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The effects of acetaldehyde, glyoxal and acetic acid on the heterogeneous reaction of nitrogen dioxide on gamma-alumina

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Heterogeneous reactions of nitrogen oxides on the surface of aluminium oxide result in the formation of adsorbed nitrite and nitrate. However, little is known about the effects of other species on these heterogeneous reactions and its products. In this study, diffuse reflectance infrared spectroscopy (DRIFTS) was used to analyze the process of the heterogeneous reaction of NO_2 on aluminium oxide particle surfaces in the presence of pre-adsorbed organic species (acetaldehyde, glyoxal and acetic acid) at 298 K and reveal the influence of these organic species on the formation of adsorbed nitrite and nitrate. It was found that the pre-adsorption of organic species (acetaldehyde, glyoxal and acetic acid) on γ-Al_2O_3 could suppress the formation of nitrate to different extents. Under the same experimental conditions, the suppression for the formation of nitrate by the pre-adsorption of acetic acid is much stronger than that by pre-adsorption of acetaldehyde and glyoxal, indicating that the influence of acetic acid on the heterogeneous reaction of NO_2 is different from that of acetaldehyde and glyoxal. Surface nitrite was formed and identified to be an intermediate product. For the heterogeneous reactions of NO_2 on the surfaces of γ-Al_2O_3 with and without the pre-adsorption of acetaldehyde and glyoxal, it was firstly formed and then gradually disappeared as the reaction proceeded, but for the reaction with the pre-adsorption of acetic acid, it was the final main product. This indicated that the pre-adsorption of acetic acid would promote the formation of nitrite while the others won’t change the trend of the formation of nitrite. Possible mechanisms for the influences of the pre-adsorption of acetaldehyde, glyoxal and

acetic acid on the heterogeneous conversion of NO_2 on γ-Al_2O_3 were proposed, and atmospheric implications based on these results were discussed.

1. Introduction

Nitrogen dioxide is an important air pollutant and its chemical reactivity is of great importance in atmospheric chemistry.[1] It can undergo various heterogeneous reactions to form adsorbed products such as adsorbed nitric acid, nitrates and nitrites.[2-4] It is well known that nitric acid plays a significant role in the formation of atmospheric secondary particles, and the formed nitrate aerosols are well known to affect the air quality, human health and climate.[5] Moreover, the heterogenous reactions of NO_2 on soot or organic films can be considered as sources of HONO which plays a fundamental role as hydroxyl radical precursor via its photolysis during daytime.[6,7] Hence the heterogeneous reactions of NO_2 have been received increasing attention in the past decades. Many previous studies have focused on the heterogeneous reactions of NO_2 on different mineral oxides,[3, 8-11] and some of the studies have discussed the synergistic effect existing in the heterogeneous reactions between NO_2 and SO_2 on different mineral oxides.[9,11] However, up to now, little attention is paid to the effect of pre-adsorbed organic species on the heterogeneous processes of NO_2 on the mineral aerosols.[12]

Acetaldehyde is one of the most abundant aldehydes in the atmosphere.[13] It can be emitted directly from combustion sources and produced by photochemical oxidation of hydrocarbons. Besides formaldehyde, acetaldehyde is also closely related to the sick building syndrome, and its effects on human health mainly depend on its levels, duration and frequency of exposure.[14] Indirectly, it can act as a chemical precursor of tropospheric ozone to compromise domestic air quality.[15] Heterogeneous reactions of CH_3CHO on oxide particles (e.g. SiO_2) have been studied,[16-19] and the results showed that through the interaction of hydrogen bonding between carbonyl groups and surface hydroxyl groups, CH_3CHO molecules are weakly and reversibly physisorbed on the surfaces of SiO_2 particles, while on the surfaces of other oxides (e. g. α-Al_2O_3, CaO and TiO_2) CH_3CHO molecules can undergo heterogeneous reactions to yield irreversibly adsorbed unsaturated carbonyl compounds with higher molecular weight. It is found that the pre-adsorbed CH_3CHO significantly suppresses the heterogeneous reaction of large amount of SO_2 on the surface of α-Fe_2O_3 and has a little influence on the uptake of small amount of SO_2.[20] Therefore, it is expected that under atmospheric conditions CH_3CHO molecules can also be adsorbed onto mineral dust aerosols,[18] and may change the surface properties of these aerosols, and thereby affect the subsequent heterogeneous uptake behaviors of NO_2 on these particles.

