ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 2, pp. 236–244. © MAIK “Nauka/Interperiodica” (Russia), 2008.
Published in Russian in Kinetika i Kataliz, 2008, Vol. 49, No. 2, pp. 249–257.

Roles of Surface Nitrogen Oxides in Propene Activation and NO Reduction on Ag/Al_2O_3[1]

F. Ouyang[a], **M. Haneda**[b], **W. Sun**[a], **Y. Kindaichi**[b], **and H. Hamada**[b]

[a] *Shenzhen Graduate School, Harbin Institute of Technology, HIT Campus, Shenzhen University Town, Xili, Shenzhen, Guangdong, 518055 China*

[b] *National Institute of Advanced Industrial Science and Technology, AIST Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan*

Received June 25, 2007

Abstract—The activation of propene in selective catalytic reduction (SCR) of NO on 4% Ag/Al_2O_3 has been studied by in situ infrared (IR) spectroscopy. Distinctive propene activation products were detected in the SCR of NO, depending on the nature of surface oxygen and nitrogen oxide species on Ag/Al_2O_3. C_3H_6 was oxidized to acetate species in an $O_2 + C_3H_6$ atmosphere on Ag/Al_2O_3 above 573 K. The addition of NO to the $C_3H_6 + O_2$ feed gas suppressed the formation of acetate species but increased the proportion of acrylate species. Acrylate species were further confirmed to be formed preferentially from C_3H_6 oxidation without the O_2 atmosphere on Ag/Al_2O_3 or nitrate-adsorbed Ag/Al_2O_3. On the other hand, adsorption of NO led to the formation of nitrito species on Ag/Al_2O_3, but the nitrito was barely oxidized to nitrate species unless there was an O_2 atmosphere at 473–673 K. Thus, the oxidation of propene to acetate species, or the formation of nitrate from nitrito, is attributed to two competitive electrophilic reactions. The formation of nitrate from nitrito species decreased electrophilic oxygen species that oxidized propene to acetate. Nevertheless, the first dehydrogenation of propene to form acrylate species on nitrate-adsorbed Ag/Al_2O_3 is a nucleophilic reaction, as it is on Ag/Al_2O_3. Furthermore, there was no decrease in reaction activity for formation of acrylate species on nitrate-adsorbed Ag/Al_2O_3 compared to Ag/Al_2O_3. This led to the total reaction occurring easily through the propene nucleophilic oxidation branch because the presence of the adsorbed nitrogen oxides changed selectively the formation rates of the surface reductants. IR spectra data further demonstrate that acrylate and acetate species, as the surface reductants, reacted with nitrate to generate isocyanate intermediates in the SCR of NO. The effect of structures of different reductants on NO reduction is discussed.

DOI: 10.1134/S0023158408020110

INTRODUCTION

Selective catalytic reduction (SCR) of NO in oxygen-rich exhaust gas of lean-burn engines remains a challenge for environmental catalysis. Iwamoto [1] and Held et al. [2] first demonstrated the high performance of a Cu-ZSM-5 catalyst for NO reduction independently in excess oxygen. However, the hydrothermal resistance of this class of catalyst is unsatisfactory [3]. Hence, much of the work related to lean de-NO_x has been performed on metal oxide-supported catalysts [4]. Metal oxide-supported Ag catalysts have been found to reduce NO efficiently in the presence of excess oxygen [5–18]. Most studies of relevant reaction mechanisms using infrared spectroscopy have focused on the formation and conversion of nitrogen oxides [5–11] and N-containing organic intermediates, such as R-NO_2 on Ag/TiO_2–ZrO_2 [10], isocyanate species (NCO) on Ag/Al_2O_3 [6, 18], and cyanide in the SCR of NO on Pt/SiO_2 [19].

A few studies have also stressed the importance of the reductants for the SCR of NO. Various reductants, such as alcohols [5–9], light alkenes [10–17], and methane [20], as well as other alkanes [21], were applied to efficiently remove NO over metal oxide-supported catalysts [4, 22, 23]. Activation of reductants is a research subject related to the formation of intermediates in SCR of NO, which differs from the selective oxidation of reductants in the presence of oxygen alone, since nitrogen oxides are possibly involved in reductant activation. Anderson and Rochester [24] found that nitric oxides enhanced propene oxidation to acrylate species in SCR of NO on Rh/Al_2O_3. We found that the allyl species from propene oxidation was involved in the formation of an amido compound in SCR of NO on Ga_2O_3–Al_2O_3 [25]. On Ag/Al_2O_3, the activation of reductants has been suggested to produce oxygenates, such as carboxylate species [5, 8–11]. Furthermore, it was also found that NO reduction efficiency was dependent on the type of reductant. For example, a higher nitrogen yield was obtained from the SCR of NO with ethanol on Ag/Al_2O_3 compared to propene [5]. Recently, a highly dispersed Ag/Al_2O_3 catalyst was found to oxidize propene to acrylate species, and a further reaction was also suggested to occur easily in the C=C bond, which gave a consecutive route of NO

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[1] This article was submitted by the authors in English.

reduction [16, 17]. However, the C_3H_6 activation, in particular, the effect of nitrogen oxides on the C_3H_6 activation mechanism has not been fully elucidated. We found that reductant activation is an important reaction step in NO reduction [26]. In this study, we focus on study of the activation mechanism of propene oxidation by nitrogen oxides and O_2, as well as the reaction of the produced oxygenates toward N-containing organic compounds on Ag/Al_2O_3.

