Electrical Promotion-Assisted Automotive Exhaust Catalyst: Highly Active and Selective NO Reduction to N2 at Low-Temperatures

Yuki Omori, Ayaka Shigemoto, Kohei Sugihara, Takuma Higo, Toru Uenishi, Yasushi Sekine

Submitted date: 07/03/2021 • Posted date: 09/03/2021
Licence: CC BY-NC-ND 4.0

Citation information: Omori, Yuki; Shigemoto, Ayaka; Sugihara, Kohei; Higo, Takuma; Uenishi, Toru; Sekine, Yasushi (2021): Electrical Promotion-Assisted Automotive Exhaust Catalyst: Highly Active and Selective NO Reduction to N2 at Low-Temperatures. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.14176577.v1

Pd catalyst (Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$) in an electric field exhibits extremely high three-way catalytic activity (TWC: NO-C$_3$H$_6$-CO-O$_2$-H$_2$O). By applying an electric field to the semiconductor catalyst, low-temperature operation of TWC can be achieved even at 473 K by virtue of the activated surface-lattice oxygen.
1. Experimental procedure

Catalyst preparation

Catalyst preparation was conducted using a citric acid complex method with aqueous solutions of Ce(NO₃)₃·6H₂O and ZrO(NO₃)₂·2H₂O (Kanto Chemical Co. Inc.), with excess amounts of citric acid and ethylene glycol (Kanto Chemical Co. Inc.). The molar ratio of metal: citric acid: ethylene glycol was 1: 3: 3. After the obtained solution was evaporated in a water bath at 353 K for 16 h, the solution was dried on a hot plate with stirring. The obtained powder was pre-calcined at 673 K for 2 h and was calcined at 1123 K for 10 h.

Next we impregnated Pd nanoparticles on it using an impregnation method with an acetone solution of Pd(OCOCH₃)₂ (Kanto Chemical Co. Inc.). We dried it at 393 K for 20 h and calcined it in air at 823 K for 3 h. Then the best performance catalyst of 0.5 wt% Pd/Ce₀.₇Zr₀.₃O₂ was obtained.

Activity tests

Catalytic activity tests were conducted in a fixed-flow-type quartz reactor at atmospheric pressure. An electric field was applied with a power supply via stainless steel electrodes, contacting...
the catalyst bed (amount of fixed catalyst was 80 or 200 mg; denoted in each caption) on the upper side and bottom side. The activity tests were performed under a simulated stoichiometric exhaust gas (2500 ppm NO, 3000 ppm CO, 500 ppm C₃H₆, 2500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) with a total flow rate of 200 mL min⁻¹. A pre-treatment for the catalyst was conducted for oxidation (5% O₂, Ar-balanced at 773 K for 15 min) and reduction (5% H₂, Ar-balanced at 773 K for 15 min) sequentially before the reaction. In the activity tests, the furnace temperature was increased stepwise from 338 to 623 K. Steady-state activity was evaluated at each temperature. To evaluate catalytic activity in an electric field, direct current of 1–12 mA was applied between the electrodes, monitoring the response voltage using an oscilloscope (TDS 2001C with a voltage probe P6015A; Tektronix Inc.). A thermocouple was set in the bottom of the catalyst bed to measure the real temperature of catalyst bed. The outlet gas was analyzed using an online GC-TCD (GC-8A; Shimadzu Corp.) and a chemiluminescent method NOx analyzer (NOA-7000; Shimadzu Corp.). The NO conversion and N₂ selectivity are defined as shown in equations (1) and (2).

\[ X_{\text{NO}} \text{(NO conversion rate / %)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100 \quad (1) \]
\[ \text{N}_2 \text{ selectivity (％) = } 2r_{\text{N}_2}/r_{\text{NO}} \times 100 \quad (2) \]

In these equations, [NO]ᵢᵢ, [NO]ₒₒ, \( r_{\text{N}_2} \), and \( r_{\text{NO}} \) conv. respectively represent the inlet NO concentration, outlet NO concentration, N₂ formation rate and NO conversion rate. The NO-CO-O₂-H₂O reaction (2500 ppm NO, 3000 ppm CO, 250 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O reaction (2500 ppm NO, 500 ppm C₃H₆, 1000 ppm O₂, 7 vol% H₂O and Ar as a balance gas) tests were conducted similarly. Partial-pressure-dependent testing of oxygen was conducted under a NO-CO-O₂-H₂O condition (2500 ppm NO, 3000 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O condition (2500 ppm NO, 500 ppm C₃H₆, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) similarly.

**Elucidation of intermediates on the catalyst**

*In-situ* DRIFTS measurements were taken using a Fourier transform infrared spectrometer (FT/IR 6200; Jasco Corp.) with an MCT detector and a ZnSe window. Catalyst sample powder (ca. 40 mg) was filled into a hand-made Teflon cell with platinum electrodes. Background spectra (donated as BKG) were measured under inert Ar gas (100 mL min⁻¹ at 373 K, 448 K, and 473 K) after the same pre-treatment as the activity tests. After the measurement of BKG, the following
measurements were taken. 3000 ppm C$_3$H$_6$ (Ar balanced) was supplied to the IR cell followed by obtaining the spectra of adsorbed species on the catalyst. To evaluate the adsorbed species on the catalyst with an electric field, DC current of 3 mA was applied between the electrodes whereas 3000 ppm C$_3$H$_6$ gas was supplied, and the spectra for the catalyst in an electric field. The spectral range was 1000–4000 cm$^{-1}$, with resolution of 4.0 cm$^{-1}$ and an accumulation of five scans.