Glyoxal, the simplest and one of the most abundant dialdehydes found in the atmosphere, is produced largely via photochemical oxidation of volatile organic compounds (VOCs).[21-24] It has recently been the focus of numerous studies due to its potential to form secondary organic aerosol (SOA).[21-27] The important aspects for quantifying the role of glyoxal in forming SOA are the chemical processing of glyoxal in aerosol and the effect of electrolyte composition on Henry's law partitioning coefficients of glyoxal in aerosol, the other important role of glyoxal in aerosol was the effect of condensed-phase chemistry on aerosol optical properties.[27] The dialdehyde glyoxal is one of several dicarbonyl species that are formed in significant yields from the photooxidation of aromatic hydrocarbons.[28-32] Glyoxal is an excellent candidate for studying heterogeneous reactions because it is significantly more reactive than most other aldehydes in hydration, polymerization, and hemiacetal formation.[33] Also, glyoxal cannot undergo aldol condensation due to its relatively special structure, which thereby reduces the complexity of observed reaction products. Previous study have reported the heterogeneous reactions of glyoxal on particulate matter including sulfate and nitrate particles,[33] however, little attention is paid to the influence of glyoxal on the heterogenous reaction of NO_2.

Organic acids are important constituents of the troposphere, for they contribute to a large fraction of the non-methane hydrocarbon mixture,[34, 35] and also contribute significantly to tropospheric free acidity. These compounds can be emitted directly into the atmosphere by mobile and stationary sources and be produced in situ by the photo-oxidation of gas-phase hydrocarbons. As sources of free radicals in the atmosphere and precursors in the formation of organic aerosols, they are major contributors to urban photochemical smog.[36,37] Acetic acid (CH_3COOH) is considered to be the important component of these acids and has low gas-phase reactivity when reacted with OH and NO_3 radicals.[38] CH_3COOH is the oxidation product of CH_3CHO which is also contributing to the occurrence of atmospheric pollution, however, few studies have explored the differences in the effects of CH_3COOH and CH_3CHO on the heterogeneous reaction of NO_2.

Mineral dust aerosol represents one of the largest natural mass fractions of the global aerosol. It is produced mainly in the arid and semiarid areas of our planet, in particular in the great deserts.[39] The impact of mineral dust particles on the Earth's atmosphere is manifold. They are believed to have a direct effect on the radiation budget of the atmosphere and therefore are expected to impact on climate.[40] In addition, the surface of such aerosol particles can provide reactive sites for heterogeneous reactions, and the potential role of which has been emphasized in several modelling studies.[41, 42] Alumina is an important component of mineral dust in the atmosphere. There are a few forms of aluminum oxide, for example, α-Al_2O_3, and γ-Al_2O_3. γ-Al_2O_3 has been widely used as a model of mineral aerosol for its higher Brunauer-Emmett-Teller (BET) surface area and better quality of spectra information, which serves to obtain useful information about the mechanism of atmospheric heterogeneous reactions.[43]

Although the role of gas phase carbonyls as a source of radicals and organic nitrates has been studied extensively,[44, 45] little is known about the influence of aldehydes and organic acids on the heterogeneous reaction of NO_2 on mineral particles. In this study, the influence of pre-adsorbed acetaldehyde, glyoxal and acetic acid on the heterogeneous reaction of NO_2 on γ-Al_2O_3 is investigated using in situ diffuse reflectance infrared Fourier spectroscopy (DRIFTS). The effect of pre-adsorption species on nitrate and nitrite formation is also discussed. This study may lead to a better understanding of the heterogeneous reaction of NO_2 on mineral aerosol particles in the troposphere, and it would also provide useful information for atmospheric chemistry studies.

2. Experimental

2.1. Chemicals.

In this study, commercially available γ-Al_2O_3 particles (99.997% purity, surface area: 50 m^2/g) purchased from Alfa Aesar were used for spectral measurements. The γ-Al_2O_3 particles was dried at 100 °C for 24 h, and some of the dried γ-Al_2O_3 particles were kept in a desiccator at 68% RH for 48 h. This treatment made some adsorbed water molecule layers be present on the particles, and the sample was still loose, fine powders after the equilibration. NO_2 (200 ppm, NO_2/N_2) was used as reactant gases, CH_3CHO (100 ppm, CH_3CHO /N_2), OHC-CHO (100 ppm, OHC-CHO /N_2) and CH_3COOH (100 ppm, CH_3COOH /N_2) (Shanghai Qingkuan Chemical Co., Ltd) were used as pre-adsorbed organic species of NO_2 respectively. O_2 (99.999% purity, Shanghai Qingkuan Chemical Co., Ltd) and Ar (99.999% purity, Shanghai Qingkuan Chemical Co., Ltd) were introduced into reaction chamber through gas dryers before use.

