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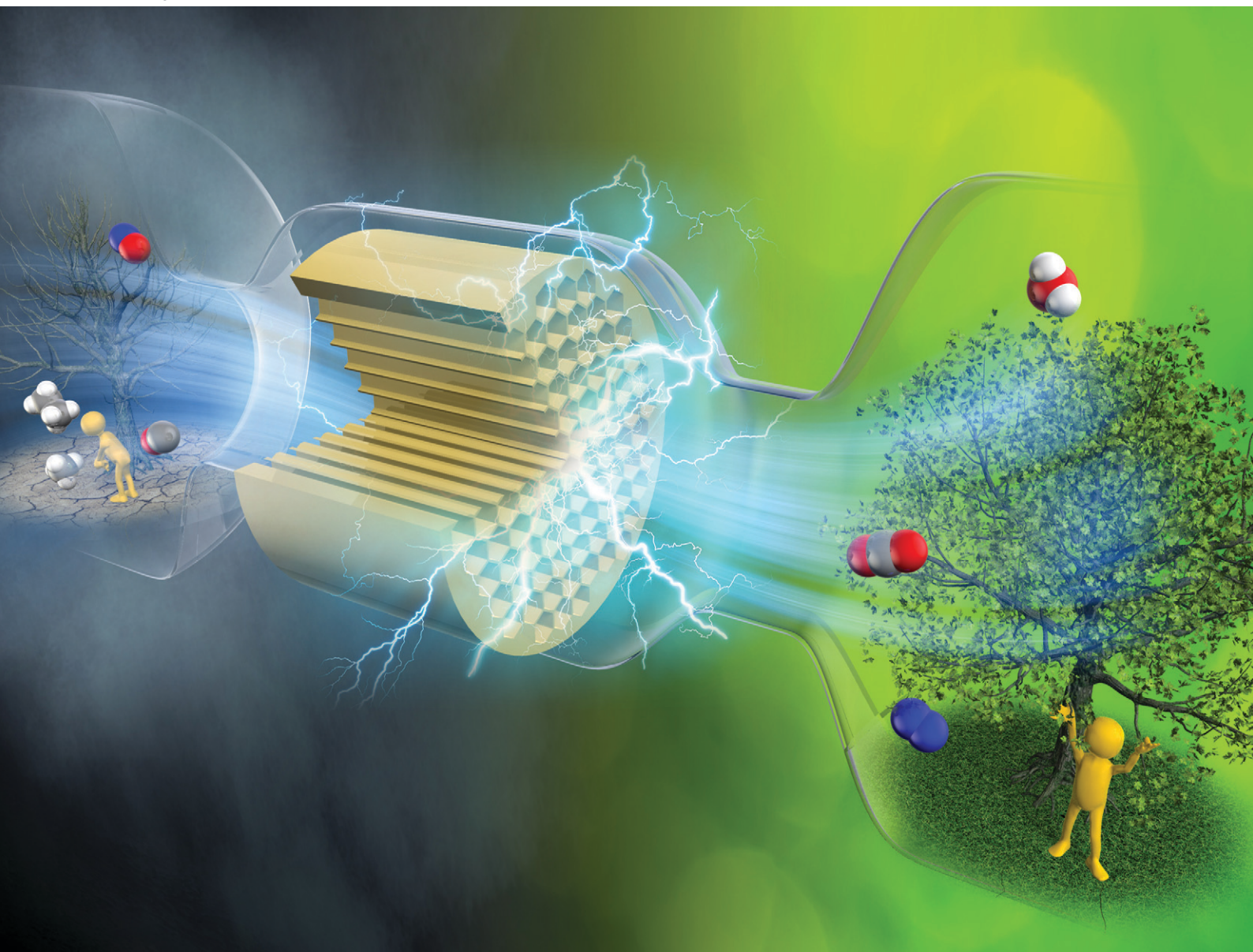
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Electrical promotion-assisted automotive exhaust catalyst: highly active and selective NO reduction to N₂ at low-temperatures†

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A 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.