**Structural characterization of the catalyst**

X-ray diffraction patterns were measured to confirm the crystalline structures of Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ catalysts (SmartLab 3; Rigaku Corp.). The Cu K$\alpha$ radiation condition was at 40 kV and 40 mA. The BET-specific surface area of the catalyst was measured using N$_2$ adsorption at 77 K (Gemini VII; Micromeritics Instrument Corp.).

XRD patterns for Ce$_{0.7}$Zr$_{0.3}$O$_2$ and Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ and BET surface area are presented in Fig. S3 and Table S2 respectively. BET surface changed slightly, but both of Ce$_{0.7}$Zr$_{0.3}$O$_2$ and Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ have a fluorite structure. Furthermore, it is expected that Pd was dispersed finely on Ce$_{0.7}$Zr$_{0.3}$O$_2$ because peaks assigned Pd metal was not observed.

2. Supplementary Tables and Figures

Table S1. Input electric power to Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ (catalyst weight was 200 mg) during activity test at each temperature.

| Gas Concentration | Injected Volume | Slope | Area | Intercept | Real Volume |
|-------------------|-----------------|-------|------|-----------|-------------|
| 1.01%             | 506.54          | 1910601.30403284 | AREA | -        | 506.54      |

Table S2. Surface area of Ce$_{0.7}$Zr$_{0.3}$O$_2$ and 0.5 wt% Pd/ Ce$_{0.7}$Zr$_{0.3}$O$_2$. |
Fig. S1 Schematic image of the reactor.

Fig. S2 NO, CO and O\textsubscript{2} reaction rate, O\textsubscript{2} conversion and N\textsubscript{2} selectivity over 0.5wt% Pd/Ce\textsubscript{0.7}Zr\textsubscript{0.3}O\textsubscript{2} under NO-CO-O\textsubscript{2}-H\textsubscript{2}O reaction (NO: 2500 ppm, CO: 3000 ppm O\textsubscript{2}: 0, 250, 500, 750, 1000 and 1500 ppm, H\textsubscript{2}O: 70000 ppm Ar balance, total flow: 200 cc min\textsuperscript{-1}) with/without the electric field at 413 K.

Fig. S3 XRD patterns of Ce\textsubscript{0.7}Zr\textsubscript{0.3}O\textsubscript{2} and Pd/ Ce\textsubscript{0.7}Zr\textsubscript{0.3}O\textsubscript{2}. 
Electrical promotion-assisted automotive exhaust catalyst: highly active and selective NO reduction to N₂ at low-temperatures

Yuki Omori¹, Ayaka Shigemoto², Kohei Sugihara³, Takuma Higo³, Toru Uenishi³, Yasushi Sekine*⁴⁵

¹ Waseda University, Applied Chemistry, 3-4-1, Okubo, Shinjuku, Tokyo 169-8555, Japan, yseikine@waseda.jp

² Toyota Motor Corp., 1200, Mishuku, Susono, Shizuoka 410-1193, Japan

Pd catalyst (Pd/Ce₀.₇Zr₀.₃O₂) in an electric field exhibits extremely high three-way catalytic activity (TWC: NO-C₃H₆-CO-O₂-H₂O). By applying an electric field to the semiconductor catalyst, low-temperature operation of TWC can be achieved even at 473 K by virtue of the activated surface-lattice oxygen.

With the development of global motorization, urban air pollution caused by automobile emissions and the excessive combustion of oil products have become global problems. Although these severe environmental problems are being addressed, there are currently very few innovative technologies to purify emissions from internal combustion engines. In recent years, the development of zero emission vehicles (ZEVs) such as battery electric vehicles (BEVs) and fuel cell electric vehicles (FCVs) has been progressing. Nevertheless, from the standpoint of infrastructure facilities and cruising range, the demand for fuel-burning vehicles such as hybrid vehicles (HV) continues. With the widespread use of "e-fuel," a novel concept fuel made from renewable H₂ and captured CO₂, it is expected that these engine-powered vehicles will continue to be used in the global market in the future. That progress notwithstanding, exhaust gas purification might become more difficult because of lower exhaust gas temperatures and tighter restrictions on hazardous gas emissions. In light of this situation, many investigations have been conducted to improve exhaust gas purification at low temperatures using electrically heated catalysts (EHC) [1,2], plasma catalytic systems [3–5], and highly active three-way catalysts (TWC) [6,7]. However, the EHC method and plasma-catalyzed reaction require higher electric power consumption [3,4,8,9]. In addition, TWCs require high temperatures to achieve high purification performance [10,11]. We found from an earlier study that various catalytic reactions can proceed even at low temperatures when a DC electric field is applied to a semiconductor support [12–16]. Since then, we have attempted to apply this finding to TWCs. In this paper, we propose a new catalytic TWC system using palladium catalyst supported on cerium-zirconia, which can function at temperatures as low as 473 K. We prepared mixed oxide of Ce₀.₇Zr₀.₃O₂ for a catalyst support which has suitable properties (i.e. electron conductivity and surface ion conductivity) for the catalytic reaction in the electric field. Catalyst preparation and reaction procedure are described in the ESI. First, we conducted NO reduction with C₃H₆ and CO on 0.5 wt% Pd/Ce₀.₇Zr₀.₃O₂ catalyst (see ESI for the structural information) with/without an electric field by 1.5 mA of direct current. The conversion of NO, C₃H₆, CO, and selectivity to N₂ with/without the electric field are presented in Fig. 1. Application of the electric field brought very high values of NO, C₃H₆, and CO conversion and N₂ selectivity, even at low temperatures (423–473 K), along with coexistence of O₂ and H₂O, as presented in Fig. 1(b). At 428.4 K, NO, C₃H₆, and CO conversion were 54.9%, 65.9%, and 96.8% respectively. Surprisingly, the selectivity to N₂ was 91.3% with the electric field. In contrast, without the electric field, NO conversion and N₂ selectivity were very low (almost 0%) at the low-temperature region (also see Fig. 1(a)). In these tests, the catalyst bed temperature was measured directly using a thermocouple attached to the catalyst to confirm the effects of Joule heating by the applied direct current on the catalytic activity. Consequently, the heated catalyst showed almost no activity. A great promotion with the electric field on the catalytic activity was confirmed. Therefore, the high activity/selectivity is not attributable to Joule heating. Additionally, the electric power consumption for applying the electric field to the catalyst bed was only up to 1.2 W at 428.4 K (see Supporting Information Table S1). Therefore, the catalysis with the electric field enables a highly efficient three-way catalyst system, even at temperatures lower than those of conventional systems.

