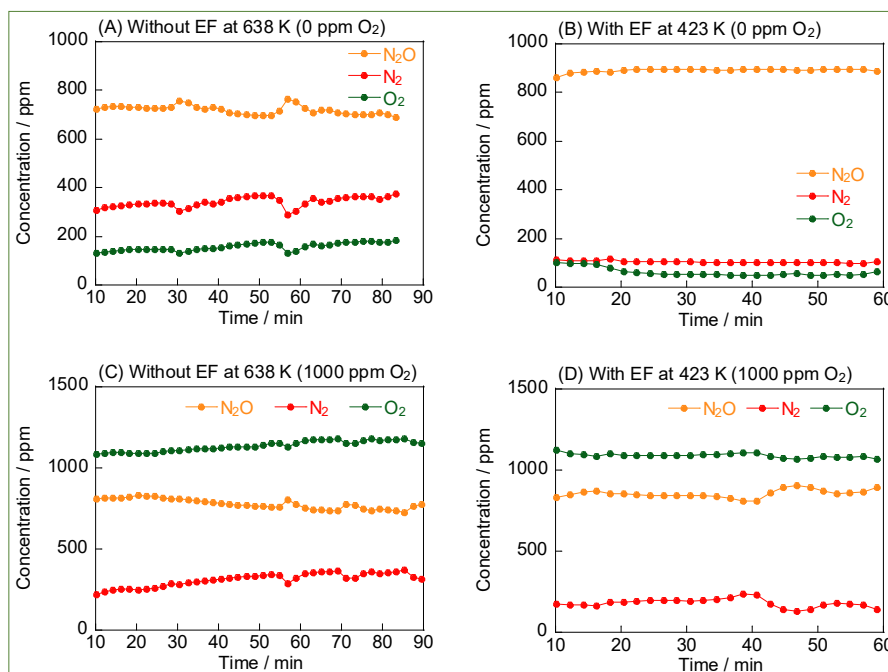


Figure S8. Outlet concentration of N_2O , N_2 and O_2 with time on stream under a flow of (A), (B) 1000 ppm N_2O + 10% H_2O , and (C), (D) 1000 ppm N_2O + 1000 ppm O_2 + 10% H_2O with an interval of Ar purge over 0.5wt%Rh/ $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst without the electric field at 638 K and with the electric field at 423 K. Weight of catalyst: 100 mg, total flow rate: 100 mL min^{-1} ; current, 0 or 6 mA.

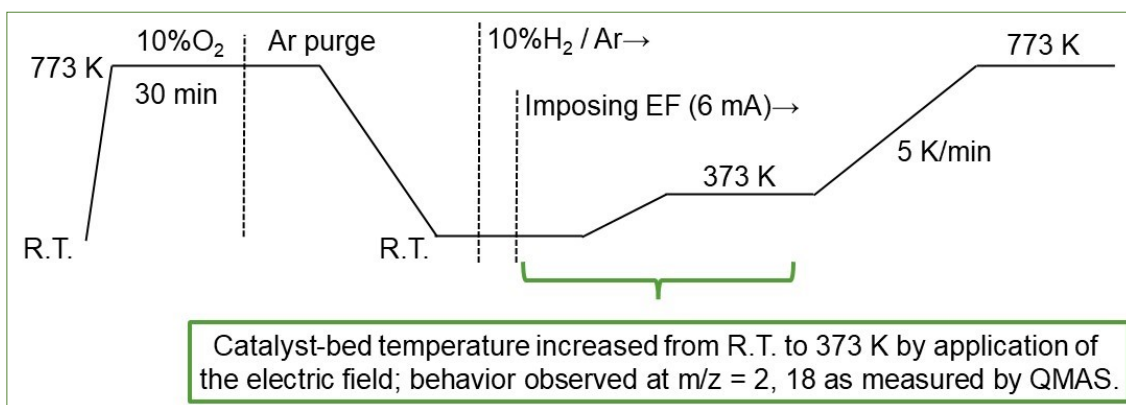


Figure S9. Experimental protocol for the evaluation of reduction performance of the 0.5wt%Rh/ $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0, 0.1$ and 0.3) catalysts with the electric field.