Introduction

With the development of global motorization, urban air pollution caused by automobile emissions and the excessive combustion of oil products have become global problems. 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 a palladium catalyst supported on ceria–zirconia ($Ce_{0.7}Zr_{0.3}O_2$), which can function at temperatures as low as 473 K. We prepared a 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.†

Results and discussion

First, we conducted the three-way catalytic reaction (NO–C_3H_6–CO–H_2O–O_2) on an 0.5 wt% Pd/$Ce_{0.7}Zr_{0.3}O_2$ catalyst (see the ESI† for the structural information of the prepared

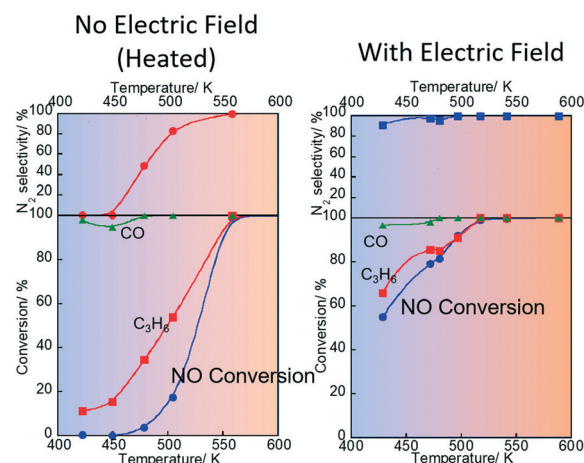**Fig. 1** NO, CO and C₃H₆ conversion and N₂ selectivity over 0.5 wt% Pd/Ce₀.₇Zr₀.₃O₂ under NO–C₃H₆–CO–O₂–H₂O reaction (NO: 2500 ppm, C₃H₆: 500 ppm CO: 3000 ppm, O₂: 2500 ppm, H₂O: 70 000 ppm, Ar balance, SV: 72 000 h⁻¹) applying 1.5 mA direct current.

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catalyst) 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 measured 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. 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 Table S1 in the ESI†). Therefore, the catalysis with the electric field enables a highly efficient three-way catalyst system, even at temperatures much lower than those of conventional systems.

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 decomposition activity tests were conducted while supplying only NO gas. The NO conversion values with no reductant (*i.e.* CO and C_3H_6 in this case) with the electric field were around 2.5% at each temperature. 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_3H_6), instead of NO direct decomposition, was promoted by

Table 2 NO conversion and N_2 selectivity over 0.5 wt% $Pd/Ce_{0.7}Zr_{0.3}O_2$ under NO–C_3H_6–CO–O_2–H_2O reaction (NO: 2500 ppm, C_3H_6: 500 ppm CO: 3000 ppm, O_2: 2500 ppm, H_2O: 70 000 ppm Ar balance, total flow: 200 cc min^{-1}), NO–CO–O_2–H_2O reaction (NO: 2500 ppm, CO: 3000 ppm O_2: 250 ppm, H_2O: 70 000 ppm Ar balance, total flow: 200 cc min^{-1}) and NO–C_3H_6–O_2–H_2O reaction (NO: 2500 ppm, C_3H_6: 500 ppm, O_2: 2500 ppm, H_2O: 70 000 ppm Ar balance, total flow: 200 cc min^{-1}) with/without an electric field at 3 mA (denoted as EF)

–Without EF–

Condition	NO conversion (N_2 selectivity)/%		
	420 K	475 K	500 K
NO–CO–O_2–H_2O	97.2 (5.2)	100 (30.4)	100 (96.2)
NO–C_3H_6–O_2–H_2O	3.6 (0.9)	3.4 (0.3)	6.2 (5.4)
NO–C_3H_6–CO–O_2–H_2O (TWC)	0.1 (0.0)	0.27 (0.0)	3.5 (13.4)

–With EF–

Condition	NO conversion (N_2 selectivity)/%		
	420 K	475 K	500 K
NO–CO–O_2–H_2O	95.8 (22.9)	99.5 (32.0)	100 (71.7)
NO–C_3H_6–O_2–H_2O	14.4 (92.4)	13.7 (100)	17.7 (100)
NO–C_3H_6–CO–O_2–H_2O (TWC)	13.7 (100)	14.4 (100)	23.0 (100)

