

Role of Acetate and Nitrates in the Selective Catalytic Reduction of NO by Propene over Alumina Catalyst as Investigated by FTIR

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The mechanism of the selective catalytic reduction (SCR) of NO by C₃H₆ on Al₂O₃ was investigated using in situ IR spectroscopy. Attention was focused on the reactivity of the adsorbed acetate and nitrates on the Al₂O₃ surface. IR spectra showed that the reaction starts with the nitrates formation from NO + O₂ followed by its reaction with C₃H₆ to form acetate, which becomes the predominant surface species in the steady-state condition. The acetate band, which was stable in He or NO, significantly decreased when the flowing gas was switched to NO + O₂. A complementary set of experiments monitoring gas composition showed that N₂ and CO_x were produced by the reaction of acetate with NO + O₂. The rate of acetate consumption in NO + O₂ exhibited the same order of magnitude as the NO reduction rate, indicating that the acetate is active as a reductant and takes part in the N₂ formation. Nitrates can oxidize both C₃H₆ and acetate, and are mostly reduced to N₂. A proposed reaction scheme explains the role of O₂ in facilitating SCR of NO.

Introduction

It is widely accepted that selective catalytic reduction (SCR) of NO by hydrocarbons is a potential method to remove NO_x practically in excess O₂.^{1,2} Although many studies on SCR are related to zeolitic catalysts, metal oxides are also of importance as promising SCR catalysts due to their high durability.^{3–5} Among oxide catalysts, γ -Al₂O₃ is one of the most active single oxides for SCR.⁵ Al₂O₃ is also used as a support of SCR catalysts and is suggested to be responsible for certain steps of this reaction.^{5,6} Thus, the catalytic functions of Al₂O₃ during SCR are of interest in terms of the surface chemistry of SCR.

Although the reaction mechanisms of SCR have been studied by many research groups, considerable disagreements are found in the literature regarding the reaction mechanism. By considering some recent proposals,^{2,5,7–9} the literature data fall into one of three main categories summarized as follows: (a) hydrocarbons are converted to some intermediates, which then interact with NO_x;^{10,11} (b) NO is oxidized to NO₂ or surface NO_y complexes, which then interact with hydrocarbons;^{12–18} (c) a redox type mechanism with the direct decomposition of NO as the crucial step.¹⁹ After extensive studies were devoted to the SCR mechanism over metal-exchanged zeolites, some data were collected on the nature of the surface complexes formed during adsorption of reagents. Among them, however, very few are focused on the kinetics of the reaction of the surface species,^{17,18,20} which can give important information on the role of the surface species.

On the other hand, rather few studies have focused on the SCR mechanism on the metal oxide catalysts. As for γ -Al₂O₃, on which redox-type mechanism c is unlikely, hypotheses b have first been proposed on the basis of some empirical evidence.^{12,13} Hypothesis a is also likely from the result that formation of carbonaceous radicals were detected during SCR on Al₂O₃ and were found to correlate with the activity.¹⁰ However, these

observations can be regarded as empirical in nature. Hence, the mechanism of SCR is still controversial even on Al₂O₃, which is among the simplest surfaces on which SCR is observed.

In this study, we have carried out in situ FTIR spectroscopic studies on the formation and the reaction of adsorbed species in SCR of NO by C₃H₆ over Al₂O₃. It was of particular interest to clarify the role of adsorbed acetate and nitrates; the transient reactions of acetate with NO + O₂ and nitrates with C₃H₆ were followed by IR and GC analysis, and the reaction rates of surface and gas-phase molecules were compared.

Experimental Section

γ -Al₂O₃ was a reference catalyst of the Catalysis Society of Japan²¹ (JRC-ALO-1A, BET surface area = 160 m² g⁻¹). The sample was pressed into a 0.1 g self-supporting wafer and mounted into a quartz IR cell with CaF windows. In situ IR spectra were recorded on a JASCO FT/IR-300 equipped with the IR cell connected to a conventional flow reaction system, which was used in our previous study.¹⁸ All the spectra were measured at the reaction temperatures, accumulating 100 scans at a resolution of 4 cm⁻¹. A reference spectrum of Al₂O₃ in He was subtracted from each spectrum. Prior to each experiment, the catalyst was (1) heated in 6.7% O₂/He at 773 K for 1 h and (2) cooled to the desired temperature and purged for 30 min with He, (3) and then various gas mixtures were fed at a flow rate of 42 mL min⁻¹. The concentrations of NO, C₃H₆, and O₂ in the gas mixtures were 1000 ppm, 300 ppm, and 6.7% with He balance, respectively. To obtain IR spectra of the adsorbed carboxylate ions, formic acid (270 μ mol g(catalyst)⁻¹), acetic acid (90 μ mol g(catalyst)⁻¹), and propionic acid (70 μ mol g(catalyst)⁻¹) were introduced onto the catalyst wafer at 573 K as a pulse in the He carrier, followed by purging in He for 60 min, and then spectra were recorded at 573 K.

