Investigation of Reaction Mechanism of NO−C₃H₆−CO−O₂ Reaction over NiFe₂O₄ Catalyst

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Supporting Information

ABSTRACT: To elucidate the reaction mechanism of NO−C₃H₆−CO−O₂ over NiFe₂O₄, we investigated the dynamics of the adsorbed and gaseous species during the reaction using operando Fourier transform infrared (FTIR). The NO reduction activity dependent on the C₃H₆ and CO concentrations suggested that NO is reduced by C₃H₆ under three-way catalytic conditions. From FTIR measurements and kinetic analysis, it was clarified that the acetate species reacted with NO−O₂ to form N₂ via NCO, and that the rate-limiting step of NO reduction was the reaction between CH₃COO⁻ and NO−O₂. The NO reduction mechanism of the three-way catalyst on NiFe₂O₄ is different to that on platinum-group metal catalysts, on which NO reduction proceeds through N−O cleavage.

INTRODUCTION

Platinum-group metals (PGMs), such as Pt, Pd, and Rh, are used as active components in automotive three-way catalysts (TWCs) to purify nitrogen oxides (NOx), unburned hydrocarbons (HC), and carbon monoxide (CO) in gasoline vehicle exhausts. Recently, the demand for PGMs has become increasing significant because of exponential increases in passenger cars in developing countries and increasingly stringent emission regulations in developed countries. However, due to the high costs and limited resources of PGMs, PGM-free automotive catalysts are highly desired.

There are few reports of PGM-free catalysts being examined under three-way catalytic conditions. Kameyama et al. reported a carburized Fe−Ce catalyst, which showed comparable activity to Pt/CeO₂ under three-way catalytic conditions. Kang et al. proposed a Cu−Ni bimetallic catalyst, which had higher activity than a monometal Cu catalyst. Some mixed oxides, for example, spinel oxides and perovskite oxides, were also reported as PGM-free TWCs. Although these catalysts exhibited moderate activities for HC and CO oxidation, the activities for NO reduction were poor, that is, the NO reduction activity dependent on the C₃H₆ and CO concentrations suggested that NO is reduced by C₃H₆ under three-way catalytic conditions. From FTIR measurements and kinetic analysis, it was clarified that the acetate species reacted with NO−O₂ to form N₂ via NCO, and that the rate-limiting step of NO reduction was the reaction between CH₃COO⁻ and NO−O₂. The NO reduction mechanism of the three-way catalyst on NiFe₂O₄ is different to that on platinum-group metal catalysts, on which NO reduction proceeds through N−O cleavage.

The NO reduction mechanism over PGM catalysts has been extensively studied with NO−CO as a model TWC reaction. Many reports have demonstrated that NO reduction proceeds with NO dissociation on a PGM catalyst by using spectroscopic techniques and theoretical calculations. Reduction of NO requires reduced M⁰ (M = metal) sites. CO removes atomic oxygen from the catalyst surface to create reduced M⁰ sites and is converted to CO₂. N−O cleavage easily occurs on the reduced catalytic sites due to the high extent of electron back donation into the molecular antibonding σ* orbital of NO, which leaves atomic nitrogen and oxygen on the surface. N₂ is produced by coupling two nitrogen atoms on the surface. The remaining oxygen atoms are removed by CO, and the reduced catalytic sites are restored. There are some reports that NCO is an intermediate species during NO reduction. Surface nitrides, which originate from NO dissociation, react with CO molecules to form NCO species. Finally, NCO is indirectly reduced NO to N₂ by removing adsorbed oxygen to restore the catalytic active sites on Rh/TiO₂. In the presence of O₂, NO reduction proceeds as described above, although the reaction rate is decreased. The reaction mechanism of NO reduction using a hydrocarbon as a reductant under stoichiometric conditions has rarely been reported. Halkides et al. reported that C₃H₆ indirectly reduced NO to N₂ by removing adsorbed oxygen to restore the catalytic active sites on Rh/TiO₂.