![Fig. 1 NO, CO and C₃H₆ conversion and N₂ selectivity over 0.5wt% Pd/Ce₀.₇Zr₀.₃O₂ under NO-C₃H₆-CO-O₂-H₂O reaction (NO: 2500 ppm, C₃H₆: 500 ppm CO: 3000 ppm, O₂: 2500 ppm, H₂O: 70000 ppm, Ar balance, total flow: 200 cc min⁻¹ SV: 72000 h⁻¹) applying 1.5 mA direct current.](image-url)
This promotional effect by the electric field differs completely from electrically heated catalyst (EHC) and plasma reactions. It has been confirmed by in-situ XAFS measurements that the local heating of the catalyst particles due to the Joule-heating by the application of electric field is negligible. To confirm whether the plasma effect can be ignored in this system, we conducted the plasma reaction on the same TWC gas composition. At 375 and 468 K, NO conversions using plasma reaction were only 5.6% and 7.4%, respectively. These values are very low compared to the catalytic activities in the electric field presented in Table 1. Therefore, the promotive effect for the TWC reaction using the electric field is much greater than the plasma reaction.

Additionally, to confirm whether the high catalytic activity of TWC in the electric field derived from a direct NO decomposition, or not, NO reduction activity tests were conducted while supplying only NO gas. The NO conversion values with no reductant (i.e. CO and C$_3$H$_6$ in this case) with the electric field were, respectively, 2.7%, 2.3%, and 2.5% at 451 K, 532 K, and 625 K. These results suggest that NO direct decomposition is unlikely to occur in this system, and suggest that the reaction between oxidants (NO, O$_2$) and reductants (CO, C$_3$H$_6$), instead of NO direct decomposition, was promoted by application of the electric field: not by plasma, and not by the heat.

**Table 1** NO conversion over 0.5 wt% Pd/ CeO$_2$-ZrO$_2$ under NO-C$_3$H$_6$-CO-O$_2$-H$_2$O reaction (NO: 2500 ppm, C$_3$H$_6$: 500 ppm CO: 3000 ppm, O$_2$: 2500 ppm, H$_2$O: 70000 ppm, Ar balance, total flow: 200 cc min$^{-1}$) for various reactions.

| Condition | 420 K | 475 K | 500 K |
|-----------|-------|-------|-------|
| NO-CO-O$_2$-H$_2$O | 97.2 (5.2) | 100 (30.4) | 100 (96.2) |
| NO-C$_3$H$_6$-O$_2$-H$_2$O | 0.7 (0.85) | 3.4 (0.29) | 6.2 (5.4) |
| NO-C$_3$H$_6$-CO-O$_2$-H$_2$O (TWC) | 0.11 (0.0) | 0.27 (0.0) | 3.5 (13.4) |

We investigated the contribution of reductants (C$_3$H$_6$ and CO) to NO reduction with the electric field at low temperatures. For this purpose, we conducted NO-C$_3$H$_6$-O$_2$-H$_2$O and NO-CO-O$_2$-H$_2$O reactions with and without the electric field at high space velocity ($SV = ca. 180000$ h$^{-1}$). Table 2 shows NO conversion with and without the electric field on each condition at a low-temperature region (catalyst-bed temperature: 420–500 K). On the NO-C$_3$H$_6$-O$_2$-H$_2$O condition, NO conversion was nearly 100% with and without the electric field. No marked difference was observed on the NO conversion. This trend suggests that the NO-CO reaction is a dominant reaction in the NO-CO-O$_2$-H$_2$O condition. A slight increase in selectivity to N$_2$ was observed by application of the electric field at 420 K. In contrast, a clear difference in NO conversion was apparent with and without electric field on the NO-C$_3$H$_6$-O$_2$-H$_2$O condition at 420–500 K. Moreover, drastic promotion of N$_2$ selectivity was observed with application of the electric field in the NO-C$_3$H$_6$-O$_2$-H$_2$O condition: almost identically to the TWC condition. This result suggests that the NO-C$_3$H$_6$ reaction and CO oxidation are dominant reactions on the TWC condition with the electric field at low temperatures (420–500 K).

