Electrical promotion-assisted automotive exhaust catalyst: highly active and selective NO reduction to N_2 at low-temperatures

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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.

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 H_2 and captured CO_2, 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 Ce$_{0.7}$Zr$_{0.3}$O$_2$ 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 C_3H_6 and CO on 0.5 wt% Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ catalyst (see ESI for the structural information) with/without an electric field by 1.5 mA of direct current. The conversion of NO, C_3H_6, CO, and selectivity to N_2 with/without the electric field are presented in Fig. 1. Application of the electric field brought very high values of NO, C_3H_6, and CO conversion and N_2 selectivity, even at low temperatures (423–473 K), along with coexistence of O_2 and H_2O, as presented in Fig. 1(b). At 428.4 K, NO, C_3H_6, and CO conversion were 54.9%, 65.9%, and 96.8% respectively. Surprisingly, the selectivity to N_2 was 91.3% with the electric field. In contrast, without the electric field, NO conversion and N_2 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.
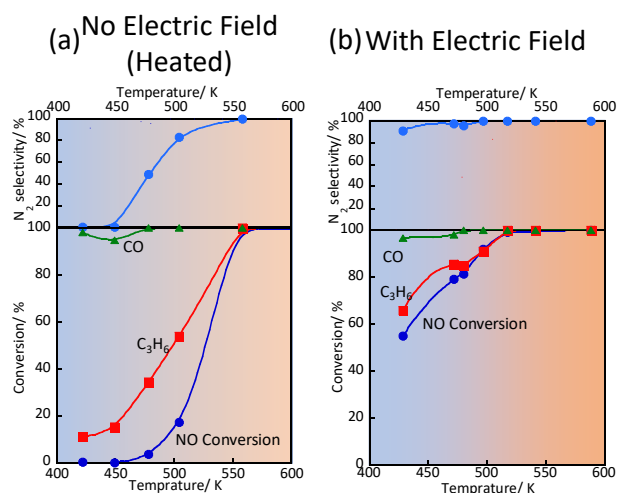

Fig. 1 NO, CO and C_3H_6 conversion and N_2 selectivity over 0.5wt% Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ under NO-C$_3$H$_6$-CO-O$_2$-H$_2$O reaction (NO: 2500 ppm, C_3H_6: 500 ppm CO: 3000 ppm, O_2: 2500 ppm, H_2O: 70000 ppm, Ar balance, total flow: 200 cc min^{-1} SV: 72000 h^{-1}) applying 1.5 mA direct current.

Table 1 NO conversion over 0.5wt%Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ 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.

	NO conversion/%		
Plasma reaction at various temperatures	5.6 (at 375 K)	7.4 (at 468 K)	
Heated catalytic reaction at various temperatures	0.0 (at 420 K)	0.3 (at 449 K)	0.26 (at 478 K)
Electric field reaction with reductant	19.1 (at 414 K)	16.5 (at 433 K)	20.5 (at 457 K)
NO decomposition in the electric field (no reductant)	2.7 (at 451 K)	2.3 (at 532 K)	2.5 (at 625 K)

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 2 NO conversion and N$_2$ selectivity over 0.5wt% Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ 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}), NO-CO-O$_2$-H$_2$O reaction (NO: 2500 ppm, CO: 3000 ppm O$_2$: 250 ppm, H$_2$O: 70000 ppm Ar balance, total flow: 200 cc min^{-1}) and NO-C$_3$H$_6$-O$_2$-H$_2$O reaction (NO: 2500 ppm, C$_3$H$_6$: 500 ppm, O$_2$: 2500 ppm, H$_2$O: 70000 ppm Ar balance, total flow: 200 cc min^{-1}) with/without an electric field (denoted as EF).

- Without EF -

	NO conversion (N$_2$ selectivity)/ %		
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	**3.6 (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)

- With EF -

	NO conversion (N$_2$ selectivity)/ %		
Condition	420 K	475 K	500 K
NO-CO-O$_2$-H$_2$O	95.8 (22.9)	99.5 (32.0)	100 (71.7)
NO-C$_3$H$_6$-O$_2$-H$_2$O	**14.4 (92.4)**	**13.7 (100)**	**17.7(100)**
NO-C$_3$H$_6$-CO-O$_2$-H$_2$O(TWC)	13.7 (100)	14.4 (100)	23.0(100)