As for base metal oxides, the NO reduction mechanism in NO−CO has also been explored by transient experiments and theoretical studies. NO reduction is usually accompanied...
by N–O bond dissociation25–30 on base metal oxides as well as on PGMs. It has been reported that N–O dissociation occurs at the oxygen vacancy or metallic sites for CeO2,26 Cu/ CeO2,29 NiO/ CeO2,27,28 and CuO–V2O5/γ-Al2O3.30 Therefore, enhancing the reducibility of catalysts, that is, the ease of formation of oxygen vacancies or metallic sites, is an essential factor for improving NO reduction activity in NO–CO–O2.6,32,33 However, this strategy did not work well in the presence of HCs.6

Base metal catalysts are widely used in NO-selective catalytic reduction by hydrocarbons (HC-SCR) in an oxygen-rich atmosphere, such as Cu/Al2O333–35 and Ag/Al2O3.36–38 The reaction mechanism of HC-SCR has been extensively studied and it was reported that NOx and/or partially oxidized hydrocarbon species are the intermediate species.35,38–42 However, the NO reduction mechanism for NO–HC–O2 in stoichiometric amounts, much less NO–HC–CO–O2 has never been reported. In this article, we investigated the NO reduction mechanism over NiFe2O4 in NO–C3H6–CO–O2, for further development of PGM-free TWCs. To the best of our knowledge, this is the first report of the elucidation of the NO reduction mechanism over metal oxide catalysts under stoichiometric TWC conditions.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of NO conversion over NiFe2O4 in NO–C3H6–CO–O2, NO–C3H6–O2, and NO–CO–O2. NO conversion in NO–C3H6–CO–O2 was the same as that in NO–C3H6–CO–O2. The C3H6 and CO conversions during each reaction are also shown in Figure S2. C3H6 conversion was also similar in NO–C3H6–CO–O2 and NO–C3H6–O2 (Figure S2A). However, NiFe2O4 exhibited higher NO reduction activity in NO–CO–O2 than that in NO–C3H6–CO–O2. These results suggest that C3H6 is involved in NO reduction over NiFe2O4 in the three-way catalytic reaction. Furthermore, we explored the effect of C3H6 and CO concentrations on NO conversion at 325 °C, at which the NO conversion was around 14%. Figure 2 shows the NO conversion as a function of C3H6 and CO concentrations. The stoichiometry was balanced by adjusting the O2 concentration, which only slightly affected the NO reduction activity (Figure S3). When the C3H6 concentration was decreased from 1200 to 500 ppm, NO conversion also slightly decreased. Further decreasing the C3H6 concentration resulted in a significant increase in NO conversion. The NO conversion in NO–CO– O2 (C3H6 = 0 ppm) was three times higher than that under TWC conditions. This result indicates that CO is a better reducing agent for NO than C3H6 and that C3H6 might have poisoned specific catalytic sites. Actually, NO conversion was almost independent of CO concentration even in the absence of CO (CO = 0 ppm). These results indicate that C3H6 is responsible for NO reduction under TWC conditions. As shown in Figure S2B, in C3H6–CO–O2 and CO–O2, CO conversion decreased in the presence of C3H6. Therefore, C3H6 suppresses the oxidation of CO by NO or O2.

Figure 2 shows the IR spectra of the adsorbed species on the NiFe2O4 surface under various reaction conditions. For NO–O2 (h), bands at 1600, 1569, 1540, 1245 cm–1, and 1210 cm–1 were observed. These bands can be assigned to the two components of the split ν2 vibration of nitrate;43,44 bridging nitrate (1600 and 1210 cm–1), bidentate nitrate (1569 and 1245 cm–1), and monodentate nitrate (1540 cm–1). As shown in spectrum (a), two strong bands at around 1549 and 1440 cm–1 assignable to ν(COO) and ν(COO) of chelating bidentate acetate45–47 were observed for C3H6–O2. Bands at 1360 and 1310 cm–1 may be assigned to δ(CH3) of acetate48 and ν(CH3) (COO) of carboxylate, respectively. In the high wavenumber region, bands at 2953 and 2873 cm–1 derived from ν(CH3) of acetate were observed.48,50 The doublet band at 2180 and 2117 cm–1 can be assigned to the R and P branches of weakly adsorbed CO. The IR spectrum for NO–C3H6–O2 (b) was almost the same as that for C3H6–O2 (a) except for a band at 2193 cm–1 assignable to ν(CO) of NCO.51,52 For NO–CO–O2 (f), NCO was not observed. It has been reported that NCO is an intermediate in NO-selective catalytic reduction by hydrocarbons (HC-SCR)35,38,40 in an O2-rich atmosphere and NO–CO.18–21 The IR spectrum for NO–C3H6–CO–O2 (c) was almost the same as that for NO–C3H6–O2 (b). The main adsorbed species on NiFe2O4 was acetate species. The bands assignable to NOx and CO were hardly observed for NO–C3H6–CO–O2.