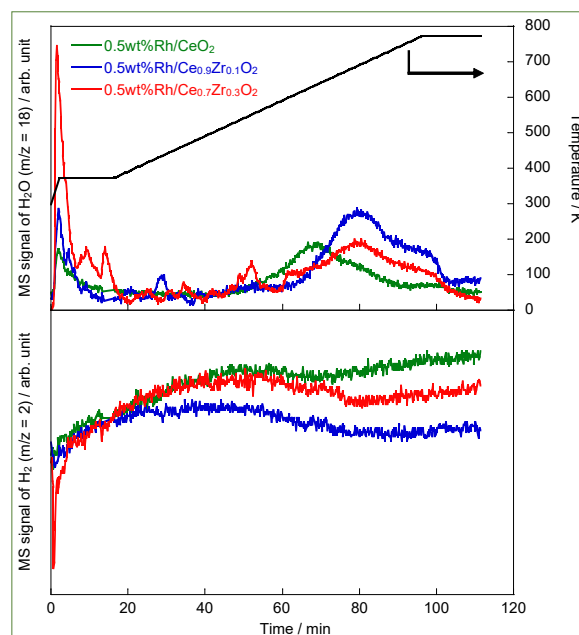


Figure S10. Reduction profile of the 0.5wt%Rh/Ce_{1-x}Zr_xO₂ ($x = 0, 0.1$ and 0.3) catalysts with the electric field.

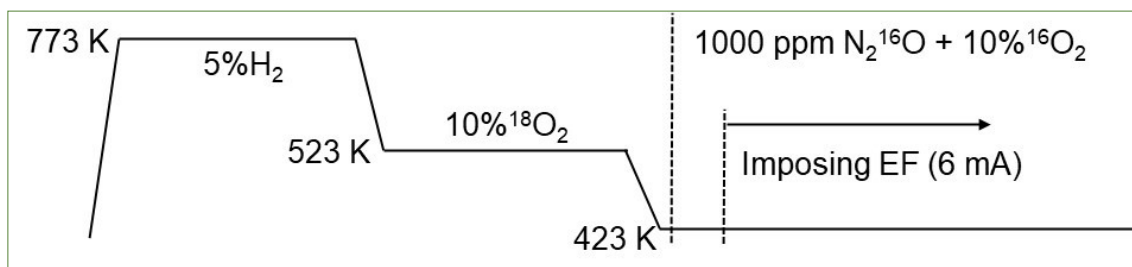
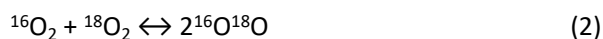
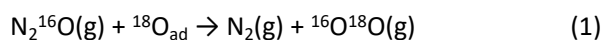


Figure S11. Experimental protocol for transient response tests switching from $^{18}\text{O}_2$ to $\text{N}_2^{16}\text{O} + ^{16}\text{O}_2$.

Figure 6 in the main text presents the isotopic responses of $m/z = 28, 34, 36$ and 44 , obtained after switching from $^{18}\text{O}_2$ to $\text{N}_2^{16}\text{O} + ^{16}\text{O}_2$ over the catalyst. When the electric field was applied to the catalyst bed, the intensity of $m/z = 44$ decreased, while the intensity of $m/z = 28$ increased, indicating N_2O decomposition and N_2 formation. Additionally, $^{16}\text{O}^{18}\text{O}$ ($m/z = 34$) and $^{18}\text{O}_2$ ($m/z = 36$) were observed immediately after the application of the electric field. Observation of ^{18}O fragment suggests that surface-lattice oxygen is migrated and removed by the application of the electric field. Here,

$^{16}\text{O}^{18}\text{O}$ is formed from Equations (1) and (2), while $^{18}\text{O}_2$ is formed from Equation (3).