application of the electric field: not by plasma, and not by the heat. We investigated the contribution of reductants (C_3H_6 and CO) to NO reduction with the electric field at low temperatures. For this purpose, we conducted NO–C_3H_6–O_2–H_2O and NO–CO–O_2–H_2O reactions with and without the electric field at high space velocity (SV = *ca.* 180 000 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_2O condition, NO conversion was nearly 100% with and without the electric field. No marked difference was observed on the NO conversion. 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_3H_6–O_2–H_2O condition at 420–500 K. Moreover, drastic promotion of N_2 selectivity was observed with application of the electric field in the NO–C_3H_6–O_2–H_2O condition: almost identically to the TWC condition. This result suggests that the NO–C_3H_6 reaction and CO oxidation are dominant reactions on the TWC condition with the electric field at low temperatures (420–500 K).
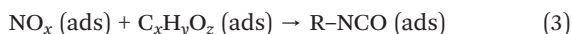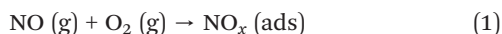
To elucidate the effect of coexistence O_2 for TWC reaction, O_2 partial-pressure-dependent tests were conducted under the NO–CO–O_2–H_2O and NO–C_3H_6–O_2–H_2O conditions with and without the electric field. As shown in Fig. S2 (ESI†), in

Table 1 NO conversion over 0.5 wt% $Pd/Ce_{0.7}Zr_{0.3}O_2$ under NO–C_3H_6–CO–O_2–H_2O reaction (NO: 2500 ppm, C_3H_6: 500 ppm CO: 3000 ppm, O_2: 2500 ppm, H_2O: 7 vol%, Ar balance, total flow: 200 cc min^{-1}) for various reactions

	NO conversion/%		
Plasma reaction	5.6 (at 375 K)	7.4 (at 468 K)	
NO decomposition in the electric field	2.7 (at 451 K)	2.3 (at 532 K)	2.5 (at 625 K)
Heated catalytic reaction	0.0 (at 420 K)	0.3 (at 449 K)	0.26 (at 478 K)
Electric field reaction with reductants (3 mA)	19.1 (at 414 K)	16.5 (at 433 K)	20.5 (at 457 K)

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the NO–CO–O_2–H_2O condition, the behavior of NO, CO and O_2 conversion rates with changing O_2 concentration was the same with and without the electric field. The NO conversion rate decreases and the CO reaction rate increases with increasing O_2 concentration. This trend suggests that CO was consumed through the CO–O_2 reaction rather than NO–CO reaction on Pd/$Ce_{0.7}Zr_{0.3}O_2$. These results demonstrate that the electric field does not contribute to the NO–CO and CO–O_2 reactions in the low-temperature region (420–500 K). In contrast, in 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 with the electric field positively depends on the O_2 concentration of 0–1000 ppm. 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 (eqn (1)–(4)).[10]

$$NO\ (g) + O_2\ (g) \rightarrow NO_x\ (ads) \tag{1}$$

$$C_xH_y\ (g) + O_2\ (g) \rightarrow C_xH_yO_z\ (ads) \tag{2}$$

$$NO_x\ (ads) + C_xH_yO_z\ (ads) \rightarrow R\text{–}NCO\ (ads) \tag{3}$$

$$NO_x\ (ads) + R\text{–}NCO\ (ads) \rightarrow N_2\ (g) + CO_2\ (g) \tag{4}$$

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 $C_xH_yO_z$ 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 DRIFT 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 1596, 1440, and 1272 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 surface of Pd/$Ce_{0.7}Zr_{0.3}O_2$ 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 band observed at 1950–1775 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. These 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
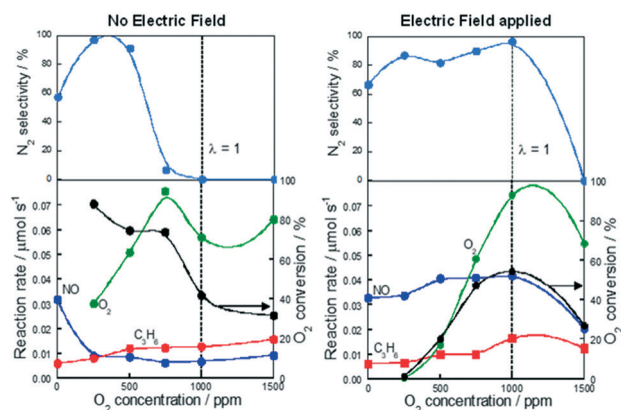