We also investigated the influence of C3H6 and CO concentrations on the adsorbed species on the NiFe2O4 catalysts (Figure 3b–f). The IR spectrum hardly changed regardless of the presence of CO (Figure 3b,c). This agrees with the result of the activity test, that is, NO reduction activity is almost independent of CO concentration. The IR spectrum negligibly changed when the concentration of C3H6 decreased to 250 ppm (d), at which NO reduction activity also hardly changed. Further decreasing the C3H6 concentration resulted in an enhancement in NO reduction activity and the appearance of a band at 1777 cm–1. The IR spectrum for NO–CO–O2 (f) was clearly different to that for NO–C3H6–CO–O2 (c) and showed a sharp band at 1777 cm–1. This band is attributable to NO adsorbed on Fe(III) and appeared when the catalyst had been pretreated with CO.53 In fact, this band did not appear for NO–O2 (h) or NO alone (g). The appearance of the band at 1777 cm–1 suggested that NO adsorbed on coordinatively unsaturated Fe sites. Theoretical calculations showed that NO–CO reactions over FeO3 clusters proceed by undergoing compositional changes between Fe2O2 and Fe2O3.51 In this report, CO was oxidized by O in FeO3 clusters and the clusters were reduced to Fe2O2. Subsequently, NO adsorbed on the less coordinated Fe sites. Accordingly, the presence of Fe(III)–NO

Figure 1. Temperature dependence of NO conversion over NiFe2O4 in NO–C3H6–CO–O2, NO–C3H6–O2, and NO–CO–O2.
suggests that NO reacted with CO through this redox mechanism. On the basis of the above results, it is suggested that NO$\rightarrow$CO reactions proceed at low C$_3$H$_6$ concentrations whereas NO$\rightarrow$C$_3$H$_6$ reactions dominantly proceed in the presence of some C$_3$H$_6$. These results are consistent with those of the activity dependence on C$_3$H$_6$ and CO concentrations, that is, NO reduction activity is high in the absence of C$_3$H$_6$, but it is low and independent of CO concentration in the presence of some C$_3$H$_6$.

Figure 4 shows the temperature dependence of the IR spectra for NO$\rightarrow$C$_3$H$_6$$\rightarrow$O$_2$. The bands of partially oxidized hydrocarbon were observed at 1638, 1557, 1433, and 1358 cm$^{-1}$ at various temperatures. As the reaction temperature increased, the intensity of partially oxidized hydrocarbon species decreased, and the bands almost disappeared above 400 °C. The band at 2180 cm$^{-1}$ assignable to the NCO species appeared above 250 °C, which is the light-off temperature of NO conversion, suggesting that NCO is an intermediate species of NO reduction over NiFe$_2$O$_4$. In the presence of H$_2$O (10 vol %), the intensity of the NCO band nearly diminished completely (Figure S4), which suggests that the NCO species hydrolyzed, as reported elsewhere.$^{54}$

The reactivity of the adsorbed species was examined based on transient changes in the IR spectra. For C$_3$H$_6$$\rightarrow$O$_2$ (Figure S5), acetate bands (1550 and 1440 cm$^{-1}$) appeared simultaneously with a negative band (ca. 3680 cm$^{-1}$), which is assignable to a hydroxyl group.$^{56,55}$ Consumption of the OH group along with the appearance of the acetate species suggest

![Figure 2](image2.png)  
**Figure 2.** Dependence of NO conversion on (A) C$_3$H$_6$ concentration and (B) CO concentration under stoichiometric conditions over NiFe$_2$O$_4$ at 325 °C. The stoichiometry was balanced by adjusting the O$_2$ concentration. The broken lines show NO conversion under standard TWC conditions.