To distinguish whether $^{16}\text{O}^{18}\text{O}$ was formed by the reaction in Equation (1) or Equation (2), an additional experiment was conducted. Following H_2 reduction, ^{16}O on the catalyst surface was replaced by $^{18}\text{O}_2$ at 523 K. Subsequently, only 10% $^{16}\text{O}_2$ was dosed onto the 0.5wt%Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst while the electric field was applied. Figure S12(A) displays the isotopic responses of $m/z = 34$ and 36, obtained after switching from $^{18}\text{O}_2$ to $^{16}\text{O}_2$ over the catalyst. The response of $^{16}\text{O}^{18}\text{O}$ ($m/z = 34$) and $^{18}\text{O}_2$ ($m/z = 36$) immediately after the electric field application aligns with the results from Figure 6. Figure S12(B) presents the superposition of the $m/z = 34$ profiles of Figure 6 (the result of transient response test switching from $^{18}\text{O}_2$ to $\text{N}_2^{16}\text{O} + ^{16}\text{O}_2$) and Figure S12(A) (the result of transient response tests switching from $^{18}\text{O}_2$ to $^{16}\text{O}_2$). It is noteworthy that equivalent intensities of $m/z = 34$ were observed, indicating that the $m/z = 34$ signal in Figure 6 predominantly arises from the oxygen exchange reaction described in Equation (2), rather than Equation (1). These experiments did not demonstrate N_2O decomposition *via* the ER mechanism but did validate the occurrence of oxygen exchange reactions facilitated by the application of the electric field.

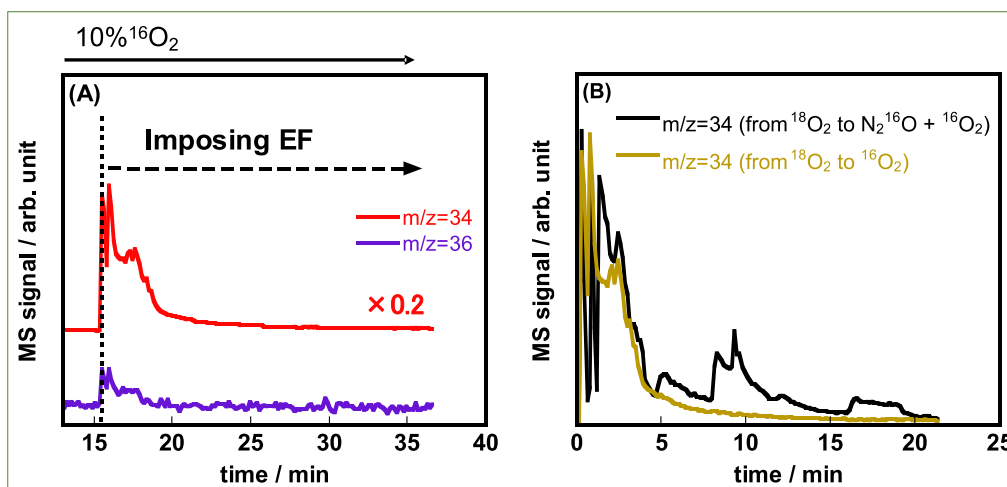


Figure S12. (A) Isotopic responses of $m/z = 34$ and 36 , obtained after switching from $^{18}\text{O}_2$ to $^{16}\text{O}_2$ over $0.5\text{wt}\%\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst. (B) Comparison of $m/z = 34$ between Figure 6 and Figure S12(A).

Furthermore, to observe in detail the oxygen exchange reaction with and without the electric field, an additional experiment was conducted. For this measurement, the surface oxygen species in $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ were filled with $^{16}\text{O}_2$ and then $^{18}\text{O}_2$ was supplied with and without the electric field at 423 K and 523 K. Then a mass spectrometer was used to analyze the produced gas. The experimental protocol is depicted in Figure S13.