EXPERIMENTAL

Preparation of catalyst. γ-Alumina (NEOBEAD), as a catalyst support, was obtained from Mizusawa Chemicals Co. and was crushed to size of 16–28 mesh (BET surface area: 190 $m^2 g^{-1}$). Ag-supported Al_2O_3 (4 wt % Ag/Al_2O_3) was prepared by the impregnation method using an aqueous $AgNO_3$ solution, followed by drying at 383 K for 24 h and calcination at 873 K for 5 h in air (BET surface area: 160 $m^2 g^{-1}$). C_3H_6, NO, O_2 (feed gas premixed from high purity gas of 99.999% and helium balanced) and acetic acid (99.7%) were used as received.

In-situ IR spectra of the catalyst. A glass evacuation system with an IR cell was connected to a mass-flow controlled setup [10]. The disc of Ag/Al_2O_3 (ca. 0.05 g) was placed in the IR cell and pretreated by evacuation at 773 K for 2 h, followed by heating in 10% oxygen flow at 773 K for 2 h (referred to as the oxygen pretreated sample). Feed gases, containing a single component or a mixture of 1000 ppm NO, 987 ppm C_3H_6, and 10% O_2 with the balance of helium, was added to the IR cell at a total rate of 60 $cm^3 min^{-1}$. Acetic acid was bubbled into the IR cell by helium pulse (60 $cm^3 min^{-1}$) through an acetic acid vessel at 300 K. IR spectra were recorded on a FT–IR spectrometer (Shimadzu 8600PC) with an MCT detector at a resolution of 4 cm^{-1}. Relevant background spectra of the catalyst have been subtracted in all shown IR spectra.

Characteristics of the catalyst. The catalyst was characterized by XRD and UV-Vis. The XRD result of Ag/Al_2O_3 shows a very similar pattern to γ-Al_2O_3. No peak attributed to the Ag and Ag_2O phase was detected, indicating the presence of Ag in highly dispersed Ag or microparticles. UV-Vis diffuse reflectance spectra of catalysts were recorded in the range of 190–700 nm with a resolution of 2 nm using a UV-Vis spectrometer (Shimadzu, UV-2400PC) equipped with an integrating sphere attachment. In the UV-Vis diffuse reflectance spectra, Ag/Al_2O_3 after calcination at 773 K exhibited absorption around 350 nm, which has been attributed to Ag_n [27] or $Ag_n^{\delta+}$ [28].

RESULTS

IR spectra of SCR of NO by propene. The 4% Ag/Al_2O_3 sample was exposed to feed gas containing 1000 ppm NO, 987 ppm C_3H_6, and 10% O_2 and its temperature was elevated from 373 to 673 K at a rate of 10 K min^{-1}. IR spectra of surface species formed on Ag/Al_2O_3 during SCR of NO are shown in Fig. 1. At 373 K, a reaction of NO with oxygen generated a nitrito species [29] (1228 and 1320 cm^{-1}, referred to as **b-NO_2^-**). The monodentate type of nitrate species [5, 29] (1546 and 1240 cm^{-1}; referred to as **NO_3^-–I**) was formed predominantly at 473 K. In addition, bands appeared at 1585 and 1296 cm^{-1}, which have been assigned tentatively to the bidentate type of nitrate species [5, 29] (referred to as **NO_3^-–II**). Characteristic bands belonging to oxidized hydrocarbons [5, 6] became apparent in the 1600–1350 cm^{-1} range at 573 K. Isocyanate [5] (very weak band near 2230 cm^{-1}) was formed at 673 K. We also detected N_2 reduced in the SCR of NO using a flow-bed reactor at this temperature, suggesting that isocyanate species act as intermediates and are finally reduced to N_2. This is consistent with previous results [5, 6, 8, 10].

The reaction of NO with O_2 on Ag/Al_2O_3. The Ag/Al_2O_3 sample was exposed to NO (1000 ppm) + helium flow at 473 K and then the sample temperature was elevated to 673 K at a rate of 10 K min^{-1}. IR spectra of surface species at various temperatures are shown in Fig. 2a. Nitrito species (1320 and 1228 cm^{-1}) appeared after the introduction of NO, but was scarcely oxidized to the NO_3^- species until 573 K. Apparently, there were surface oxygen species (O_s) on the metal oxide catalyst, where a NO reaction occurred to form nitrito species. However, it was not oxidized easily to NO_3^- species by O_s.