![Figure 3](image3.png)  
**Figure 3.** IR spectra at (A) 3000–1100 cm$^{-1}$ and (B) 2300–1700 cm$^{-1}$ on NiFe$_2$O$_4$ at 325 °C in a flow of (a) C$_3$H$_6$$\rightarrow$O$_2$, (b) NO$\rightarrow$C$_3$H$_6$$\rightarrow$O$_2$, (c–e) NO$\rightarrow$C$_3$H$_6$$\rightarrow$CO$\rightarrow$O$_2$, (f) NO$\rightarrow$CO$\rightarrow$O$_2$, (g) NO, and (h) NO$\rightarrow$O$_2$. The concentrations of NO and CO were fixed at 1000 and 4000 ppm, respectively. The concentration ratios of C$_3$H$_6$/O$_2$ were (a–c) 1000/6000 ppm, (d) 250/3125 ppm, and (e) 125/2563 ppm.
that the OH group was removed or substituted with mainly acetate.\textsuperscript{45,56} Figure 5A shows the IR spectrum for NO$^-$O$_2$ over NiFe$_2$O$_4$ at 300 °C after treatment with C$_3$H$_6$−O$_2$. The intensity of the acetate band decreased for NO$^-$O$_2$. At the same time, the NCO band at 2177 cm$^{-1}$ appeared and the intensity subsequently decreased (Figure 5B), which is similar to the dynamics of the intermediate species concentration for sequential reactions. The band attributed to NO$_x$ was hardly observed. For a flow of O$_2$ alone, NCO was not observed, although the band intensity of CH$_3$COO$^-$ decreased (Figure S6). These results suggest a sequential reaction from CH$_3$COO$^-$, via NCO, and finally to gaseous species in flowing NO$^-$O$_2$. Figure 6 shows the effluent gas composition from the IR cell measured by a NO$_x$/CO/CO$_2$ analyzer and a mass spectrometer. When NO$^-$O$_2$ was supplied over the CH$_3$COO$^-$ preadsorbed catalyst, the signal of m/e = 28 increased. Because CO concentration was negligible, this signal was attributed to N$_2$. Therefore, CH$_3$COO$^-$ reacted with NO$^-$O$_2$ to form NCO, and NCO was finally converted to N$_2$ over NiFe$_2$O$_4$.

In a similar manner, the dynamics of the adsorbed NO$_x$ species in C$_3$H$_6$−O$_2$ was examined. The intensity of the bands assigned to nitrate species (1600, 1566, 1540, 1245, and 1213 cm$^{-1}$) increased and that of the hydroxyl group decreased (Figure S7), which suggests that NO$_x$ also reacted or substituted with surface $-$OH groups.\textsuperscript{57} After exposure of NiFe$_2$O$_4$ to NO$^-$O$_2$, C$_3$H$_6$−O$_2$ was fed to the catalyst. As shown in Figure 7A, after switching NO$^-$O$_2$ to C$_3$H$_6$−O$_2$, the intensity of the bands attributed to NO$_x$ rapidly decreased and the bands for CH$_3$COO$^-$ appeared. NCO was not observed in this procedure and gaseous NO was formed (Figure 7B). The amount of NO$_x$ was calculated from the IR band area of nitrate (1095−1355 cm$^{-1}$) using an adsorption coefficient of 15.9 cm$^{-1}$ cm$^{-2}$/μmol. The amounts of desorbed NO$_x$ (3.0 μmol; measured by the NO$_x$ analyzer) and adsorbed NO$_x$ (3.0 μmol; measured by IR) were almost the same. Therefore, NO$_x$ desorbed as a gaseous species and N$_2$ was not produced in flowing C$_3$H$_6$−O$_2$ over the NO$_x$-treated catalyst.