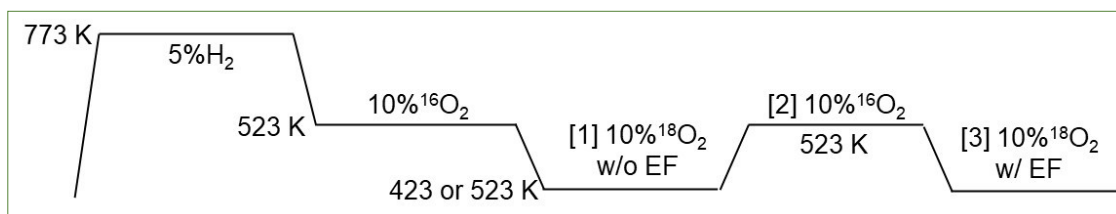


Figure S13. Experimental protocol for transient response tests switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$.

Figure S14 displays the isotopic responses of $m/z = 32, 34$ and 36 , obtained after switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ over the catalyst with and without the electric field. As can be seen in Figure S14(A), the response of $^{16}\text{O}^{18}\text{O}$ ($m/z = 34$) was immediate at 423 K when the electric field was applied but absent in its absence. Similarly, as shown in Figure S14(B), $^{16}\text{O}^{18}\text{O}$ was observed at 523 K both with and without the electric field, although the intensity of $^{16}\text{O}^{18}\text{O}$ was lower when the electric field was not applied. These findings suggest that surface lattice oxygen can be migrated and removed by the application of the electric field at low temperature, even when Joule heating is taken into account.

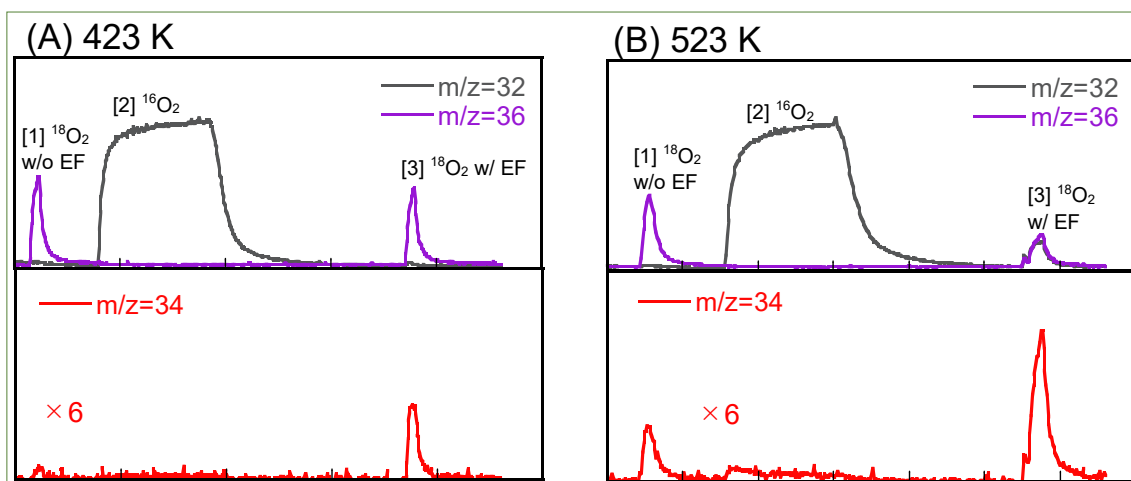


Figure S14. Isotopic responses of $m/z = 32, 34$ and 36 , obtained after switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ over 0.5wt%Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst with and without the electric field at 423 and 523 K.