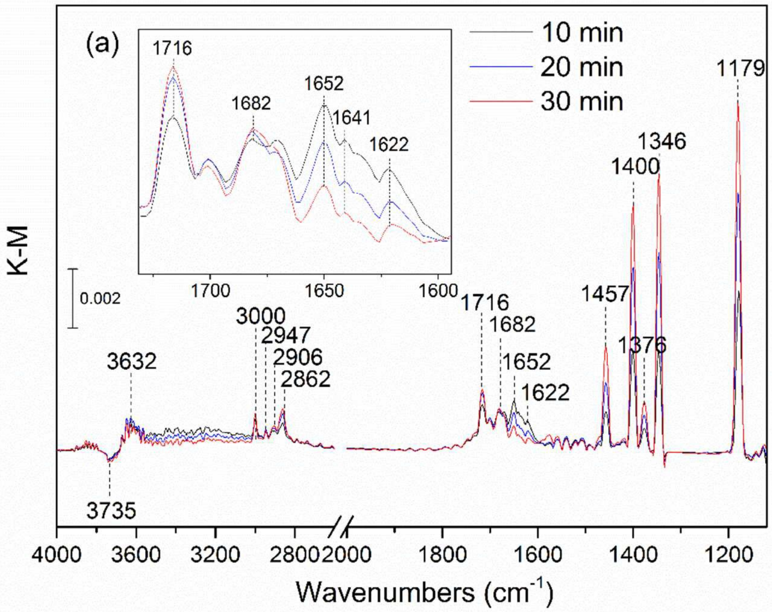
2.2. *In situ* DRIFTS experiment.

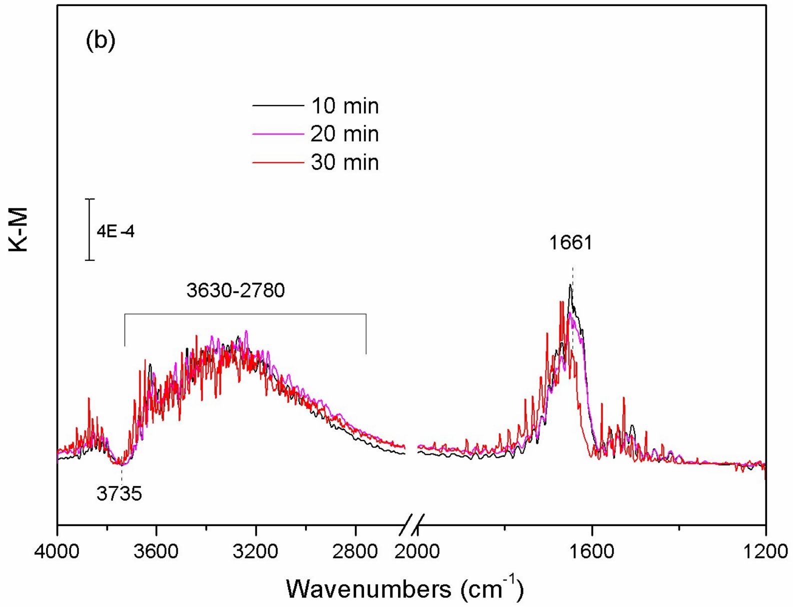
In this study the heterogeneous reactions of NO_2 on humid γ-Al_2O_3 in the presence and absence of organic species have been studied by using in situ DRIFTS technique. The DRIFTS spectra were recorded using the Nicolet Avatar 360 FTIR spectrometer, equipped with a Spectra-Tech diffuse reflectance accessory and a high-sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N_2. About 14 mg (± 0.02

mg) γ-Al_2O_3 sample was placed into the ceramic crucible in the chamber. The sample temperature in the chamber was kept at 298 K by using an automatic temperature controller. After the reaction chamber was purged with a mixture of O_2 (21% v/v) and Ar (79% v/v) at a total flow rate of 100 mL/min for 60 min, the pre-adsorbed organic species (CH_3CHO, OHC-CHO and CH_3COOH) (79 mL/min) with O_2 (21 mL/min) was introduced into the chamber to perform the pre-adsorption respectively, then the mixture of O_2 (21% v/v) and Ar (79% v/v) was used to purge the chamber for 60 min again, and then a background spectrum was recorded. After collecting the background spectrum, a mixture of gases [NO_2 (1.12×10^{15} molecules cm^{-3}), O_2 (21% v/v) and Ar (59% v/v)] was introduced into the chamber at a total flow rate of 100 mL/min for 120 min. When the mixture of gases was introduced, the IR spectra were recorded automatically every 10 minutes. All the IR spectra were recorded at a resolution of 4 cm^{-1} for 100 scans. For each reaction condition, experiments were repeated at least 3 times.