The Ag/Al_2O_3 sample was exposed to 1000 ppm of NO + 10% O_2 at 573 K, and the IR spectrum of surface species is shown in Fig. 2b. Bands at 1228, 1320, and 1630 cm^{-1} were initially observed in the spectrum. The band at 1630 cm^{-1} disappeared after removal of NO, which was attributed to absorption of gaseous NO_2 (1630 cm^{-1}) [29] or its weakly adsorbed species. After NO in the feed gas was cut off (leaving oxygen alone), the band at 1228 cm^{-1} decreased in intensity and shifted to 1240 cm^{-1}, accompanied by an increase in intensity of the band at 1240 cm^{-1}, indicating that NO_3^- (1545 and 1240 cm^{-1}) was yielded from the oxidation of nitrito species by oxygen species produced from the activation of gaseous O_2. Thus, the reaction is represented as

$$NO + O_s \xrightarrow[+e]{} NO_2^- \xrightarrow[1/2O_2]{} NO_3^-. \qquad (I)$$

Oxidative activation of propene by oxygen over Ag/Al_2O_3. The Ag/Al_2O_3 catalyst was exposed to $C_3H_6 + O_2$ flow (987 ppm and 10%) at 423 K, followed by heating to 673 K (10 K min^{-1}) in the presence of $C_3H_6 + O_2$. The spectra of the surface species measured

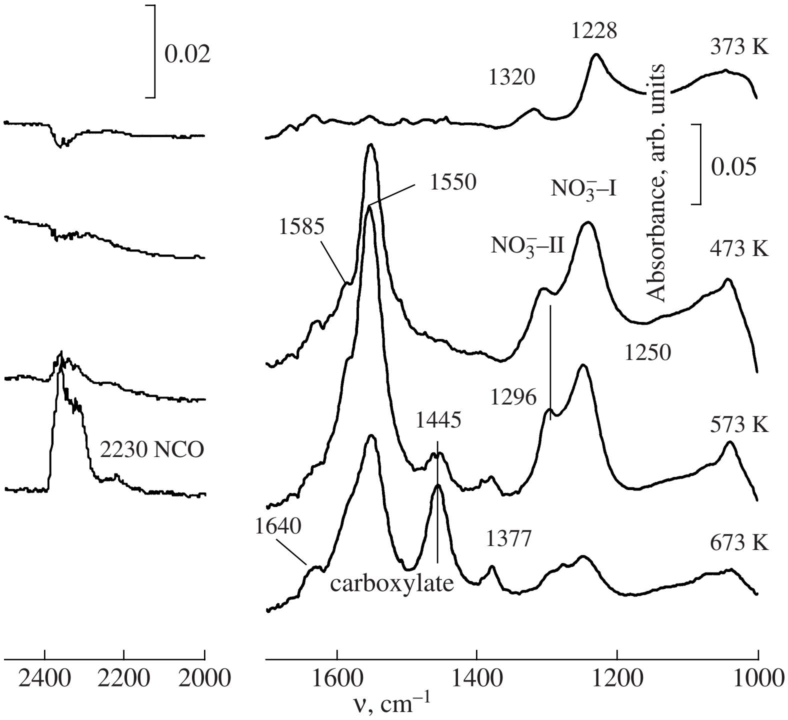


Fig. 1. IR spectra of surface species at various temperatures after oxygen pretreated 4% Ag/Al_2O_3 was exposed to 1000 ppm NO + 987 ppm C_3H_6 + 10% O_2 at 373 K and subsequently increased temperature (10 K min^{-1}) to 673 K.

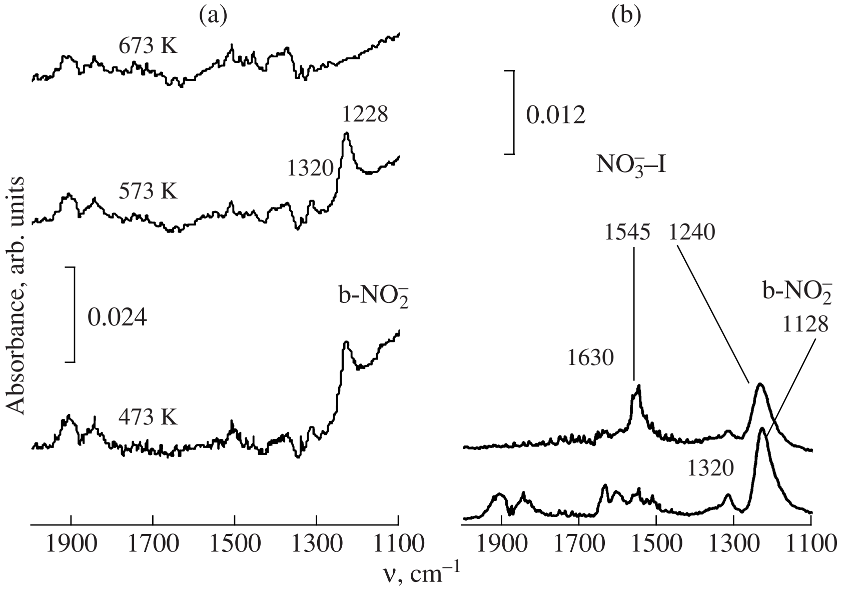


Fig. 2. (a) IR spectra of surface species at various temperatures after oxygen pretreated 4% Ag/Al_2O_3 was exposed to 1000 ppm of NO at 473 K and subsequently increased temperature (10 K min^{-1}) to 673 K. (b) IR spectra of surface species on Ag/Al_2O_3 after the catalyst was exposed to 1000 ppm of NO + 10% O_2 at 573 K for 2 min, followed by exposing to 10% of O_2 for 5 min.