The extinction coefficient of the nitrates on Al₂O₃ was determined in the following fashion. The catalyst in the IR cell was first exposed to a flow of NO + O₂ for various exposure times at 573 K. After purging in He for 30 min, IR spectra of

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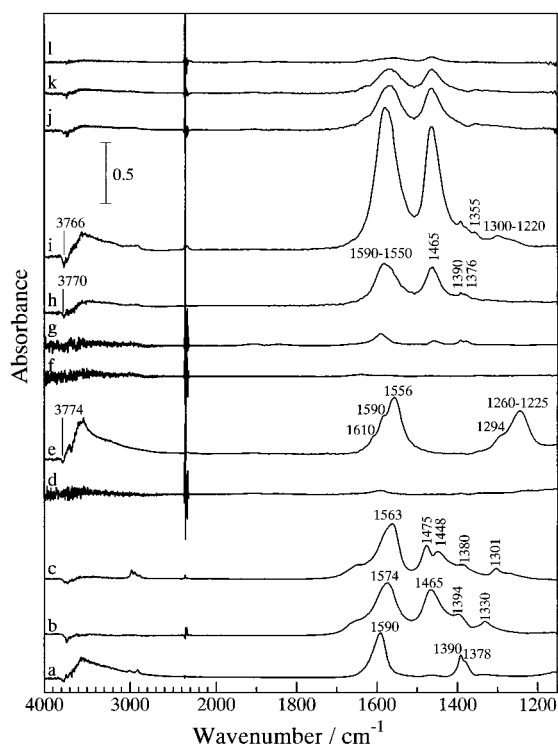


Figure 1. IR spectra of adsorbed species on Al_2O_3 taken at 573 K (a–i) and at various temperatures (j–l): (a) formic acid, (b) acetic acid, (c) propionic acid, after flowing (d) NO for 200 min, (e) NO + O_2 for 200 min, (f) C_3H_6 for 200 min, (g) C_3H_6 + NO for 200 min, (h) C_3H_6 + O_2 for 600 min, after flowing NO + C_3H_6 + O_2 (i) at 573 K for 600 min, (j) at 623 K for 200 min, (k) at 673 K for 200 min, and (l) at 773 K for 200 min.

nitrates on the catalyst were recorded. Then, the catalyst was heated in He to 823 K (10 K/min) while monitoring the amount of desorbed NO_x ($\text{NO} + \text{NO}_2$) by an on-line NO_x analyzer, and thus the total amount of adsorbed nitrates was estimated. A good linear plot was obtained between the amount of nitrates and the peak area of the nitrates band (in the range 1162–1350 cm^{-1}). The extinction coefficient of nitrates determined from the slope of this line was $1.3 \times 10^{-17} \text{ cm}^{-1} \text{ cm}^2/\text{molecule}$.

The extinction coefficient of the acetate on Al_2O_3 was determined in the following fashion. Various amounts of acetic acid ($<150 \mu\text{mol g}(\text{catalyst})^{-1}$) was introduced to the catalyst wafer at 573 K, and IR spectra of the acetate on the catalyst were recorded. On-line GC analysis confirmed that all the acetic acid was adsorbed on the catalyst. A good linear plot was obtained between the amount of acetic acid introduced and the peak area of the acetate band. The extinction coefficient of acetate determined from the slope of this line was $1.7 \times 10^{-17} \text{ cm}^{-1} \text{ cm}^2/\text{molecule}$.

To determine the steady-state and transient activity for the reaction, separate experiments were performed in a conventional flow reactor with 7.0 g of a catalyst at a flow rate of 100 mL min^{-1} under the condition where both NO and C_3H_6 conversions were mostly below 30%. Product analysis was performed by a gas chromatograph and NO_x analyzer (Best BCL-100 uH). The pretreatment of the sample and the concentrations of reaction mixtures were the same as in the corresponding IR experiments.

Results

1. Identification of the Adsorbed Species. Figure 1 shows the IR spectra of surface species on Al_2O_3 formed at 573 K in flowing various gas mixtures and from reference compounds

(formic acid, acetic acid, and propionic acid). In $\text{NO} + \text{O}_2$ (spectrum e), the bands at 1610, 1590, 1556, 1294, and around 1225–1260 cm^{-1} were observed. In the literature, the couples of bands in the region 1650–1500 cm^{-1} and 1170–1300 cm^{-1} are often assigned to the ν_3 split stretching vibration of the nitrates on the metal oxides.^{22–24} Previously, Parkyn²⁴ reported the IR spectrum of NO_2 adsorbed on Al_2O_3 , and assigned the bands at 1570 and 1290 cm^{-1} to unidentate nitrate and the bands at 1590 and 1610 cm^{-1} with the corresponding unresolved band at around 1225–1250 cm^{-1} to bidentate and bridging nitrates, respectively. The bands at 1556 and 1294 cm^{-1} and the bands at 1590 and 1610 cm^{-1} with the corresponding unresolved band at around 1225–1260 cm^{-1} observed in this study are almost consistent with those observed by Parkyn and are assigned to unidentate, bidentate, and bridging nitrates, respectively. In NO (spectrum d), a band assignable to nitrate was observed at around 1600 cm^{-1} , though its intensity was much less than in $\text{NO} + \text{O}_2$.