3. Results and discussion

To investigate the impact of pre-adsorbed species on the heterogeneous reaction of NO_2, the following aspects are studied: 1) Investigation of heterogeneous uptake of acetaldehyde, glyoxal and acetic acid on pure γ-Al_2O_3 particles, respectively. 2) Investigation of heterogeneous reaction of NO_2 on γ-Al_2O_3 particles with and without pre-adsorption of these organic compounds. 3) The effect of pre-adsorbed species on the formation of nitrate. 4) The effect of the pre-adsorbed species on the formation of nitrite.


(a)
10 min
20 min
30 min
K-M
0.002
1716
1682
1652
1641
1622
1700
1650
1600
3632
3735
3000
2947
2906
2862
1716
1682
1652
1622
1457
1400
1376
1346
1179
4000
3600
3200
2800
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


(b)
10 min
20 min
30 min
K-M
4E-4
3630-2780
1661
3735
4000
3600
3200
2800
2000
1600
1200
Wavenumbers (cm^{-1})

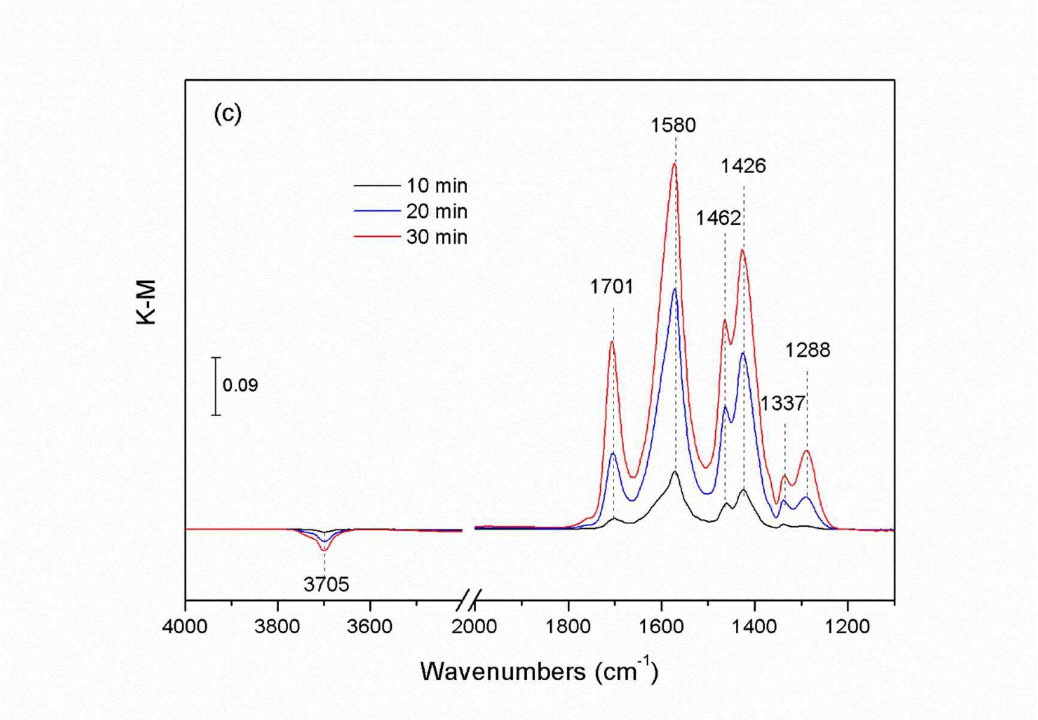


Figure 1. DRIFTS spectra of surface products during the reaction of humid γ-Al_2O_3 with pre-adsorbed species as a function of reaction time. (a) acetaldehyde (2.21× 10^{15} molecules cm^{-3}), (b) glyoxal (2.21×10^{15} molecules cm^{-3}), (c) acetic acid (2.21× 10^{15} molecules cm^{-3}). The inset in Figure 1a is the enlarged spectral region from 1730 to 1590 cm^{-1}.