Figure 4. Temperature dependence of IR spectra in a flow of NO−C$_3$H$_6$−O$_2$ over NiFe$_2$O$_4$.

Figure 5A shows the IR spectrum for NO−O$_2$ over NiFe$_2$O$_4$ at 300 °C after treatment with C$_3$H$_6$−O$_2$. The intensity of the acetate band decreased for NO−O$_2$. At the same time, the NCO band at 2177 cm$^{-1}$ appeared and the intensity subsequently decreased (Figure 5B), which is similar to the dynamics of the intermediate species concentration for sequential reactions. The band attributed to NO$_x$ was hardly observed. For a flow of O$_2$ alone, NCO was not observed, although the band intensity of CH$_3$COO$^-$ decreased (Figure S6). These results suggest a sequential reaction from CH$_3$COO$^-$, via NCO, and finally to gaseous species in flowing NO−O$_2$. Figure 6 shows the effluent gas composition from the IR cell measured by a NO$_x$/CO/CO$_2$ analyzer and a mass spectrometer. When NO−O$_2$ was supplied over the CH$_3$COO$^-$ preadsorbed catalyst, the signal of m/e = 28 increased. Because CO concentration was negligible, this signal was attributed to N$_2$. Therefore, CH$_3$COO$^-$ reacted with NO−O$_2$ to form NCO, and NCO was finally converted to N$_2$ over NiFe$_2$O$_4$.

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Figure 5. Dynamic changes of (A) IR spectra and (B) IR intensities of each band as a function of time in a flow of NO−O$_2$ at 300 °C over NiFe$_2$O$_4$ on which acetate species were preadsorbed.
From the above results, it can be concluded that the activation of \( \text{C}_3\text{H}_6 \) to partially oxidized species is an important step for NO reduction, and NCO is the intermediate species during NO reduction.

We carried out kinetic analyses to explore the reaction between \( \text{CH}_3\text{COO}^- \) and \( \text{NO}^-\text{O}_2 \) during the TWC reaction. The initial rate of \( \text{CH}_3\text{COO}^- \) consumption, \( \frac{d[\text{CH}_3\text{COO}^-]}{dt} \) (Figure S8), in \( \text{NO}^-\text{O}_2 \) was calculated from the transient reaction of acetate with \( \text{NO}^-\text{O}_2 \). The concentration of \( \text{CH}_3\text{COO}^- \) was estimated using the Lambert–Beer equation,

\[
A = \frac{\varepsilon CW}{S}
\]

where \( A \), \( \varepsilon \), \( C \), \( W \), and \( S \) represent the absorbance of the IR spectra at 1430 cm\(^{-1}\), the extinction coefficient of \( \text{CH}_3\text{COO}^- \), the concentration of \( \text{CH}_3\text{COO}^- \), the weight of the catalyst, and the geometric area of the IR disk, respectively. The extinction coefficient of \( \text{CH}_3\text{COO}^- \) (0.124 cm\(^{-1}\) cm\(^2\)/μmol) was determined from the IR intensity of \( \text{CH}_3\text{COO}^- \) when \( \text{CH}_3\text{COOH} \) was injected into the IR disk. The amount of adsorbed \( \text{CH}_3\text{COO}^- \) was determined from \( \text{CH}_3\text{COOH} \) reacting with \( \text{O}_2 \) at 500 °C and the analysis of the amount of \( \text{CO} \) and \( \text{CO}_2 \) in the effluent gas. Initial rates of \( \text{CH}_3\text{COO}^- \) consumption at each temperature (260, 275, 300, and 325 °C) were investigated in the same manner as described above. Figure 8 displays the Arrhenius plots for the \( \text{CH}_3\text{COO}^- \) consumption rates measured in transient reactions by Fourier transform infrared (FTIR) as well as for the reaction rates of NO reduction, \( \text{C}_3\text{H}_6 \) oxidation, and \( \text{CO} \) oxidation measured in the flow reactor under TWC conditions. Table 1 shows the reaction rates and activation energies of each reaction. The activation energy of \( \text{CH}_3\text{COO}^- \) consumption was almost the same as those of NO reduction and \( \text{C}_3\text{H}_6 \) oxidation during the TWC reaction. The consumption rate of \( \text{CH}_3\text{COO}^- \) was of the same order as the oxidation rate of \( \text{C}_3\text{H}_6 \) under the TWC conditions. These results demonstrate that the reaction between \( \text{CH}_3\text{COO}^- \) and \( \text{NO}^-\text{O}_2 \) occurs during the TWC reaction and is the rate-limiting step for NO reduction. The activation energy of CO oxidation was entirely different to that of NO reduction and \( \text{C}_3\text{H}_6 \) oxidation under the TWC conditions, which supports the previous argument that CO does not contribute to NO reduction.