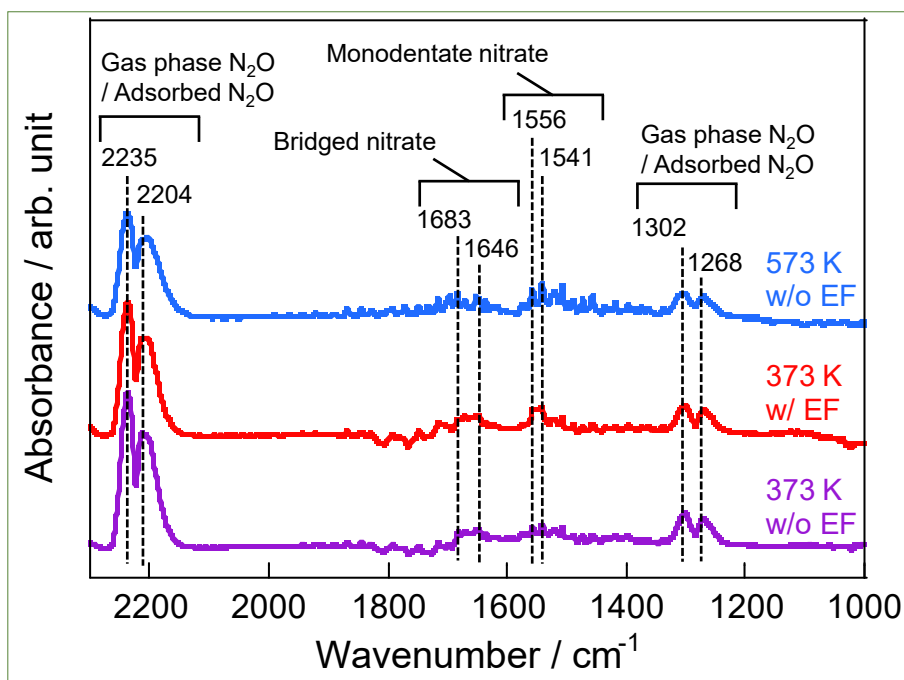


Figure S15. Transmission infrared spectroscopy spectra during N_2O decomposition over $0.5\text{wt}\%\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst with and without the electric field. Condition: $1000\text{ ppm N}_2\text{O} + 10\%\text{O}_2$ in Ar balance, total flow rate: 100 mL min^{-1} , current: 0 or 6 mA.

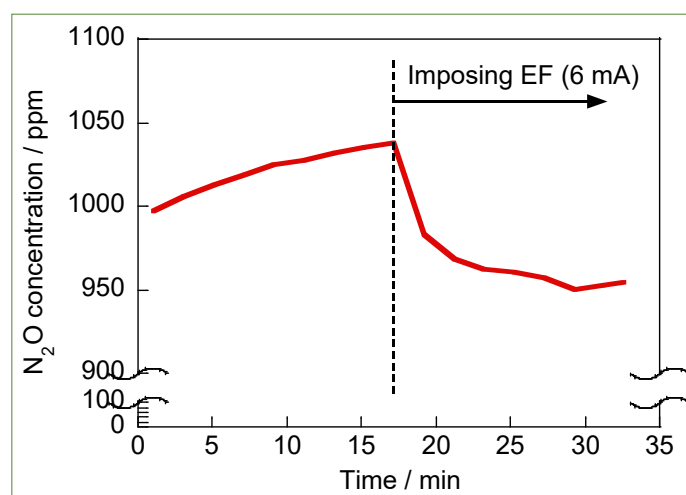


Figure S16. N_2O concentration measured during the TIRS-MS experiment performed with $0.5\text{wt}\%\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst with and without the electric field at 373 K. Condition: $1000\text{ ppm N}_2\text{O} + 10\%\text{O}_2$ in Ar balance, total flow rate: 100 mL min^{-1} , current: 0 or 6 mA.