at various temperatures are shown in Fig. 3. At 523 K, some bands appeared at 1650–1300 cm^{-1} and became evident at 1645, 1573, 1556, 1460, and 1380 cm^{-1} at 573 K. Two intense bands at 1573 and 1460 cm^{-1} increased in intensity up to 673 K, while the band at 1380 cm^{-1} decreased in intensity. The intense bands at

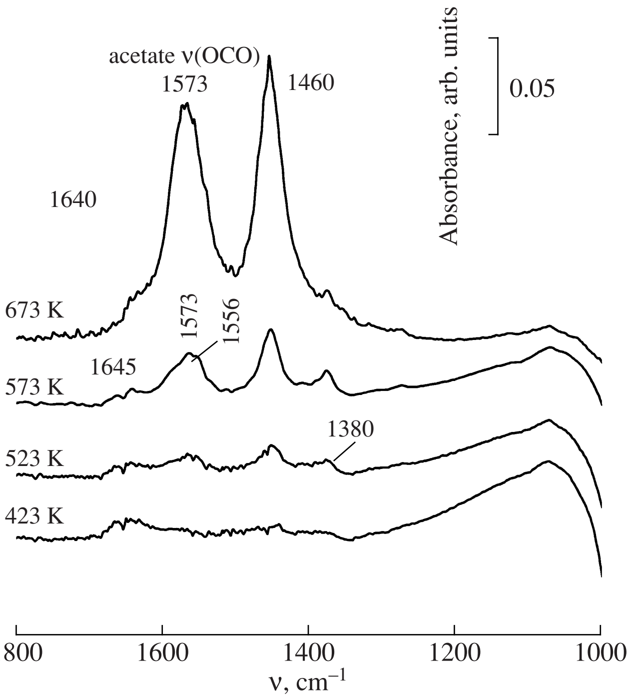


Fig. 3. IR spectra of surface species on Ag/Al_2O_3 in the presence of $C_3H_6 + O_2$ at 423 K, and subsequently increasing temperature to 673 K (10 K min^{-1}).

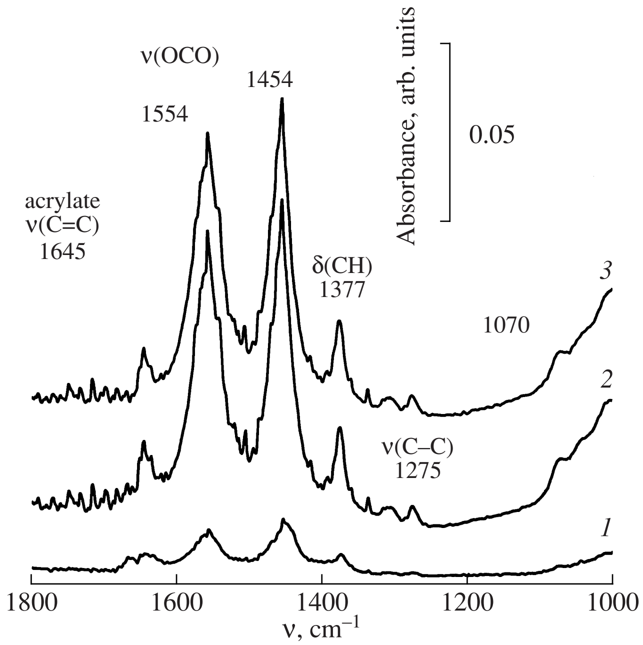


Fig. 4. IR spectra of surface species with change of time on oxygen pretreated Ag/Al_2O_3 in the presence of C_3H_6 at 573 K for 5 min (*1*), 30 min (*2*), and finally, a helium purge for 30 min (*3*).

1573 and 1460 cm^{-1} have been ascribed to characteristic absorptions due to carboxylate species over other catalysts [30–32]. They also formed from the oxidation of propene or alcohols in the SCR of NO [8, 11].

To identify the carboxylate species, the adsorption of acetic acid was examined. Ag/Al_2O_3 was exposed to acetic acid bubbled by the helium carriage gas at 573 K. The IR spectra assignments were summarized in the table. Since the bands related to the oxidation of propene at 673 K corresponded exactly to two intense bands due to bidentate acetate species (Fig. 3), we suggest that the propene oxidation reaction occurred to form surface acetate species in the presence of O_2 and represent the reaction as follows:

$$CH_3\text{–}CH{=}CH_2 + 2O_2 \xrightarrow[-3H]{} CH_3\text{–}COO_s + CO_2 \qquad \text{(II)}$$

in which H was oxidized possibly to H_2O or formed OH groups.