It has been reported that \( \text{CH}_3\text{COO}^- \) and \( \text{HCOO}^- \) are intermediate species during NO reduction for HC-SCR. To investigate the reactivity of \( \text{CH}_3\text{COO}^- \) and \( \text{HCOO}^- \), we conducted the transient reaction of adsorbed \( \text{CH}_3\text{COO}^- \) and \( \text{HCOO}^- \) in \( \text{NO}^-\text{O}_2 \). After injection of \( \text{CH}_3\text{COOH} \) or \( \text{HCOOH} \) (2 μL) and adsorption of \( \text{CH}_3\text{COO}^- \) or \( \text{HCOO}^- \) on the catalyst disk, \( \text{NO}^-\text{O}_2 \) was fed to the catalyst. Consumption of adsorbed \( \text{CH}_3\text{COO}^- \) and formation of NCO were observed (Figure S9). The consumption rate of \( \text{CH}_3\text{COO}^- \) in \( \text{NO}^-\text{O}_2 \) (3.7 μmol s\(^{-1}\)) is close to that of...
C₃H₆−O₂ treated catalysts (3.8 μmol s⁻¹). However, after adsorption of HCOOH, NCO was not formed, although the intensity of the bands assigned to HCOO⁻ decreased (Figure S10). On the basis of the stoichiometry, CH₃COO⁻ reacts with 3.5 mol of NO, whereas HCOO⁻ only reacts with 0.5 mol of NO. Accordingly, it is suggested that the contribution of CH₃COO⁻ to NO reduction is major but that of HCOO⁻ is negligible. The reaction mechanism of the transformation from CH₃COO⁻ to NCO has been considered in previous reports as follows: the reaction between CH₃COO⁻ and NO₂ gives the aci-anion of nitromethane,⁵⁹ which easily decomposes to NCO species (Scheme S1).⁵⁹,⁶⁰