In flowing $\text{C}_3\text{H}_6 + \text{O}_2$ (spectrum h), two strong bands at around 1550–1590 and 1465 cm^{-1} and two weak bands at 1390 and 1376 cm^{-1} were observed. The frequencies of the bands at around 1550–1590 and 1465 cm^{-1} are in good agreement with those of acetic acid adsorbed on the same catalyst (spectrum b). Similar bands were also reported in a previous study with acetic acid adsorbed on Al_2O_3 .²⁵ Thus, the bands at around 1550–1590 and 1465 cm^{-1} are assignable to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ of adsorbed acetate. This indicates that acetate ion is formed on the surface of Al_2O_3 from the reaction of $\text{C}_3\text{H}_6 + \text{O}_2$. The frequencies of the weak bands at 1390 and 1376 cm^{-1} are in good agreement with those of formic acid adsorbed on the same catalyst (spectrum a) and those found in previous studies with formate adsorbed on Al_2O_3 .^{26,27} Thus, the bands at 1390 and 1376 cm^{-1} are assignable to $\nu_{\text{s}}(\text{COO})$ and $\delta(\text{CH})$ of adsorbed formate, respectively. In $\text{C}_3\text{H}_6 + \text{NO}$ (spectrum g), the acetate bands were observed, though their intensity was much less than in $\text{C}_3\text{H}_6 + \text{O}_2$. In C_3H_6 (spectrum f), the acetate bands were hardly observed.

IR spectra of adsorbed species in $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ at various temperatures (573–773 K) in the steady states are also shown in Figure 1 (spectra i–l). Two strong bands at around 1550–1590 and at 1465 cm^{-1} due to the acetate were observed. A band at 1355 cm^{-1} may be assignable to $\delta(\text{CH}_3)$ of acetate.^{28,29} It was found that the main surface species formed during the reaction is the acetate over a wide range of temperatures. In addition, weak bands due to nitrates (1297 cm^{-1} with a shoulder at 1245 cm^{-1}) and formate (1390 and 1376 cm^{-1}) were also observed at 573 K.

In the O–H stretching region of the spectra, bands with negative absorbance appeared at around $3770 \pm 4 \text{ cm}^{-1}$ during exposure to $\text{C}_3\text{H}_6 + \text{O}_2$, $\text{NO} + \text{O}_2$, and $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$. This result can be interpreted that the formation of nitrates and acetate results in the consumption of OH group having the same nature. The OH band at around 3760–3780 cm^{-1} was identified as being coordinated to an tetrahedral Al site and termed the I-a group by Knozinger et al.,³⁰ and it is generally ascribed to the basic hydroxyl group.^{30,31} Eischens et al.³² reported that higher frequency OH bands (above 3700 cm^{-1}) were consumed during carboxylate formation on $\gamma\text{-Al}_2\text{O}_3$ and concluded that the formation of carboxylate is related to the basic hydroxyl groups. On the other hand, Boehm³³ studied the adsorption of NO_2 on $\eta\text{-Al}_2\text{O}_3$ and suggested that formation of nitrate is related to the basic OH[−] groups. Parkyns proposed that nitrate on Al_2O_3 is held by coordination through its oxygen atoms to the exposed Al^{3+} cation site.²⁴ From the above-mentioned, it is suggested