Oxidation of propene on Ag/Al_2O_3 in the absence of O_2 at 573 K. Changes in the formed surface species with reaction time were examined in detail. Oxygen-pretreated Ag/Al_2O_3 was exposed to C_3H_6 flow (987 ppm) at 573 K, and several typical spectra are shown in Fig. 4. The bands at 1645 (sharp and weak),

Assignments of propene oxidation products

Vibration	V_2O_5/TiO_2 [30]		1.5–6%Ag/Al_2O_3 [17] (acrylate)	4%Ag/Al_2O_3 [present study]		
	acrylate	acetate		acrylate	acetate*	acetate**
ν(C=C)	1635 (sh, w)	–	1642	1641–1645 (sh, w)	–	–
$\nu(OCO)_{as}$	1495 (b, i)	1530	1575	1554 (b, i)	1573 (b, i)	1572 (b, i)
$\nu(OCO)_s$	1440 (b, i)	1442	1456–1458	1456 (b, i)	1460 (b, i)	1565 (b, i)
δ(CH)	1375 (sh, m)	1350	1378–1392	1377 (sh, m)	–	–
ν(C–C)	1275 (w)	–	1296–1298	1275 (w)	–	–

* Arising from acetic acid adsorption.

** Arising from propene oxidation, see Figs. 3 and 4.
sh—sharp; b—broad; w—weak in intensity; i—intense; m—mediate.

1554 (intense), 1454 (intense), 1377 (sharp and mediate), 1275 (weak), and 1070 cm^{-1} (weak) appeared and grew as the reaction progressed. The intensity of the bands was close to a constant after a helium purge for 30 min. A parallel increase in intensity of all the bands and the same thermal stability in helium gas indicated that the bands corresponded to a dominant surface species. The band at 1645 cm^{-1} was not attributed to C=C vibration of propene since it was not removed after the He purge at 573 K. Acrylate species could be produced from the oxidation of propene or the adsorption of acrylic acid, on V_2O_5/TiO_2 [30], V–Sb-oxides catalyst [31], and Co_3O_4 [32]. The band at ~1640 cm^{-1} has been attributed to C=C vibrations of these species. Iglesías-Juez et al. have suggested that acrylate species was formed from propene oxidation near 670 K over 1.5–6% Ag/Al_2O_3 prepared by inverse microemulsion [17]. The relevant assignments were also summarized in the table. Based on the similarity in spectra, not only in the frequency but also in the relative intensity, we attributed the bands at 1645, 1554, 1454, 1377, and 1275 cm^{-1} to acrylate species. As known previously [30, 31], acrylate species are formed via the oxidation of propene by surface oxygen:

$$CH_2{=}CH{-}CH_3 + 2O_s \xrightarrow[-3H]{} CH_2{=}CH{-}COO_s. \qquad (III)$$

In the reaction, the first step is H abstraction from CH_3 groups of propene by nucleophilic O^{2-} ions, then the propyl species is further oxidized to acrylate species. In addition, other caboxylate species do not show identified features in the present spectra. For example, a strong band at 1573 cm^{-1}, due to acetate species, was not visible. The characteristic bands at 1590 (intense), 1390 (mediate), and 1380 cm^{-1} due to formate [12] were not observed as well. This means that the acrylate species was the main surface product from propene activation on the catalyst.

Oxidative activation of propene by preadsorbed nitrate on Ag/Al_2O_3. The nitrate-adsorbed surface was prepared by the exposure of Ag/Al_2O_3 to NO + O_2 for 30 min at 573 K, followed by a helium purge for 30 min at the same temperature. Figure 5 shows several typical IR spectra related to the reaction of the nitrate species with propene (987 ppm) at 573 K. The acrylate species (1643, 1556, 1456, 1377, and 1278 cm^{-1}) was formed and grew as the reaction progressed on Ag/Al_2O_3, while half of NO_3^-–I (1549 and 1248 cm^{-1}) and NO_3^-–II (~1300 cm^{-1}) decreased rapidly in the first 5 min and the remainder disappeared after 30 min. Bands due to the other surface species, such as NCO and formate, were not visible. We concluded that the nitrate species was involved in oxidation activation of propene and was removed during the reaction.

Figure 6 compares the changes in the intensity of the band at 1377 cm^{-1} with time on the nitrate preadsorbed or oxygen pretreated Ag/Al_2O_3. The relative rate for acrylate formation on the nitrate preadsorbed Ag/Al_2O_3 was slightly higher than on the oxygen pretreated Ag/Al_2O_3 in the first reaction stage (10 min). The reaction still occurred preferentially toward the formation of acrylate species on the nitrate preadsorbed surface, as shown in the following:

$$\begin{gathered} CH_2{=}CH{-}CH_3 + NO_3^- \\ \xrightarrow[-3H,\,(x-1)O]{} CH_2{=}CH{-}COO^- + NO_{x(x\,=\,1,\,2)}. \end{gathered} \qquad (IV)$$

Formation of acrylate over Ag/Al_2O_3 in the presence of C_3H_6 + NO + O_2. After the exposure of Ag/Al_2O_3 to C_3H_6 + O_2 flow for 40 min at 573 K, NO (1000 ppm) was added into the C_3H_6 + O_2 feed gas. The changes in the IR spectra with time at 573 K are shown in Fig. 7. After the reaction in C_3H_6 + O_2 for 40 min, the spectrum was similar to that of acetate species in Fig. 3, showing the formation of acetate species (1560 and 1456 cm^{-1}) from the oxidation of propene. NCO species (2225 cm^{-1}) appeared immediately after the addition of NO and then remained constant after the reaction for 5 min. Meanwhile, the acetate species (1571 cm^{-1}) decreased with increasing acrylate species (1377 cm^{-1}) in the initial 20 min. These results may be explained by the fact that the acetate formation rate was lower than the consumption rate, while the acrylate formation rate was higher than the consumption rate, leading, consequently, to an increase in the proportion of the acrylate species. Finally, no change was further observed in the spectra after 20 min, showing that the reaction was close to the steady state. We still found that the addition of NO enhanced formation of acrylate species at 673 K. At this temperature we detected that NO was reduced in the flow reactor. This demonstrated that acrylate species, as a reductive intermediate, contributed to NO reduction. In addition, the initial decrease of acetate species with the appearance of NCO species indicated that the acetate species was another intermediate for the NO reduction.