To elucidate the effect of coexistence of $O_2$ for TWC reaction, $O_2$ partial-pressure-dependent tests were conducted under the NO-CO-O$_2$-H$_2$O and NO-C$_3$H$_6$-O$_2$-H$_2$O conditions with and without the electric field. Under the NO-CO-O$_2$-H$_2$O condition, no difference was found for the reaction rates of NO, CO, and $O_2$ as presented in Fig. S2 (ESI). The NO reaction rate decreases concomitantly with increasing $O_2$ concentration with and without the electric field. However, the CO reaction rate increases concomitantly with increasing $O_2$ concentration with and without the electric field. This trend suggests that CO was not consumed through the NO-CO reaction, but through the CO-$O_2$ reaction with and without the electric field. This result is
consistent with the results obtained for the stoichiometric NO-CO$_2$-H$_2$O reaction. Therefore, results show that CO does not play the role of redundant for NO in the low-temperature region (423–500 K) with or without the electric field.

We conducted in-situ DRIFTS measurements to elucidate details of the contribution of surface oxygen on the reaction in the electric field. The DRIFTS spectra for Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ catalyst in a C$_2$H$_6$ flow (3000 ppm C$_2$H$_6$ balanced Ar gas) are portrayed in Fig. 3. Three peaks at 1594, 1441, and 1281 cm$^{-1}$ increased. New notable peaks observed at 1908 and 1841 cm$^{-1}$ were assigned to the vibration of C=O [21–24] (spectrum a). The change of spectrum shows that the oxygenate species are formed on the catalyst surface by application of the electric field. The findings suggest that the propylene is oxidized by the surface lattice oxygen of catalyst because no oxygen source exists in the atmosphere. The same IR measurements at 423–473 K were performed to elucidate the influence of Joule heating by the EF application (spectra c and d). No peak attributable to C=O vibration is found in these spectra, which demonstrates that C$_2$H$_6$ oxidation below 473 K proceeds only slightly on the Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ catalyst without the electric field.

This study investigated catalytic NO reduction with an electric field at low temperatures. Electric field promotion over 0.5 wt% Pd/Fe$_{0.7}$Zr$_{0.3}$O$_2$ catalyst enables high activity, even at low temperatures (423–473 K) and even with coexisting O$_2$ and H$_2$O. For surface reactions with the electric field, the NO–C$_2$H$_6$ reaction is the dominant reaction on the three-way catalyst conditions in low-temperature regions (423–473 K). Furthermore, the NO reaction rate depends positively on O$_2$ concentrations of 0–1000 ppm under a NO-C$_2$H$_6$-O$_2$-H$_2$O atmosphere. Application of the electric field promoted the formation of partially oxidized hydrocarbon (C$_8$H$_{18}$O$_4$) using lattice oxygen in the catalyst support, as confirmed by in-situ
DRIFTS measurements. The activated surface lattice oxygen contributes to the formation of intermediates and accelerates NO reduction by the application of the electric field, even at low temperatures. This finding is expected to engender the development of highly efficient three-way catalyst systems.

References

1. S. R. Khan, M. Zeeshan, and S. Iqbal, Chem. Eng. Commun., 2018, 205, 680–688.
2. R. M. Heck and R. J. Farrauto, Appl. Catal. A: Gen., 2001, 221, 443–457.
3. S. Bröer and T. Hammer, Appl. Catal. B: Environ., 2000, 28, 101.
4. B. M. Penetrante, R. M. Brusasco, B. T. Merritt, and G. E. Vogtlin, Pure Appl. Chem., 1999, 71, 1829.
5. M. A. Malik and K. H. Schoenbach, Int. J. Plasma Environ. Sci. Technol., 2011, 5 (1), 50–57.
6. M. V. Twigg, Appl. Catal. B: Environ., 2007, 70, 2–15.
7. H. S. Gandhi, G. W. Graham, and R. W. McCabe, J. Catal., 2003, 216, 433–442.
8. J. Gao, G. Tian, and A. Sorniotti, Energy Sci. Eng., 2019, 7, 2383–2397.
9. W. Maus, R. Brück, R. Konieczny, and A. Scheeder, MTZ Worldwide, 2010, 71, 34–39.
10. R. Burch, J. P. Breen, and F. C. Meunier, Appl. Catal., B: Environ., 2002, 39, 283–303.
11. T. Higo, K. Ueno, Y. Omori, H. Tsuchiya, S. Ogo, S. Hirose, H. Mikami, and Y. Sekine, RSC Adv., 2019, 9, 22721–22728.
12. K. Murakami, Y. Tanaka, R. Sakai, Y. Hisai, S. Hayashi, Y. Mizutani, T. Higo, S. Ogo, J.-G. Seo, H. Tsuneki, and Y. Sekine, Chem. Commun., 2020, 56, 3365–3368.
13. M. Torimoto, S. Ogo, D. Harjowinoto, T. Higo, J.-G. Seo, S. Furukawa, and Y. Sekine, Chem. Commun., 2019, 55, 6693–6695.
14. A. Sato, S. Ogo, K. Kamata, Y. Takeno, T. Yabe, T. Yamamoto, S. Matsumura, M. Hara, and Y. Sekine, Chem. Commun., 2019, 55, 4019–4022.
15. K. Takise, A. Sato, K. Murakami, S. Ogo, J.-G. Seo, K. Imagawa, S. Kado, and Y. Sekine, RSC Adv., 2019, 9, 5918–5924.
16. R. Manabe, H. Nakatsubo, A. Gondo, K. Murakami, S. Ogo, H. Tsuneki, M. Ikeda, A. Ishikawa, H. Nakai, and Y. Sekine, Chem. Sci., 2017, 8, 5434–5439.
17. L. Zhao, Y. Zhang, S. Bia, and Q. Liu, RSC Adv., 2019, 9, 19236–19242.
18. L. Q. Nguyen, C. Salim, and H. Hinode, Appl. Catal. B: Environ., 2010, 96, 299–306.
19. M. Haneda, Y. Kintaichi, M. Inaba, and H. Hamada, Catal. Today, 1998, 42, 127–135.
20. K. Shimizu, H. Kawabata, A. Satsuma, and T. Hattori, J. Phys. Chem. B, 1999, 103, 5240–5245.
21. B. Liu, Y. Zhang, and L. Tang, Int. J. Hydrogen Energy, 2009, 34, 435–439.
22. S. Hamoudi, F. Larachi, and A. Sayari, J. Catal., 1998, 177, 247–258.
23. M. Haneda, N. Bion, M. Daturi, J. Saussey, J. C. Lavalley, D. Duprez, and H. Hamada, J. Catal., 2002, 206, 114–124.
24. L. Cheng and X. P. Ye, Catal. Lett., 2009, 130, 100–107.
Electrical promotion-assisted automotive exhaust catalyst: highly active and selective NO reduction to N₂ at low-temperatures