Fig. 2 NO, C_3H_6 and O_2 reaction rate, O_2 conversion and N_2 selectivity over 0.5 wt% Pd/$Ce_{0.7}Zr_{0.3}O_2$ under NO–C_3H_6–O_2–H_2O reaction (NO: 2500 ppm, C_3H_6: 500 ppm O_2: 0, 250, 500, 750, 1000 and 1500 ppm, H_2O: 7 vol%, balance gas: Ar, total flow: 200 cc min^{-1}) with/without the electric field (3 mA) at each temperatures (with: 373 K, without: 503 K).
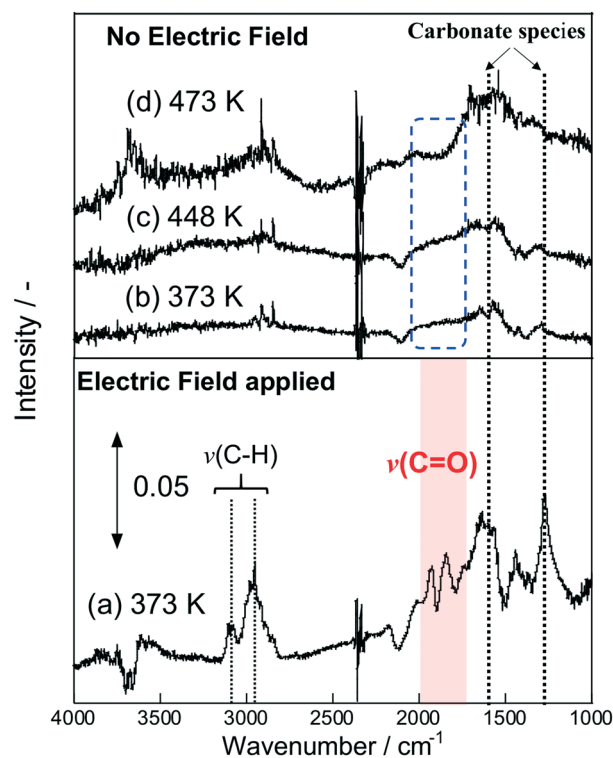

Fig. 3 DRIFT spectra of Pd/$Ce_{0.7}Zr_{0.3}O_2$ during Ar + 3000 ppm C_3H_6 flow with (a) and without (b–d) electric field (3 mA) at each temperature.

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measurements at 420–473 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.

Conclusions

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 (420–473 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 (420–473 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.

Conflicts of interest

There are no conflicts to declare.

Notes and 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*, 2001, **221**, 443–457.

3 S. Bröer and T. Hammer, *Appl. Catal., B*, 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*, 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 Worldw.*, 2010, **71**, 34–39.

10 R. Burch, J. P. Breen and F. C. Meunier, *Appl. Catal., B*, 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 H. Abdulhamid, J. Dawody, E. Fridell and M. Skoglundh, *J. Catal.*, 2006, **244**, 169–182.

18 Y. Ji, T. J. Toops, J. A. Pihl and M. Crocker, *Appl. Catal., B*, 2009, **91**, 329–338.

19 M. Haneda, Y. Kintaichi, M. Inaba and H. Hamada, *Catal. Today*, 1998, **42**, 127–135.

20 W. S. Epling, C. H. F. Peden and J. Szanyi, *J. Phys. Chem. C*, 2008, **112**, 10952–10959.

21 I. V. Yudanov, R. Sahnoun, K. M. Neyman, N. Rösch, J. Hoffmann, S. Schauermann, V. Johánek, H. Unterhalt, G. Rupprechter, J. Libuda and H. J. Freund, *J. Phys. Chem. B*, 2003, **107**, 255–264.

22 H. Tiznado, S. Fuentes and F. Zaera, *Langmuir*, 2004, **20**, 10490–10497.

23 M. Haneda, N. Bion, M. Daturi, J. Saussey, J. C. Lavalley, D. Duprez and H. Hamada, *J. Catal.*, 2002, **206**, 114–124.

24 T. Baidya, P. Bera, B. D. Mukri, S. K. Parida, O. Kröcher, M. Elsener and M. S. Hegde, *J. Catal.*, 2013, **303**, 117–129.

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