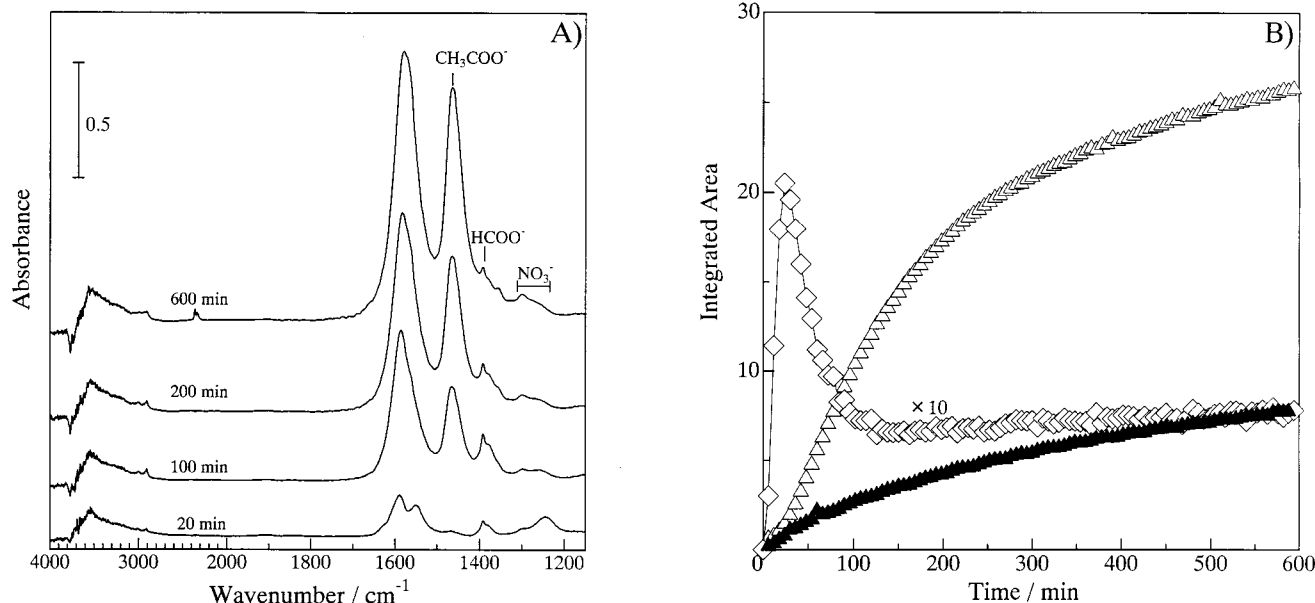


Figure 2. (A) IR spectra of adsorbed species on Al_2O_3 recorded as a function of time in flowing $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ at 573 K. (B) Time dependence of the integrated areas of the band in the range $1417\text{--}1506\text{ cm}^{-1}$ (Δ , acetate) and in the range $1193\text{--}1319\text{ cm}^{-1}$ (\diamond , nitrate). (\blacktriangle) denotes the change of the acetate band area in flowing $\text{C}_3\text{H}_6 + \text{O}_2$ at 573 K.

that the basic OH group is reactive and removed or exchanged upon formation of nitrates and acetate, resulting in coordination of nitrates and acetate on the Al–O site with an anion vacancy ($\text{Al}_{\text{CUS}}\text{--O}$ site).

2. Dynamic Changes of Surface Molecules during SCR.

Figure 2A shows the change of the IR spectra of adsorbed species recorded during $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ reaction at 573 K. After 20 min exposure, the bands due to nitrates (1245 and 1297 cm^{-1}) and formate (1390 and 1376 cm^{-1}) were observed, together with a weak band due to acetate (1465 cm^{-1}). Figure 2B shows the changes in the integrated intensities of the bands due to acetate (in the region $1417\text{--}1506\text{ cm}^{-1}$) and nitrates ($1193\text{--}1319\text{ cm}^{-1}$) with time on stream. The total intensity of the nitrates bands sharply increased at first, reached a maximum after 20 min, and then decreased and became constant. The intensity of the acetate band exhibited an induction period for 20 min and then increased with time on stream. These results indicate that the nitrates are first formed on the surface of Al_2O_3 in a flow of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$, and then nitrates may be consumed and/or substituted by acetate. In a steady-state condition, acetate is considered to be the most abundant species on the Al_2O_3 surface during SCR.

The IR result of the hydroxyl group region in Figure 2A shows that intensity of the negative band at 3766 cm^{-1} due to the basic OH group increased with time on stream in a flow of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$, which is likely to coincide with an increase of the acetate band. This result suggests again the coordination of acetate on the $\text{Al}_{\text{CUS}}\text{--O}$ site.

Acetate was also formed in $\text{C}_3\text{H}_6 + \text{O}_2$ as shown in Figure 1. Figure 2B includes the change in the intensity of the acetate band during the reaction of $\text{C}_3\text{H}_6 + \text{O}_2$ at 573 K. The initial rate of acetate formation in $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ is about 5 times higher than that in $\text{C}_3\text{H}_6 + \text{O}_2$.

3. Reactivity of Nitrates. The reactivity of nitrates toward hydrocarbon reductant was evaluated by the transient response of the IR spectra at 573 K (Figure 3A). Tests were made by exposure of the catalyst to flowing $\text{NO} + \text{O}_2$ for 200 min, followed by purging in He for 180 min, and then exposure to flowing C_3H_6 . During the tests, IR spectra were recorded as a function of time. Figure 3B shows the time course of the nitrates

concentration estimated from the integrated intensities of the nitrate bands (in the range $1162\text{--}1350\text{ cm}^{-1}$) and extinction coefficient of nitrates. As shown in the figures, nitrates decreased only slightly in He, indicating that nitrates are relatively stable in an inert gas. However, when the flowing gas was switched to C_3H_6 , the nitrate bands significantly decreased. Simultaneously, an acetate band appeared and its intensity increased with time. After 600 min, the nitrate bands disappeared and the spectrum was analogous to that in a flow of $\text{C}_3\text{H}_6 + \text{O}_2$ shown in Figure 1. These results indicate the consumption of the adsorbed nitrates through the reaction with C_3H_6 and simultaneous C_3H_6 oxidation to the acetate. It should be noted that the rate of the increase of the nitrate band in $\text{NO} + \text{O}_2$ was about 3 times larger than that of the decrease in the reaction with C_3H_6 , indicating that the reaction rate of nitrate with C_3H_6 is lower than that of nitrate formation in the $\text{NO} + \text{O}_2$ reaction.