Yuki Omori*, Ayaka Shigemoto*, Kohei Sugihara*, Takuma Higo*, Toru Uenishi*, Yasushi Sekine**

a Waseda University, Applied Chemistry, 3-4-1, Okubo, Shinjuku, Tokyo 169-8555, Japan, ysekine@waseda.jp
b Toyota Motor Corp., 1200, Mishuku, Susono, Shizuoka 410-1193, Japan

Pd catalyst (Pd/Ce₀.₇Zr₀.₃O₂) in an electric field exhibits extremely high three-way catalytic activity (TWC: NO-C₃H₆-CO-O₂-H₂O). By applying an electric field to the semiconductor catalyst, low-temperature operation of TWC can be achieved even at 473 K by virtue of the activated surface-lattice oxygen.

With the development of global motorization, urban air pollution caused by automobile emissions and the excessive combustion of oil products have become global problems. Although these severe environmental problems are being addressed, there are currently very few innovative technologies to purify emissions from internal combustion engines. In recent years, the development of zero emission vehicles (ZEVs) such as battery electric vehicles (BEVs) and fuel cell electric vehicles (FCVs) has been progressing. Nevertheless, from the standpoint of infrastructure facilities and cruising range, the demand for fuel-burning vehicles such as hybrid vehicles (HVs) continues. With the widespread use of “e-fuel,” a novel concept fuel made from renewable H₂ and captured CO₂, it is expected that these engine-powered vehicles will continue to be used in the global market in the future. That progress notwithstanding, exhaust gas purification might become more difficult because of lower exhaust gas temperatures and tighter restrictions on hazardous gas emissions. In light of this situation, many investigations have been conducted to improve exhaust gas purification at low temperatures using electrically heated catalysts (EHC) [1,2], plasma catalytic systems [3–5], and highly active three-way catalysts (TWC) [6,7]. However, the EHC method and plasma catalysis with the electric field enables a highly efficient three-way catalyst system, even at temperatures lower than those of conventional systems.

In these tests, the catalyst bed temperature was measured (almost 0%) at the low-temperature region (also see Fig. 1(a)). The electric field brought very high values of NO, C₃H₆, NO conversion and N₂ selectivity over 0.5wt% Pd/Ce₀.₇Zr₀.₃O₂ catalyst supported on cerium-zirconia, which can function at temperatures as low as 473 K. We prepared mixed oxide of Ce₀.₇Zr₀.₃O₂ for a catalyst support which has suitable properties (i.e. electron conductivity and surface ion conductivity) for the catalytic reaction in the electric field. Catalyst preparation and reaction procedure are described in the ESI.

First, we conducted NO reduction with C₃H₆ and CO on 0.5 wt% Pd/Ce₀.₇Zr₀.₃O₂ catalyst (see ESI for the structural information) with/without an electric field by 1.5 mA of direct current. The conversion of NO, C₃H₆, CO, and selectivity to N₂ with/without the electric field are presented in Fig. 1. Application of the electric field brought very high values of NO, C₃H₆, and CO conversion and N₂ selectivity, even at low temperatures (423–473 K), along with coexistence of O₂ and H₂O, as presented in Fig. 1(b). At 428.4 K, NO, C₃H₆, and CO conversion were 54.9%, 65.9%, and 96.8% respectively. Surprisingly, the selectivity to N₂ was 91.3% with the electric field. In contrast, without the electric field, NO conversion and N₂ selectivity were very low (almost 0%) at the low-temperature region (also see Fig. 1(a)). In these tests, the catalyst bed temperature was measured directly using a thermocouple attached to the catalyst to confirm the effects of Joule heating by the applied direct current on the catalytic activity. Consequently, the heated catalyst showed almost no activity. A great promotion with the electric field on the catalytic activity was confirmed. Therefore, the high activity/selectivity is not attributable to Joule heating. Additionally, the electric power consumption for applying the electric field to the catalyst bed was only up to 1.2 W at 428.4 K (see Supporting Information Table S1). Therefore, the catalysis with the electric field enables a highly efficient three-way catalyst system, even at temperatures lower than those of conventional systems.