DISCUSSION

Surface species IR spectra assignment and thermal stability. SCR of NO with propene is a most complex reaction, in which a number of organic N-containing compounds are formed. Most of these surface products exhibit bands at 1300–1650 cm^{-1}, creating problems in the identification of IR spectra. Therefore, analysis of the thermal stability and a comparison of the relative intensity of concomitant bands due to surface products are used as supporting evidence. Occasionally, adsorption of a pure agent is also necessary for accurate absorption assignments on the same catalyst. We identified acetate species arising from the oxidation of propene (Fig. 3) by the similarity in IR spectra of adsorbed acetic acid. The peak center of the $\nu(COO)$ vibration of acetate appeared at 1571 cm^{-1}, while acrylate species exhibited a band at 1554 cm^{-1} and its concomitant bands appeared at 1645 and 1377 cm^{-1}

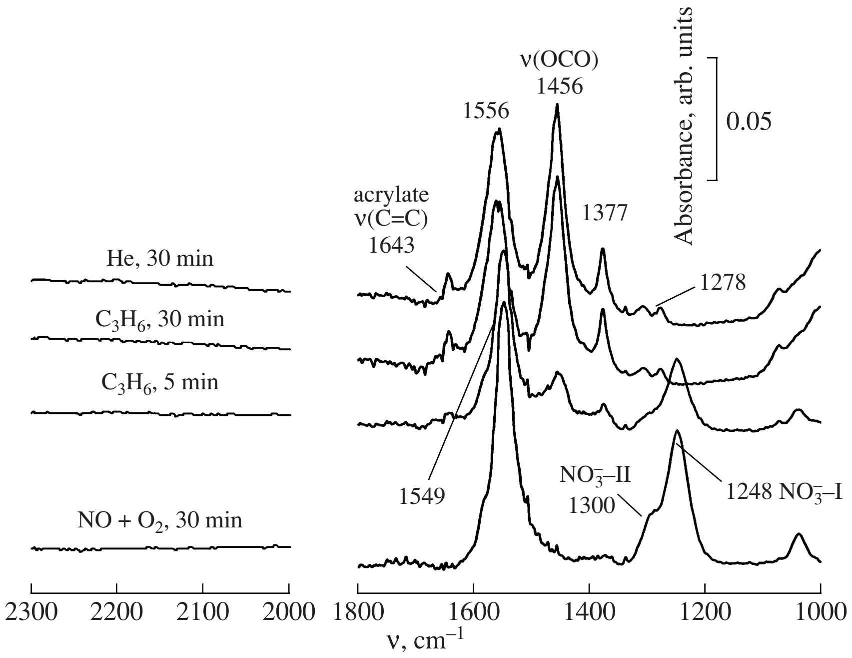


Fig. 5. IR spectra of surface species with change of time on nitrate preadsorbed Ag/Al_2O_3 by the reaction of NO + O_2 for 30 min, followed by a helium purge at 573 K for 30 min, the introduction of C_3H_6 for 5 min, 30 min, and a subsequent helium purge for 30 min.

(Fig. 4). Thus, we roughly distinguished the acrylate from the acetate species. The assignment for bands due to acrylate species was consistent with that from the adsorption of acrylic acid, not only in vibration frequencies but also in the relative intensity of the relevant bands, as reported previously [30].

The bands due to formate species, formed possibly by the oxidation of propene, are also situated in the region of 1350–1650 cm^{-1}. Meunier et al. [11] and Iglesías-Jues et al. [17] reported a difference in products from propene oxidation between Al_2O_3 and 1.2–6% Ag-load Al_2O_3, respectively. They suggested that the acrylate species was formed on the Ag-loaded Al_2O_3, displaying bands at 1645, 1580, 1460, and 1390 cm^{-1} [11, 17], while the formate species, characterized by bands at 1590, 1390, and 1380 cm^{-1}, was formed on the Al_2O_3 support. We did not observe any intense bands, due to the formate species, that should arise independently at 1590 cm^{-1} rather than the other band at 1460 cm^{-1} in the presence of $C_3H_6 + O_2$ (Fig. 3). Hence, we consider that formate could be produced at a low-loaded Ag/Al_2O_3, as reported by Meunier et al. [11] and Iglesías-Jues et al. [17], but not as a main surface species on our 4% Ag/Al_2O_3.