Figure 4 shows the results of another set of experiments to determine the rate of gaseous product formation in the reaction of adsorbed nitrates with C_3H_6 . When the catalyst, pretreated in a flow of $\text{NO} + \text{O}_2$ for 360 min, was exposed to a stream of C_3H_6 , N_2 and CO_x (CO_2 and CO) were produced with a gradual decrease in their formation rates as shown in the figure. It should be noted that a very small amount of NO formation and no formation of NO_2 or N_2O were observed. These results indicate that the nitrates adsorbed on the Al_2O_3 surface were mostly reduced to N_2 through the reaction with C_3H_6 as a reductant.

The rates of nitrate consumption, $d[\text{NO}_3^-]/dt$, during the above transient reaction were determined by numerically differentiating the data in Figure 3B and were plotted in Figure 4. Clearly, the rates of nitrates consumption were very close to those of N_2 and CO_x formation. Further, the rate of nitrates consumption was almost twice as much as the rate of N_2 formation. From these results, it is quantitatively confirmed that most of the nitrates are reduced to N_2 with participation of C_3H_6 as a reductant.

4. Reactivity of Acetate. The reactivity of the acetate was evaluated in essentially the same manner as above. The catalyst wafer was first exposed to a flow of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ for 600 min to produce the adsorbed acetate (spectrum a in Figure 5A). After switching the flowing gas to He (spectrum b), the acetate

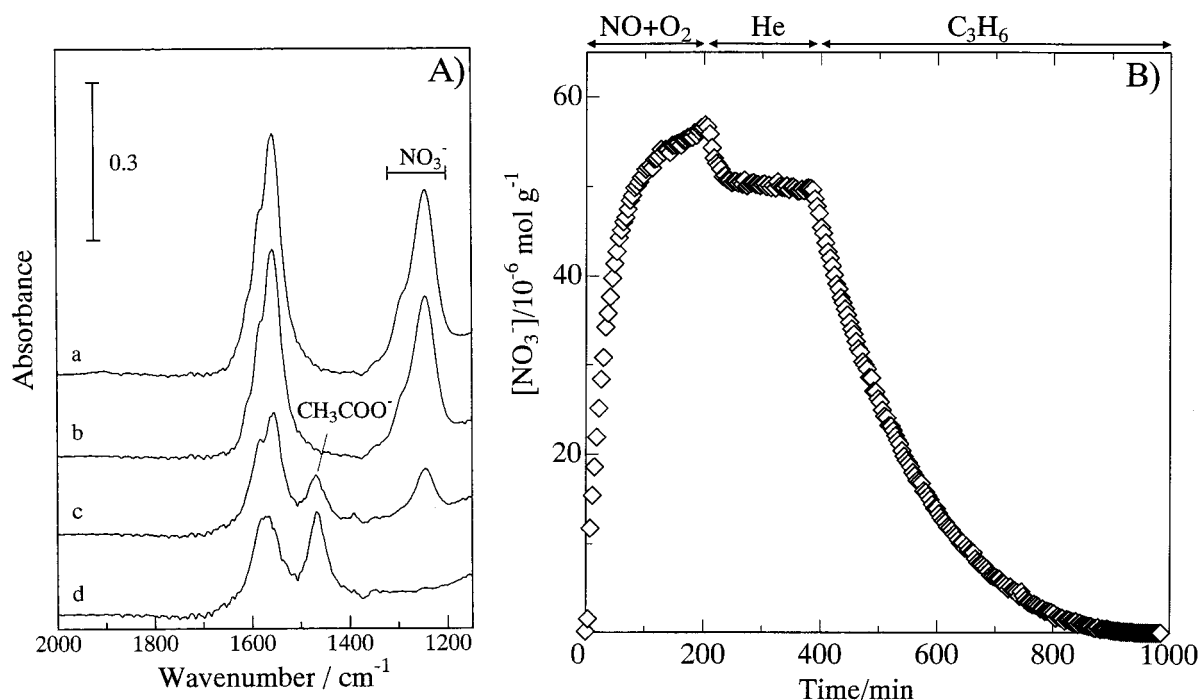


Figure 3. (A) IR spectra of adsorbed species on Al_2O_3 at 573 K. The spectra were measured (a) after flowing $\text{NO} + \text{O}_2$ for 200 min, followed by (b) He purge for 180 min, and by switching to flowing C_3H_6 for (c) 200 min and (d) 600 min. (B) Time dependence of the nitrate concentration.