(a) No Electric Field (Heated) (b) With Electric Field

Fig. 1 NO, CO and C₃H₆ conversion and N₂ selectivity over 0.5wt% Pd/Ce₀.₇Zr₀.₃O₂ under NO-C₃H₆-CO-O₂-H₂O reaction (NO: 2500 ppm, C₃H₆: 500 ppm, CO: 3000 ppm, O₂: 2500 ppm, H₂O: 70000 ppm, Ar balance, total flow: 200 cc min⁻¹ SV: 72000 h⁻¹) applying 1.5 mA direct current.
Table 1 NO conversion over 0.5wt%Pd/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_{2} under NO-C_{2}H_{6}-CO-O_{2}-H_{2}O reaction (NO: 2500 ppm, C_{2}H_{6}: 500 ppm CO: 3000 ppm, O_{2}: 2500 ppm, H_{2}O: 70000 ppm, Ar balance, total flow: 200 cc min\(^{-1}\)) for various reactions.

| Electric field reaction | Plasma reaction | Heated catalyst reaction at various temperatures | NO decomposition in the electric field (no reductant) |
|-------------------------|-----------------|-----------------------------------------------|-----------------------------------------------|
| with reductant           |                 |                                               |                                               |
| NO decomposition         |                 |                                               |                                               |
| without the electric field| 5.8 (at 375 K) | 7.4 (at 468 K)                                | 2.7 (at 451 K)                                |
| at various temperatures  |                 |                                               | 2.1 (at 532 K)                                |
| at 420 K                 |                 | 0.1 (at 440 K)                                | 0.26 (at 478 K)                               |
| at 444 K                 |                 |                                               |                                               |
| electric field           |                 |                                               |                                               |

Table 2 NO conversion and N\(_2\) selectivity over 0.5wt% Pd/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_{2} under NO-C_{2}H_{6}-CO-O_{2}-H_{2}O reaction (NO: 2500 ppm, C_{2}H_{6}: 500 ppm CO: 3000 ppm, O_{2}: 2500 ppm, H_{2}O: 70000 ppm Ar balance, total flow: 200 cc min\(^{-1}\)) for various conditions.

| Condition | 420 K | 475 K | 500 K |
|-----------|-------|-------|-------|
| NO-\text{CO}-O_{2}-\text{H}_{2}O | 97.2 (5.2) | 100 (30.4) | 100 (96.2) |
| NO-\text{C}_{2}\text{H}_{6}-\text{O}_{2}-\text{H}_{2}O | 3.6 (0.85) | 3.4 (0.29) | 6.2 (5.4) |
| NO-\text{C}_{2}\text{H}_{6}-\text{CO}-\text{O}_{2}(\text{TWC}) | 0.11 (0.0) | 0.27 (0.0) | 3.5 (13.4) |

This promotional effect by the electric field differs completely from electrically heated catalyst (EHC) and plasma reactions. It has been confirmed by in-situ XAFS measurements that the local heating of the catalyst particles due to the Joule-heating by the application of electric field is negligible. To confirm whether the plasma effect can be ignored in this system, we conducted the plasma reaction on the same TWC gas composition. At 375 and 468 K, NO conversions using plasma reaction were only 5.6% and 7.4%, respectively. These values are very low compared to the catalytic activities in the electric field presented in Table 1. Therefore, the promotive effect for the TWC reaction using the electric field is much greater than the plasma reaction.

Additionally, to confirm whether the high catalytic activity of TWC in the electric field derived from a direct NO decomposition, or not, NO reduction activity tests were conducted while supplying only NO gas. The NO conversion values with no reductant (i.e. CO and C_{2}H_{6} in this case) with the electric field were, respectively, 2.7%, 2.3%, and 2.5% at 451 K, 532 K, and 625 K. These results suggest that NO direct decomposition is unlikely to occur in this system, and suggest that the reaction between oxidants (NO, O_{2}) and reductants (CO, C_{2}H_{6}), instead of NO direct decomposition, was promoted by application of the electric field: not by plasma, and not by the heat.

We investigated the contribution of reductants (C_{2}H_{6} and CO) to NO reduction with the electric field at low temperatures. For this purpose, we conducted NO-C_{2}H_{6}-O_{2}-H_{2}O and NO-CO-O_{2}-H_{2}O reactions with and without the electric field at high space velocity (SV = ca. 180000 h\(^{-1}\)). Table 2 shows NO conversion with and without the electric field on each condition at a low-temperature region (catalyst-bed temperature: 420–500 K). On the NO-CO-O_{2}-H_{2}O condition, NO conversion was nearly 100% with and without the electric field. No marked difference was observed on the NO conversion. This trend suggests that the NO–CO reaction is a dominant reaction in the NO-CO-O_{2}-H_{2}O condition. A slight increase in selectivity to N\(_2\) was observed by application of the electric field at 420 K. In contrast, a clear difference in NO conversion was apparent with and without electric field on the NO-C_{2}H_{6}-O_{2}-H_{2}O condition at 420–500 K. Moreover, drastic promotion of N\(_2\) selectivity was observed with application of the electric field in the NO-C_{2}H_{6}-O_{2}-H_{2}O condition: almost identically to the TWC condition. This result suggests that the NO–C_{2}H_{6} reaction and CO oxidation are dominant reactions on the TWC condition with the electric field at low temperatures (420–500 K).