Tanaka et al. [33] have successfully identified N-containing organic intermediates based on analysis of the relative intensity. They found an intense absorption in IR spectra recorded from NO reduction by propene on Pt/SiO_2 (which did not belong to carboxylate species at 1400–1600 cm^{-1}) and assigned it to nitroorganic species. We have also confirmed formation of R-NO_2 in SCR of NO on Ag/TiO_2–ZrO_2 by a nitrogen isotope shift [10]. A mediate band at 1377 cm^{-1} (Fig. 7) might be assigned to absorption of the N-containing organic compounds on our Ag/Al_2O_3. However, intense bands at 1554 and 1454 cm^{-1} indicated that carboxylate must be present. To estimate the error, we compared the intensity ratios between the bands at 1377 and

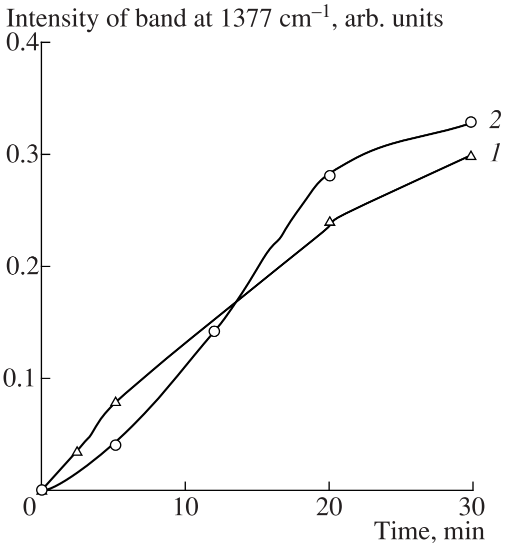


Fig. 6. The changes in the intensities of bands at 1377 cm^{-1} with reaction C_3H_6 + NO_3^- time during the conditions related to Figs. 4 and 5.

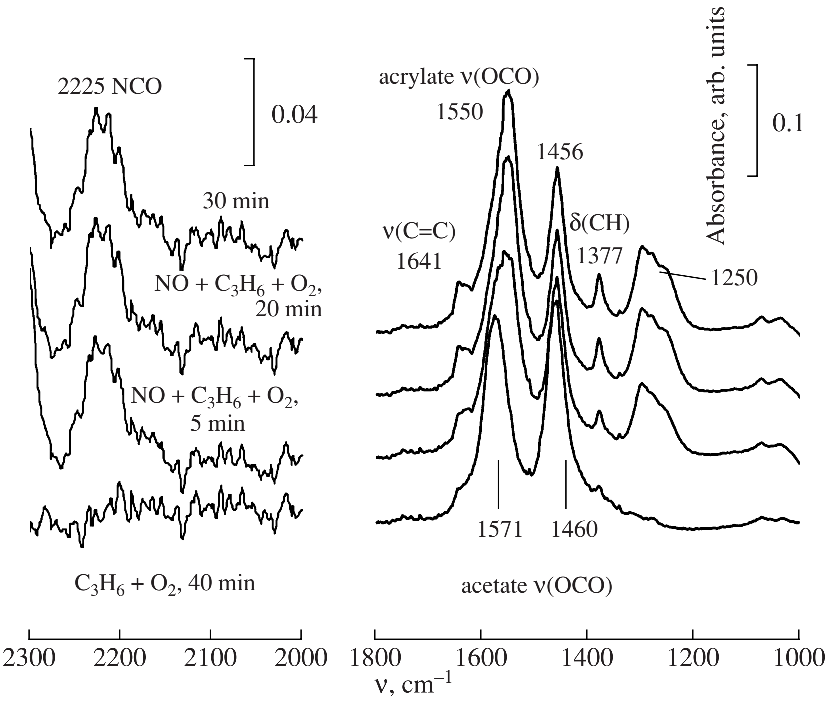
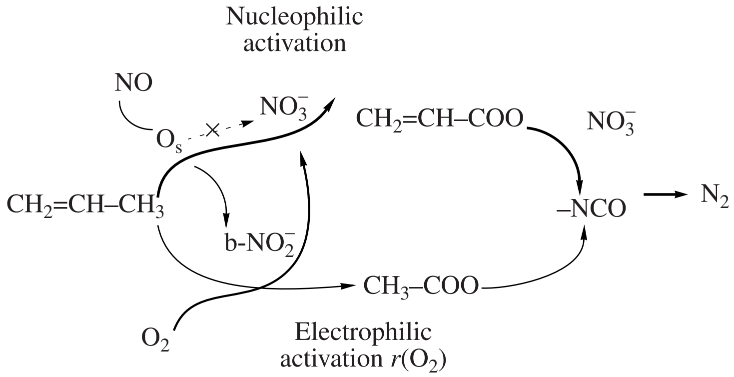


Fig. 7. The IR spectra of surface species on Ag/Al_2O_3 at 573 K after Ag/Al_2O_3 was exposed to $C_3H_6 + O_2$ for 40 min and followed by a helium purge for 30 min, the addition of NO to $C_3H_6 + O_2$ for 5 min, 20 min, and 30 min at the same temperature.