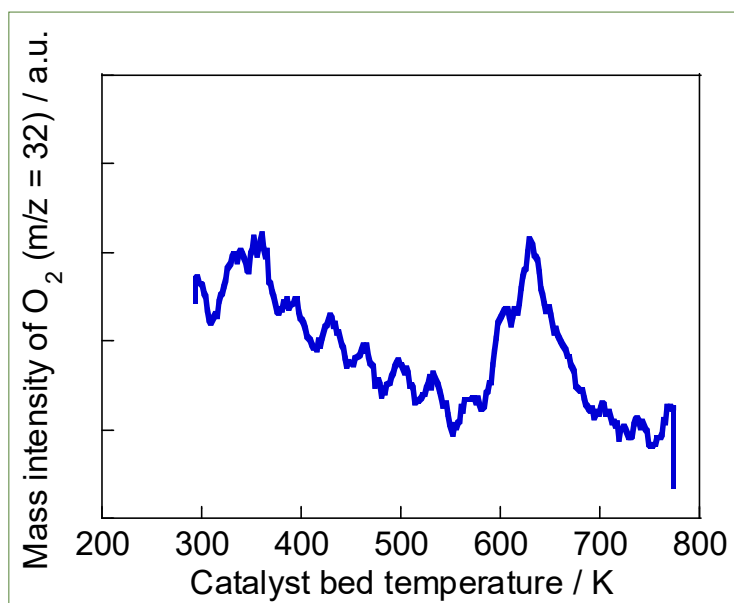


Figure S17. TPD profile of O₂ for 0.5wt%Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst. Weight of catalyst: 100 mg, total flow rate: 100 mL min⁻¹.

Table S1. Precursors used for catalyst synthesis.

Elements	Precursor
Rh	Rh(NO ₃) ₃
Fe	Fe(NO ₃) ₃ •9H ₂ O
Co	Co(NO ₃) ₂ •6H ₂ O
Ni	Ni(NO ₃) ₂ •6H ₂ O
Cu	Cu(NO ₃) ₂ •3H ₂ O

Table S2. BET surface area and Rh particle size of prepared catalysts.

Sample	S_{BET} [$\text{m}^2 \text{g}^{-1}$]	Rh particle size ^{*1} [nm]
0.5wt%Rh/CeO ₂	4.4	5.49
0.5wt%Rh/Ce _{0.9} Zr _{0.1} O ₂	7.2	3.31
0.5wt%Rh/Ce _{0.7} Zr _{0.3} O ₂	12.7	2.76
0.5wt%Rh/Ce _{0.5} Zr _{0.5} O ₂	17.5	2.33
5wt%Fe/Ce _{0.7} Zr _{0.3} O ₂	18.1	–
5wt%Co/Ce _{0.7} Zr _{0.3} O ₂	13.1	–
5wt%Ni/Ce _{0.7} Zr _{0.3} O ₂	17.6	–
5wt%Cu/Ce _{0.7} Zr _{0.3} O ₂	18.9	–

*1: estimated by CO pulse chemisorption

Table S3. BET surface area and Rh particle size of Ce_{0.7}Zr_{0.3}O₂ and 0.5wt%Rh/Ce_{0.7}Zr_{0.3}O₂ catalysts before and after the reaction with the electric field.

Sample	S_{BET} [$\text{m}^2 \text{g}^{-1}$]	Rh particle size ^{*1} [nm]
Ce _{0.7} Zr _{0.3} O ₂ –Fresh	17.8	–
Ce _{0.7} Zr _{0.3} O ₂ –After the reaction	18.3	–
0.5wt%Rh/Ce _{0.7} Zr _{0.3} O ₂ –Fresh	12.7	2.76
0.5wt%Rh/Ce _{0.7} Zr _{0.3} O ₂ –After the reaction	11.3	3.31

*1: estimated by CO pulse chemisorption

Table S4. Rh particle size of Rh/Ce_{0.7}Zr_{0.3}O₂ used for TOF calculation.

Metal loading amount [wt%]	Rh particle size ^{*1} [nm]	N ₂ O decomposition rate with EF at 373 K [mmol min^{-1}]	N ₂ O decomposition rate without EF at 573 K [mmol min^{-1}]
0.5	2.0	9.12×10^{-4}	6.23×10^{-4}
3	10.3	10.35×10^{-4}	5.86×10^{-4}
5	17.9	9.29×10^{-4}	6.52×10^{-4}

*1: estimated by CO pulse chemisorption