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-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$_3$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 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-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.
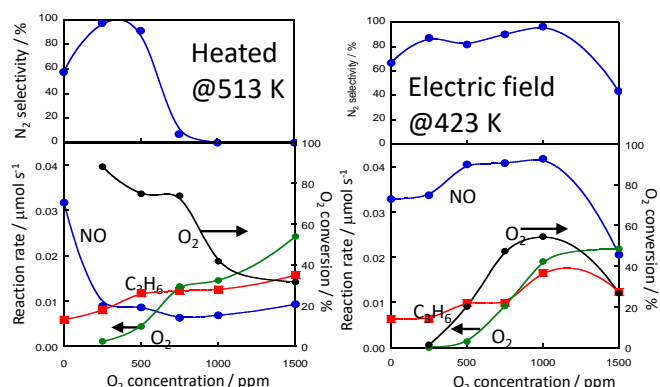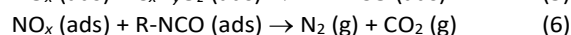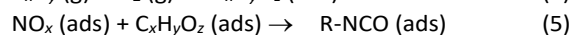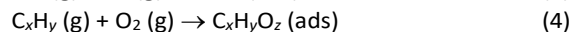

Fig. 2 NO, C_3H_6 and O_2 reaction rate, O_2 conversion and N_2 selectivity over 0.5wt% Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ under NO-C_3H_6-O_2-H_2O reaction (NO: 2500 ppm, C_3H_6: 500 ppm O_2: 0, 250, 500, 750, 1000 and 1500 ppm, H_2O: 70000 ppm Ar balance, total flow: 200 cc min^{-1}) with/without the electric field at each temperatures.

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$_x$ selective catalytic reduction by hydrocarbons (HC-SCR). NO$_x$ was reduced by hydrocarbons through these pathways (equations 3–6) [10].

$$NO\ (g) + O_2\ (g) \rightarrow NO_x\ (ads) \qquad (3)$$
$$C_xH_y\ (g) + O_2\ (g) \rightarrow C_xH_yO_z\ (ads) \qquad (4)$$
$$NO_x\ (ads) + C_xH_yO_z\ (ads) \rightarrow\ R\text{-}NCO\ (ads) \qquad (5)$$
$$NO_x\ (ads) + R\text{-}NCO\ (ads) \rightarrow N_2\ (g) + CO_2\ (g) \qquad (6)$$
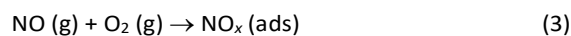
As those reactions show, NO and hydrocarbons were oxidized by O_2 (g) to form NO_2^-, NO_3^-, and $C_xH_yO_z$ (partially oxidized species of hydrocarbons), which are the key intermediate species for HC-SCR. Subsequently, NO$_x$ is reduced by $C_xH_yO_z$ to N_2 *via* R-NCO species. Higo *et al.* also reported that the partially oxidized species of hydrocarbons ($C_xH_yO_z$) are an extremely important intermediate species for HC-SCR over Pd/perovskite catalyst [11]. The catalyst shows high NO$_x$ reduction activity by virtue of the partially oxidized C_xH_y 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 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_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 acetate and carbonate species [17–20]. This result demonstrates that C_3H_6 was oxidized by the active oxygen species on the Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ catalyst to form these oxygenate adsorbates. 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 (spectra 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/Ce$_{0.7}$Zr$_{0.3}$O$_2$ catalyst without the electric field.
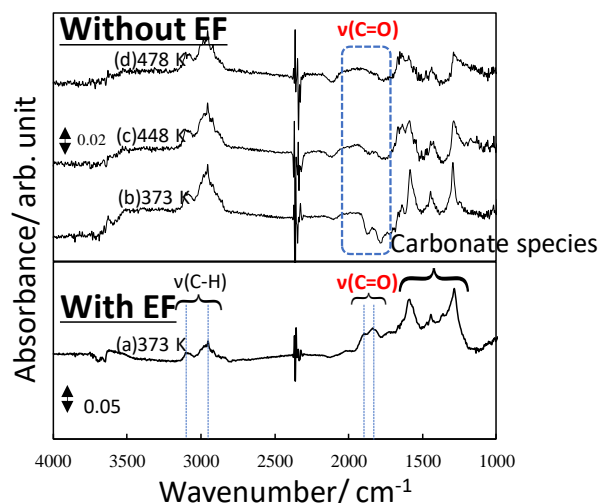

Fig. 3 DRIFT spectra of Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ during Ar + 3000 ppm C_3H_6 flow with/without electric field at each temperature.

This study investigated catalytic NO reduction with an electric field at low temperatures. Electric field promotion over 0.5 wt% Pd/Ce$_{0.7}$Zr$_{0.3}$O$_2$ catalyst enables high activity, even at low temperatures (423–473 K) and even with coexisting O_2 and H_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 ($C_xH_yO_z$) 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.

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