The consumption rates of CH₃COO⁻ under NO, O₂ alone, or NO₂ were also investigated (Figures S11, S6, and S12, respectively, and Figure S8 and Table S1). The consumption rate of CH₃COO⁻ under NO (0.38 μmol s⁻¹) was much lower than that under NO−O₂ (3.8 μmol s⁻¹). In a flow of O₂, the CH₃COO⁻ consumption rate (2.9 μmol s⁻¹) was moderate, and was three quarters of that in a flow of NO−O₂. The ratio of the CH₃COO⁻ consumption rate in O₂ to that in NO−O₂ (2.9/3.8 = 0.76) is similar to the selectivity for the reaction of C₃H₆ with O₂ in C₃H₆−NO−O₂ (0.76) roughly estimated from activity tests (detailed in Supporting Information). It is suggested that the selectivity of the reaction of C₃H₆ with NO or O₂ under TWC conditions was determined by that of CH₃COO⁻ with NOx or O₂, which is a critical factor for determining the NO reduction activity. In a flow of NO, the consumption rate of CH₃COO⁻ under NO (0.38 μmol s⁻¹) was much lower than that under NO−O₂ (3.8 μmol s⁻¹), and the bands assignable to Fe(NO) (1820, 1777 cm⁻¹) and NCO (2180 cm⁻¹) appeared (Figure S11). The band of N₂O continued to increase in a flow of NO, unlike that in a flow of NO−O₂. The formation of N₂ was observed in a flow of NO−O₂ (Figure 6) and NO (Figure S11), and the amount of N₂ was higher in NO−O₂ than that in NO. These results suggest N₂O was not necessary for the decomposition of NCO to N₂O₂, however, O₂ promoted the reaction.⁶⁹ The consumption rate of CH₃COO⁻ under NO₂ (1.1 μmol s⁻¹) was higher than that under NO (0.38 μmol s⁻¹), showing that NO₂ reacted with CH₃COO⁻ more easily than did NO. We also investigated the CH₃COO⁻ consumption rate dependent on the O₂ partial pressures in NO−NO₂ (1.1−10 vol %) and NO (Figure S13). The consumption rate declined with decreasing O₂ partial pressures and dropped steeply without O₂. The above results suggest the role of O₂ in the reaction of CH₃COO⁻ was the oxidation of NO to NO₂, which easily reacted with CH₃COO⁻ to lead to the formation of N₂O₂. Furthermore, the effect of H₂O (10 vol %) on the CH₃COO⁻ consumption rate was examined (Figure S14). The addition of H₂O deteriorated the consumption rate by a factor of 0.35 (Table S1) and nearly diminished the intensity of the NCO band.

On the basis of the above results, the overall reaction pathway is proposed, as shown in Scheme 1. C₃H₆ is responsible for NO reduction under NO−C₃H₆−CO−O₂ reaction. CH₃COO⁻, derived from the partial oxidation of C₃H₆, reacts with NO−O₂ and NO converts to N₂ via NCO. The reaction between CH₃COO⁻ and NO−O₂ is the rate-limiting step. Accordingly, the reactivity of CH₃COO⁻ is an essential factor for determining the NO reduction activity under TWC conditions. The reaction mechanism of NO-selective catalytic reduction by hydrocarbons (HC-SCR) in an O₂-rich atmosphere was reported as follows:③⁵,⑥⁸−⁶⁰,⁶¹,⁶²−⁶⁶ NO and the hydrocarbon are oxidized to NOX and partially oxidized the hydrocarbon species (acetate, formate, enolate, or acrylate), respectively. NOX and the partially oxidized hydrocarbon species react together and convert to N₂ via NCO and/or CN species. The mechanism of NO reduction in NO−H₂−CO−O₂ on NiFe₂O₄ is entirely different to that on PGM catalysts⑩−⑬ and is similar to that under HC-SCR on base metal oxides. NO reduction on PGM catalysts is accompanied with N−O dissociation and NO does not directly interact with the reductant (CO or C₃H₆). Figures 3A and S13 show the IR spectra for NiFe₂O₄ and Rh (1 wt %)/Al₂O₃, respectively, under TWC conditions. The bands derived from NO (1896 cm⁻¹; Rh(NO)⁶²−⁶⁴ and CO (2015 and 2091 cm⁻¹; Rh(CO)₂)⁶²−⁶⁴ were observed on Rh/Al₂O₃. However, the bands attributed to NO and CO on NiFe₂O₄ were not observed and partially oxidized hydrocarbon species were predominantly adsorbed. The Rh/Al₂O₃ catalyst maintained its metallic sites to adsorb NO in the presence of O₂, which are effective for NO dissociation. However, the surface of the NiFe₂O₄ catalyst was mostly covered by oxygen during the reaction. Therefore, the reaction pathway via oxygenates similar to SCR under oxygen-rich conditions may be preferable for base metal oxide catalysts. Even in the presence of C₃H₆, adsorption of NO and CO was observed on Rh/Al₂O₃ but was not observed on NiFe₂O₄. This might be why the reaction between NO and CO did not occur on NiFe₂O₄. The coverage of adsorbates should be one of the essential factors for the determination of the reaction mechanism under TWC conditions.