To elucidate the effect of coexistence of O\(_2\) for TWC reaction, O\(_2\) partial-pressure-dependent tests were conducted under the NO-CO-O_{2}-H_{2}O and NO-C_{2}H_{6}-O_{2}-H_{2}O conditions with and without the electric field. Under the NO-CO-O_{2}-H_{2}O condition, no difference was found for the reaction rates of NO, CO, and O\(_2\) as presented in Fig. S2 (ESI). The NO reaction rate decreases concomitantly with increasing O\(_2\) concentration with and without the electric field. However, the CO reaction rate increases concomitantly with increasing O\(_2\) concentration with and without the electric field. This trend suggests that CO was
not consumed through the NO–CO reaction, but through the CO–O_2 reaction with and without the electric field. This result is consistent with the results obtained for the stoichiometric NO-CO-O_2-H_2O reaction. Therefore, results show that CO does not play the role of reductant for NO in the low-temperature region (423–500 K) with or without the electric field.

For the NO-C_3H_6-O_2-H_2O condition, a drastic difference is apparent in the dependence of the NO reaction rate on O_2 concentration, as depicted in Fig. 2. Without the electric field, a negative dependence on the O_2 concentration was observed for the NO reaction rate (Fig. 2 left). However, the NO reaction rate positively depends on O_2 concentration of the 0–1000 ppm O_2 concentration. At 1000–1500 ppm O_2, the NO reaction rate decreases considerably, which suggests that the NO reduction by C_3H_6 was prevented by the competitive adsorption of O_2. It caused excess adsorption of O_2 on Pd metal, which is the active site of the NO-C_3H_6 reaction. In contrast, O_2 contributes to the positive effect on NO-C_3H_6 reaction at 0–1000 ppm O_2. Burch et al. reported that O_2 contributes to the NO selective catalytic reduction by hydrocarbons (HC-SCR). NO was reduced by hydrocarbons through these pathways (equations 3–6) [10].

\[
\begin{align*}
\text{NO (g) + O}_2 (g) & \rightarrow \text{NO}_2 (ads) \\
\text{C}_3\text{H}_6 (g) + \text{O}_2 (g) & \rightarrow \text{C}_3\text{H}_6\text{O}_2 (ads) \\
\text{NO}_2 (ads) + \text{C}_3\text{H}_6\text{O}_2 (ads) & \rightarrow \text{R-NCO (ads)} \\
\text{NO}_2 (ads) + \text{R-NCO (ads)} & \rightarrow \text{N}_2 (g) + \text{CO}_2 (g)
\end{align*}
\]

As those reactions show, NO and hydrocarbons were oxidized by O_2 (g) to form NO_2, NO_3, and C_3H_6O_2 (partially oxidized species of hydrocarbons), which are the key intermediate species for HC-SCR. Subsequently, NO_2 is reduced by C_3H_6O_2 to N_2 via R-NCO species. Higo et al. also reported that the partially oxidized species of hydrocarbons (C_3H_6O_2) are an extremely important intermediate species for HC-SCR over Pd/perovskite catalyst [11]. The catalyst shows high NO reduction activity by virtue of the partially oxidized C_3H_6 which is produced by high-mobility lattice oxygen in the catalyst-support material. The oxygen species is expected to contribute to the formation of intermediates and to accelerate NO reduction by application of an electric field.

We conducted in-situ DRIFTS measurements to elucidate the details of the contribution of surface oxygen on the reaction in the electric field. The DRIFTS spectra for Pd/\text{Ce}_0.7\text{Zr}_{0.3}\text{O}_2 catalyst in a C_3H_6 flow (3000 ppm C_3H_6, balanced Ar gas) are portrayed in Fig. 3. Three peaks at 1594, 1441, and 1281 cm^{-1} observed without the electric field (spectrum b) can be assigned to acetylate and carbonate species [17–20]. This result demonstrates that C_3H_6 was oxidized by the active oxygen species on the Pd/\text{Ce}_0.7\text{Zr}_{0.3}\text{O}_2 catalyst to form these oxygenate adsorbrates. Then, after applying the electric field in the C_3H_6 flow, absorbance at 1950–1200 cm^{-1} increased. New notable peaks observed at 1908 and 1841 cm^{-1} were assigned to the vibration of C=O [21–24] (spectrum a). The change of spectrum shows that the oxygenate species are formed on the catalyst surface by application of the electric field. The findings suggest that the propylene is oxidized by the surface lattice oxygen of catalyst because no oxygen source exists in the atmosphere. The same IR measurements at 423–473 K were performed to elucidate the influence of Joule heating by the EF application (spectrum c and d). No peak attributable to C=O vibration is found in these spectra, which demonstrates that C_3H_6 oxidation below 473 K proceeds only slightly on the Pd/\text{Ce}_0.7\text{Zr}_{0.3}\text{O}_2 catalyst without the electric field.

![Fig. 2 NO, C_3H_6 and O_2 reaction rate, O_2 conversion and N_2 selectivity over 0.5wt% Pd/\text{Ce}_0.7\text{Zr}_{0.3}\text{O}_2, under NO-C_3H_6-O_2-H_2O reaction (NO: 2500 ppm, C_3H_6: 500 ppm O_2: 0, 250, 500, 750, 1000 and 1500 ppm, H_2O: 70000 ppm Ar balance, total flow: 200 cc min^{-1}) with/without the electric field at each temperatures.]

![Fig. 3 DRIFTS spectra of Pd/\text{Ce}_0.7\text{Zr}_{0.3}\text{O}_2 during Ar + 3000 ppm C_3H_6 flow with/without electric field at each temperature.]