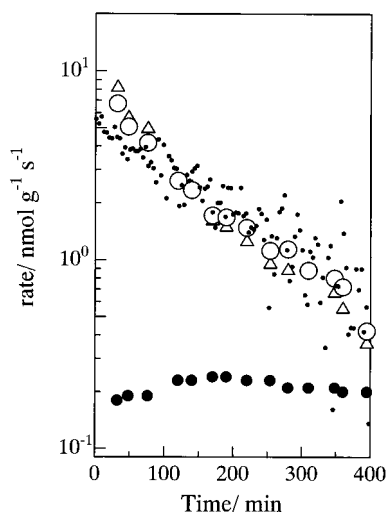


Figure 4. Rate of the nitrates consumption (small dots) and the formation rates of $2 \times \text{N}_2$ (O), NO (●), and CO_x (Δ) in flowing C_3H_6 as a function of time. Before the measurement, the catalyst was pretreated in $\text{NO} + \text{O}_2$ for 360 min at 573 K.

band (1465 cm^{-1}) was hardly changed. In contrast, when the gas was switched to $\text{NO} + \text{O}_2$ (spectra c and d), the intensity of the acetate band decreased with time and the nitrate bands appeared. Figure 5B shows the change in the integrated intensity of acetate band as a function of time after the feed was switched from $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ to He, O_2 , NO, or $\text{NO} + \text{O}_2$. The intensity hardly decreased in He or in NO, indicating that the acetate is stable in an inert gas and NO. The acetate band fairly decreased in O_2 , indicating that the acetate fairly reacts with O_2 . In contrast, the band significantly decreased in $\text{NO} + \text{O}_2$, indicating that the acetate has high reactivity with $\text{NO} + \text{O}_2$.

Figure 6 shows the results of another set of experiments to determine the rate of gaseous products formed during the transient reaction. The catalyst was first pretreated at 573 K for 600 min in a flow of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$, and the steady-state activity was obtained. The catalyst was then exposed to a

stream of He, O_2 , NO, or $\text{NO} + \text{O}_2$ at 573 K. When the pretreated catalyst was exposed to a flow of $\text{NO} + \text{O}_2$, N_2 and CO_x (CO_2 and CO) were produced with a gradual decrease in their formation rates. In contrast, N_2 was hardly produced on the exposure of pretreated catalyst to He, O_2 , and NO. In O_2 , CO_x was fairly produced with a gradual decrease in its formation rate.

By using the IR data in Figure 5 and the extinction coefficient of the acetate, the rates of acetate consumption, $d[\text{CH}_3\text{COO}^-]/dt$, during the above transient reaction of CH_3COO^- with $\text{NO} + \text{O}_2$ were determined. As shown in Figure 7, the rate of acetate consumption was on the same order of magnitude as the rates of NO reduction to N_2 and CO_x formation during the same transient reaction. This result semiquantitatively confirms a reaction pathway that the acetate is oxidized by $\text{NO} + \text{O}_2$ to produce N_2 and CO_x . A difference between the rate of acetate consumption and the rates of NO reduction and CO_x formation observed in the initial period of the transient reaction would suggest that this step is not a simple reaction.

Discussion

1. Role of Oxygen as an Initiator of SCR. Since the addition of O_2 dramatically enhances the rate of NO reduction on Al_2O_3 and other SCR catalysts,^{1,5,34,35} it is generally accepted that the role of oxygen is of primary importance to discuss the reaction mechanism of SCR.^{2,5,7-9} Some published data suggest that oxygen plays an important role for the activation of one of the reactants, NO¹²⁻¹⁸ or hydrocarbon,¹⁰ in the first step of the overall process. Here, we begin our discussion as to how the SCR of NO on Al_2O_3 begins in view of the role of oxygen.

From our IR results (Figure 1), it was shown that NO hardly adsorbed on the surface of Al_2O_3 . However, the formation of nitrates (adsorbed NO_2 species) was observed in $\text{NO} + \text{O}_2$. These imply that the formation of nitrates is greatly promoted by the presence of O_2 . It is considered that the formation of nitrates proceeds by NO oxidation and the subsequent adsorption of NO_2 on basic oxygen sites.