Although the NO reduction mechanism during the TWC reaction on NiFe₂O₄ (Scheme 1) is similar to that during NO-selective catalytic reduction (under O₂-rich conditions), NiFe₂O₄ exhibited low NO reduction activity under O₂-rich conditions (λ > 1).⁶³ The density of the adsorbed CH₃COO⁻ on NiFe₂O₄ in C₃H₆−O₂ was 3.02 nm² cm⁻³, which was calculated from the amount of adsorbed CH₃COO⁻ and the Brunauer–Emmett–Teller surface area. This value indicates that the CH₃COO⁻ species almost completely covered the NiFe₂O₄ surface (detailed in Supporting Information).⁶⁵ Further, the basic OH group was removed or exchanged upon adsorption of CH₃COO⁻ and NOx (Figures S5 and S7), suggesting that both were adsorbed on the same sites (M⁻−O sites).⁶⁵ NOx species hardly adsorbed on NiFe₂O₄ during steady-state TWC reactions because of competitive adsorption of hydrocarbon oxygenates, which may adsorb more strongly on NiFe₂O₄. Accordingly, CH₃COO⁻ reacted with gaseous NO or weakly adsorbed NOx species. The unbalanced adsorption of the C₃H₆− and NO-derived species may be the reason for the low selectivity of CH₃COO⁻ as a reductant of NOx. In other words, adsorption of NOx in the presence of C₃H₆ may enhance the NOx reduction activity during the TWC reaction on NiFe₂O₄ catalyst.

### CONCLUSIONS

The TWC reaction mechanism on NiFe₂O₄ was investigated using in situ and operando FTIR measurements, and was elucidated to be as follows: CH₃COO⁻, which originates from C₃H₆−O₂, reacts with NO−O₂ to form N₂ via NCO on NiFe₂O₄ under three-way catalytic conditions. The reaction

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**Scheme 1. Reaction Mechanism on NiFe₂O₄ under TWC Conditions**

\[ C_3H_6 + O_2 \rightarrow CH_3COO^⁻ + NO + O_2 \rightarrow N_2 \]
between CH₃COO⁻ and NO−O₂ is the rate-limiting step during NO reduction. The results of the present work give us a distinct strategy for the further development of base metal oxide TWCs, such as controlling the adsorption energy of the CH₃COO⁻ species.

**METHODS**

NiFe₂O₄ catalysts were prepared by a reverse strike coprecipitation method described elsewhere. Fe(NO₃)₃·9H₂O (purity 99%, Kishida Chemical Co., Ltd, Japan) and Ni(NO₃)₂·6H₂O (purity 98%, Kishida Chemical Co., Ltd, Japan) in an atomic ratio of Fe/Ni = 2:1 were dissolved in 100 mL of distilled water. An aqueous solution of Fe and Ni nitrates were prepared as a balance (NO, C₃H₆, and CO were stoichiometric conditions (for the NO–C₃H₆–O₂ reaction), or 1500 ppm (for the NO–O₂ reaction)) to balance the stoichiometric conditions.) C₃H₆–O₂ (NO 1000 ppm and O2 4000 ppm) was fed to the catalyst in a flow of NO–O₂ after pretreatment of the catalyst in a flow of NO–O₂. The FTIR cell was connected to a NOx/CO/CO₂ analyzer (Horiba VIA-3100) and a quadrupole mass spectrometer (MicrotracBEL BELMass) to analyze the effluent gas composition. In particular, N₂ and CO can be distinguished by the combination of the mass spectrometer (mass-to-charge ratio, m/e, is 28) and the CO analyzer.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00165.

Synchrotron XRD pattern, temperature dependence of C₃H₆ and CO conversion, dependence of NO conversion on O₂ concentration, IR spectra in the presence of H₂O, dynamic changes of IR spectra as a function of time in various gases, adsorbed CH₃COO⁻ concentration as a function of time under each gas condition, the CH₃COO⁻ consumption rate under each gas condition, and IR spectra on Rh/Al₂O₃ (PDF)

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Notes

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