This study investigated catalytic NO reduction with an electric field at low temperatures. Electric field promotion over 0.5 wt % Pd/\text{Ce}_0.7\text{Zr}_{0.3}\text{O}_2 catalyst enables high activity, even at low temperatures (423–473 K) and even with coexisting O_2 and H_2O. For surface reactions with the electric field, the NO–C_3H_6 reaction is the dominant reaction on the three-way catalyst conditions in low-temperature regions (423–473 K). Furthermore, the NO reaction rate depends positively on O_2 concentrations of 0–1000 ppm under a NO-C_3H_6-O_2-H_2O atmosphere. Application of the electric field promoted the
formation of partially oxidized hydrocarbon \((\text{C}_x\text{H}_y\text{O}_z)\) using lattice oxygen in the catalyst support, as confirmed by \textit{in-situ} DRIFTS measurements. The activated surface lattice oxygen contributes to the formation of intermediates and accelerates NO reduction by the application of the electric field, even at low temperatures. This finding is expected to engender the development of highly efficient three-way catalyst systems.

References
1. S. R. Khan, M. Zeeshan, and S. Iqbal, \textit{Chem. Eng. Commun.}, 2018, \textbf{205}, 680–688.
2. R. M. Heck and R. J. Farrauto, \textit{Appl. Catal. A: Gen.}, 2001, \textbf{221}, 443–457.
3. S. Bröer and T. Hammer, \textit{Appl. Catal. B: Environ.}, 2000, \textbf{28}, 101.
4. B. M. Penetrante, R. M. Brusasco, B. T. Merritt, and G. E. Vogtlin, \textit{Pure Appl. Chem.}, 1999, \textbf{71}, 1829.
5. M. A. Malik and K. H. Schoenbach, \textit{Int. J. Plasma Environ. Sci. Technol.}, 2011, \textbf{5} (1), 50–57.
6. M. V. Twigg, \textit{Appl. Catal. B: Environ.}, 2007, \textbf{70}, 2–15.
7. H. S. Gandhi, G. W. Graham, and R. W. McCabe, \textit{J. Catal.}, 2003, \textbf{216}, 433–442.
8. J. Gao, G. Tian, and A. Sorniotti, \textit{Energy Sci. Eng.}, 2019, \textbf{7}, 2383–2397.
9. W. Maus, R. Brück, R. Konieczny, and A. Scheeder, \textit{MTZ Worldwide}, 2010, \textbf{71}, 34–39.
10. R. Burch, J. P. Breen, and F. C. Meunier, \textit{Appl. Catal., B: Environ.}, 2002, \textbf{39}, 283–303.
11. T. Higo, K. Ueno, Y. Omori, H. Tsuchiya, S. Ogo, S. Hirose, H. Mikami, and Y. Sekine, \textit{RSC Adv.}, 2019, \textbf{9}, 22721–22728.
12. K. Murakami, Y. Tanaka, R. Sakai, Y. Hisai, S. Hayashi, Y. Mizutani, T. Higo, S. Ogo, J.-G. Seo, H. Tsuneki, and Y. Sekine, \textit{Chem. Commun.}, 2020, \textbf{56}, 3365–3368.
13. M. Torimoto, S. Ogo, D. Harjowinoto, T. Higo, J.-G. Seo, S. Furukawa, and Y. Sekine, \textit{Chem. Commun.}, 2019, \textbf{55}, 6693–6695.
14. A. Sato, S. Ogo, K. Kamata, Y. Takeno, T. Yabe, T. Yamamoto, S. Matsumura, M. Haru, and Y. Sekine, \textit{Chem. Commun.}, 2019, \textbf{55}, 4019–4022.
15. K. Takise, A. Sato, K. Murakami, S. Ogo, J.-G. Seo, K. Imagawa, S. Kado, and Y. Sekine, \textit{RSC Adv.}, 2019, \textbf{9}, 5918–5924.
16. R. Manabe, H. Nakatsuho, A. Gondo, K. Murakami, S. Ogo, H. Tsuneki, M. Ikeda, A. Ishikawa, H. Nakai, and Y. Sekine, \textit{Chem. Sci.}, 2017, \textbf{8}, 5434–5439.
17. L. Zhao, Y. Zhang, S. Bia, and Q. Liu, \textit{RSC Adv.}, 2019, \textbf{9}, 19236–19242.
18. L. Q. Nguyen, C. Salim, and H. Hinode, \textit{Appl. Catal. B: Environ.}, 2010, \textbf{96}, 299–306.
19. M. Haneda, Y. Kintaichi, M. Inaba, and H. Hamada, \textit{Catal. Today}, 1998, \textbf{42}, 127–135.
20. K. Shimizu, H. Kawabata, A. Satsuma, and T. Hattori, \textit{J. Phys. Chem. B}, 1999, \textbf{103}, 5240–5245.
21. B. Liua, Y. Zhang, and L. Tang, \textit{Int. J. Hydrogen Energy}, 2009, \textbf{34}, 435–439.
22. S. Hamoudi, F. Larachi, and A. Sayari, \textit{J. Catal.}, 1998, \textbf{177}, 247–258.
23. M. Haneda, N. Bion, M. Datrai, J. Saussje, J. C. Lavalle, D. Duprez, and H. Hamada, \textit{J. Catal.}, 2002, \textbf{206}, 114–124.
24. L. Cheng and X. P. Ye, \textit{Catal. Lett.}, 2009, \textbf{130}, 100–107.