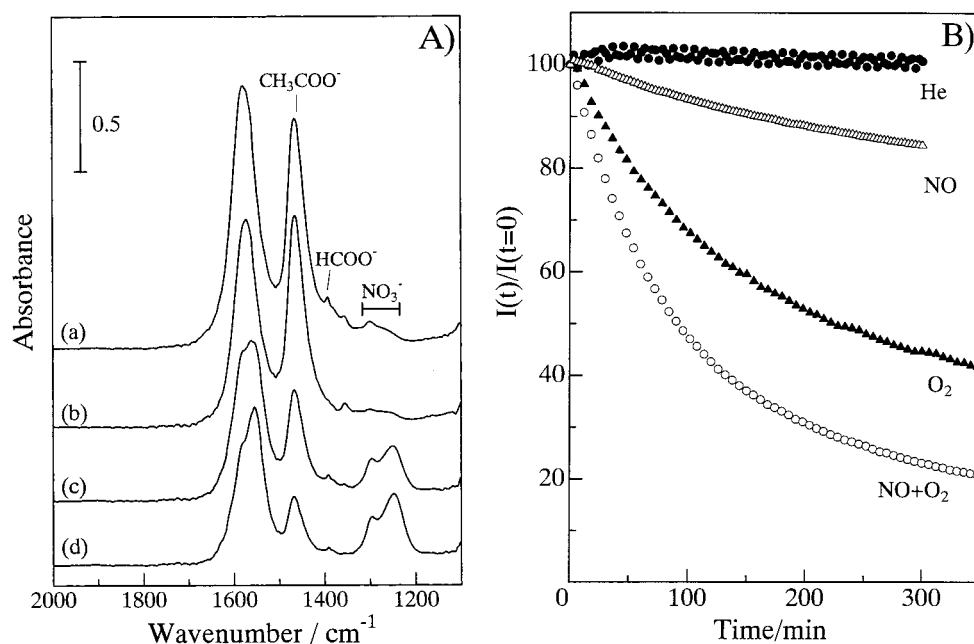


Figure 5. (A) IR spectra of adsorbed species on Al_2O_3 at 573 K taken (a) after flowing $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ for 600 min, followed by (b) He purge for 100 min, in flowing $\text{NO} + \text{O}_2$ after (a) for (c) 100 min and (d) 200 min. (B) Time dependence of the relative intensities of the acetate band (in the range $1417\text{--}1506\text{ cm}^{-1}$) normalized by initial intensity in (○) $\text{NO} + \text{O}_2$, (▲) O_2 , (△) NO , and (●) He. Before the measurements, the catalyst was pretreated in $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ for 600 min at 573 K.

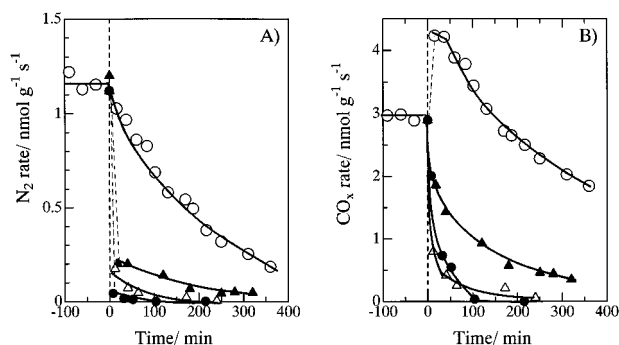


Figure 6. Formation rates of N_2 (A) and CO_x (B) as a function of time in flowing (○) $\text{NO} + \text{O}_2$, (▲) O_2 , (△) NO , and (●) He. Before the measurements, the catalyst was pretreated in $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ for 600 min at 573 K.

A reactivity test of the nitrates in the presence of gas-phase C_3H_6 (Figure 3A) showed that nitrates can react with C_3H_6 to form the acetate adspecies on the Al_2O_3 surface. Since introduction of C_3H_6 on the Al_2O_3 surface hardly produced acetate (Figure 1), nitrates are found to oxidize C_3H_6 to the acetate. As shown in Figure 2, acetate was also formed in $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ and in $\text{C}_3\text{H}_6 + \text{O}_2$ and the rate of acetate formation was higher in the former reaction. Taking into account that nitrates were present on the surface in $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ (Figure 2A), it is shown that the rate of C_3H_6 oxidation to the acetate is increased in the presence of nitrates. From these results, it is revealed that one of the roles of the nitrates during SCR is to promote C_3H_6 oxidation to the acetate. In our previous study of SCR on Na-H-mordenite catalyst, it was also shown that nitrate oxidizes C_3H_6 to surface organic species.¹⁸ By consequence, it can be concluded that oxygen acts as an initiator of SCR through the activation of both reactants.

2. Role of Acetate and Nitrates. As shown in Figure 1, the main adspecies during $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ on Al_2O_3 was the acetate. When the acetate formed by $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ was exposed to $\text{NO} + \text{O}_2$ (Figures 5 and 6), the acetate reacted and N_2 and CO_x were produced. Whereas, in He or NO , acetate did