1456 cm^{-1} (Figs. 4, 7), and found the ratio obtained from a steady SCR of NO (Fig. 7) was only slightly higher (close to 20%) than from the oxidation of propene by surface oxygen (Fig. 4). Thus, though we cannot determine the presence of an N-containing organic compound (1380 cm^{-1}; if it is present, the amount must be low), it supports the dominance of acrylate species on the surface in the SCR of NO. This is in agreement with the thermal stability of the two species. It is known that the acrylate species was basically stable in helium at 573 K (Fig. 5), whereas R-NO_2 species decomposed to isocyanate and cyanide species above 523 K on Ag/Al_2O_3 [7]. Thus, thermal stable acrylate species must be a main surface species on the Ag/Al_2O_3 at 573 K.

Propene activation routes and dynamic analysis. As is known, acrylate and acetate species were indeed formed through two different reaction pathways in the partial oxidation of propene, allylic oxidation at the methyl group, or oxidative cleavage of the C=C double bond in propene [30]. Lattice O^{2-} ion is nucleophilic, which resulted in the acrylate species through the initial attack on the methyl group of propene. On the other hand, some electrophilic oxygen species, such as O_2^- and O_2^{2-}, may be generated in the progressive transformation of gaseous O_2 to the lattice O^{2-} over catalysts [34]. Bogdanchikova et al. [28] have suggested that the Ag metallic clusters act as active sites for oxidation of NO. Similarly, we also detected such a cluster by UV and concluded that the primary nucleophilic reaction of lattice O^{2-} ion with propene led to the formation of acrylate species on Ag/Al_2O_3 (Fig. 4). On the other hand, it is reasonable to consider that electrophilic oxygen species could be generated during O_2 activation on Ag/Al_2O_3 above 573 K, which oxidized the C=C bond of propene to form acetate species (Fig. 3). In addition, the formation of nitrate species from nitrito oxidation also reduced electrophilic oxygen species (Eq. (I)). Thus, there was competition of the two electrophilic reactions between the formation of nitrate and acetate species on Ag/Al_2O_3 (Eqs. (I) and (II)). A comparison of reaction temperatures revealed that the nitrate formation reaction occurred more actively (473 K) than acetate formation (573 K; Fig. 1). Consequently, the electrophilic oxygen species was consumed in the formation of nitrate species, resulting in a reduced acetate formation rate. However, the acrylate formation rate on the nitrate-covered surface was still close to that on the surface pretreated with oxygen (Fig. 6). This results in an increase in the proportion of acrylate species in SCR of NO (Fig. 7). The relative reaction rates [$r(x)$, where x is the reaction condition related to nitrogen oxides or oxygen species] are in the order: $r(NO_3^-) \geq r(O_2^-)$ for propene activation to acrylate and $r(NO + O_2) < r(O_2)$ for propene activation to acetate. In addition, the oxygenate formation temperature is higher than NO_3^-; therefore, oxygenate formation was regarded as a key



Scheme 1.

step for NO reduction. Based on the above results, the reaction pathway is shown by Scheme 1.

Importance of reductant activation. NO_3^-, N-containing compounds, and oxygenates ($C_xH_yO_z$) are the main intermediates for SCR of NO [5–8, 10, 12]. The efficiency of the NO reduction depended on the types and contents of oxygenates. Iglesías-Jues et al. [17] proposed that acrylate due to its C=C bond may benefit for NO reduction. We found that acrylate species was formed favorably, as NO_x participated in the selective activation of propene. The superior formation of acrylate relative to other types of carboxylate species could increase the NO reduction efficiency due to the availability of acrylate species for further NO reduction. This means that involvement of nitrate into propene activation is a positive effect for NO reduction. We previously found that absorbed SO_x promoted NO reduction (which is attributed to the suitability of SO_x species for hydrocarbon activation). The activated products, such as alcoholates, are capable of reacting with nitrate species at low temperatures [26]. This is consistent with other results in the literature, in which alcoholate species could reduce NO at low temperature [5]. In the present study, the low temperature reaction was not observed since propene could not be activated at low temperature. Nevertheless, we found that propene was activated favorably to acrylate species under NO reduction condition. The relationship of the formed reductive intermediate structure with high performance of the catalyst needs further study.

CONCLUSIONS

We have assigned IR spectra of surface products from the SCR of NO with propene on 4% Ag/Al_2O_3 and used acetate and acrylate as identification to reveal the roles of nitrogen oxide species in propene activation. We find that nitrate species, like lattice O^{2-}, were nucleophilic and benefited the formation of acrylate species via the initial H abstraction step at the CH_3 group of propene. On the other hand, electrophilic oxygen species produced from gaseous O_2 were involved in two competitive reactions: (1) oxidation of propene to acetate species; (2) the formation of nitrate species. Since nitrate formation decreased the electrophilic oxygen species concentration, addition of NO to $C_3H_6 + O_2$ flow suppressed the electrophilic oxidation of propene and favored nucleophilic activation of propene, leading to decreased acetate proportion but increased acrylate. Since acetate and acrylate were important reductive intermediates in the different routes, the total NO reduction reaction progressed preferentially via a branch where propene was activated to an acrylate intermediate and, then, as a reductant, reduced NO below 723 K.

ACKNOWLEDGMENTS

This work was supported by the Guangdong Nature Science Foundation.

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