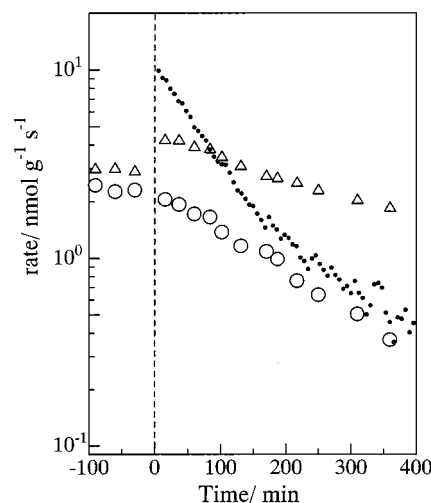
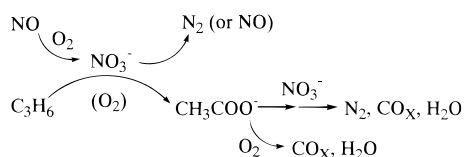


Figure 7. Rate of the acetate consumption (small dots) and the formation rates of $2 \times \text{N}_2$ (○) and CO_x (△) in flowing $\text{NO} + \text{O}_2$ as a function of time. Before the measurement, the catalyst was pretreated in $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ for 600 min at 573 K.

not react and N_2 was hardly produced. Further, the rate of NO reduction to N_2 during the reaction of the acetate with $\text{NO} + \text{O}_2$ and the acetate consumption rate determined by IR were on the same order of magnitude (Figure 7). It should be noted that the acetate formed by the reaction of $\text{C}_3\text{H}_6 + \text{O}_2$ also reacted preferentially in $\text{NO} + \text{O}_2$ to produce N_2 , CO , and CO_2 .³⁶ From these results, combined with the result that the nitrates were immediately formed in $\text{NO} + \text{O}_2$ (Figure 3B), it is shown that the acetate is an active reductant which can react with $\text{NO} + \text{O}_2$, or in other words, with the nitrates.

However, the subsequent steps are not clear yet. As proposed in our previous study,¹⁸ the consecutive reaction of surface organic species, such as N-containing hydrocarbon species, with nitrates could proceed to form N_2 as a final product. These steps may explain a higher rate of acetate consumption than the rates of NO reduction (Figure 7). Further investigations are in progress to answer this question.

SCHEME 1



When the nitrates formed by $\text{NO} + \text{O}_2$ were exposed to C_3H_6 , N_2 and CO_x were produced in the gas phase. The nitrates consumption rate and N_2 formation rate were on the same order of magnitude, and the ratio of these rates was around 2:1 (Figure 4). Therefore, it is quantitatively confirmed that nitrates are the reactive species, which are reduced to N_2 with participation of C_3H_6 as a reductant.

3. Possible Reaction Pathways. The above results can be summarized as in Scheme 1, which shows possible pathways of this reaction. The reaction starts with the formation of adsorbed nitrates via the NO oxidation by O_2 , which is followed by the formation of acetate via the partial oxidation of propene with nitrates and possibly with O_2 . The formation of N_2 occurs when the nitrates are reduced by C_3H_6 and the acetate. These two routes are the possible pathways of NO reduction on the Al_2O_3 surface, and the dominant NO reduction pathway during the reaction can change depending on the reaction condition. Acetate can also react with O_2 and produced CO_x (Figure 5B and 6B). This pathway is the unselective oxidation of the hydrocarbon reductant with O_2 .

Among the Al_2O_3 surface, the basic hydroxyl group (termed I-a) is reactive and removed or exchanged upon the formation of the nitrates and the acetate. The $\text{Al}_{\text{CUS}}-\text{O}$ site thus produced could be available for the coordination of these adsorbed species and can be regarded as one of the active sites for SCR.

As for the SCR mechanism on Al_2O_3 , Hamada et al.^{5,12,13} first suggested the notion of NO_2 intermediacy. On the basis of the result that it was easier to reduce NO_2 than NO, they suggested that the reaction is initiated by the oxidation of NO to NO_2 , followed by a subsequent reaction of hydrocarbons with NO_2 . Another possible route of SCR is that the hydrocarbon is first activated to an oxygenated surface intermediate. Obuchi et al. suggested that carbonaceous radicals, which may be produced from the carbon deposits through partial oxidation of C_3H_6 with O_2 , is an active species for SCR on Al_2O_3 .¹⁰ In view of this situation, the mechanism we proposed involves two of the most typical SCR mechanisms proposed in the literature. The mechanism also explains the role of oxygen in facilitating the reduction of NO by C_3H_6 ; oxygen activates both NO and C_3H_6 into the reactive species in the initial steps of the reaction.

Conclusion

The role of the adsorbed acetate and nitrates during SCR of NO by C_3H_6 on Al_2O_3 has been investigated, and following conclusions can be drawn. The reaction starts with the formation of nitrates by $\text{NO} + \text{O}_2$ and its subsequent reaction with C_3H_6

to form the acetate, which becomes the predominant surface species in the steady-state condition. The acetate is active as a reductant and takes part in the N_2 formation through the reaction with nitrates. Nitrates can oxidize both C_3H_6 and acetate and are reduced to N_2 . A possible reaction scheme is proposed which explains the role of oxygen in facilitating SCR; oxygen can activate both NO and C_3H_6 into the reactive species in the initial steps of the reaction.

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