3.1 Uptake of acetaldehyde on the surface of γ-Al_2O_3 particles.

Heterogeneous uptake of acetaldehyde onto the surface of γ-Al_2O_3 particles at 298 K is investigated at first. DRIFTS spectra following the exposure of CH_3CHO (79 ppm) in the mixture of O_2 (21% v/v) and Ar on γ-Al_2O_3 particles as a function of time are shown in Figure 1a. The exposure of alumina to acetaldehyde results in appearance of some sharp bands at 3000, 2862, 1716, 1457, 1400, 1376, 1346 and 1179 cm^{-1}, and several weak bands at 3735, 3632, 2947, 2906, 1682, 1652, 1641 and 1622 cm^{-1}. The C-H stretch region of the infrared spectrum shows bands at 3000, 2947, 2906, and

2862 cm^{-1}. The bands observed at 2862 cm^{-1} (ν (CH)), 1716 cm^{-1} (ν(C=O)) and 1346 cm^{-1} ($\delta_s(CH_3)$) could be assigned to physisorbed acetaldehyde, while the bands at 3000 cm^{-1} ($\nu_{as}(CH_3)$), 2947 cm^{-1} ($\nu_{as}(CH_3)$) and 1400 cm^{-1} ($\delta_s(CH_3)$) are probably due to oligomeric acetaldehyde such as paraldehyde or metaldehyde.[46] The decrease in intensity of ν (O-H) band of surface isolated hydroxyl groups at 3735 cm^{-1} indicates that acetaldehyde can be adsorbed onto alumina via H-bonding interaction of the carbonyl group with isolated OH group.[18, 46] The band at 1682 cm^{-1} corresponding to ν(C=O) of acetaldehyde shifts to lower wavenumbers with respect to the ν(C=O) band in the gas phase spectrum, indicating that some acetaldehyde molecules are coordinated with Lewis sites through the carbonyl oxygen. These results suggest that acetaldehyde molecules are adsorbed on the surface of alumina not only via H-bonding but also via strong interaction of the carbonyl group with Lewis sites, most probably coordination-unsaturated Al^{3+}.[47, 48]

The weak bands at 1652 and 1641/1622 cm^{-1} are assigned to the ν(C=O) and ν(C=C) modes of crotonaldehyde, respectively,[46, 49-51] and the former is most likely due to the crotonaldehyde coordinated with Lewis sites through the carbonyl oxygen. This result indicates that aldehyde condensation occurs and small amount of crotonaldehyde is formed on the surface of γ-Al_2O_3.[50, 51] However, it should be pointed out that the intensities of these bands have decreased almost synchronously with increasing exposure time since it is formed at the initial stage of adsorption, indicating the loss of crotonaldehyde. In addition, the band around 1273 cm^{-1} due to δ(C-OH) of 3-hydrobutanal surface intermediate is not observed in the region of

1330-1200 cm^{-1} after exposure of the γ-Al_2O_3 surface to acetaldehyde,[50] which may be due to the rapid 3-hydrobutanal dehydration to crotonaldehyde on γ-Al_2O_3.[46] But it is more likely that both results mentioned above may suggest a termination of the aldol condensation on the humid γ-Al_2O_3 surface after a short exposure time. This is consistent with the previous study that have demonstrated that the aldolization reaction on rutile TiO_2 at 313 K can be terminated after a short exposure time, and the desorption of the formed crotonaldehyde via aldolization reaction occurs with increasing exposure.[52] One possible explanation is that only a small fraction of the surface sites on the humid γ-Al_2O_3 are capable of carrying out aldolization, and reaction products such as H_2O, OH, or the higher molecular products of multiple aldolization events may poison or block the access of reactant molecules to the active sites.[52]

The bands at 1457 ($\delta_{as}(CH_3)$), 1376 ($\delta_s(CH_3)$) and 1179 (ν(C-O-C)) cm^{-1} are observed, which may also suggest that small amounts of gem-diol [$CH_3CH(OH)_2$] and dimer [$CH_3CH(OH)OCH(OH)CH_3$] are formed on the humid γ-Al_2O_3.[11, 19, 20, 53] This is because that the adsorbed acetaldehyde coordinated to Lewis sites through the carbonyl oxygen has a positively polarized carbonyl carbon, which may make it more susceptible to nucleophilic attack by H_2O and produce a gem-diol. Meanwhile, the Lewis acid sites may also catalyze the subsequent polymerization reaction between the hydroxyl groups of gem-diol and adsorbed acetaldehyde or dehydration between gem-diol molecules to produce the dimer.[54, 55]

In addition, acetate is usually associated with the ν_a(COO) bands observed around

1580 cm^{-1} (surface-coordinated acetate) and 1550 cm^{-1} (acetate ions),[56, 57] but in this study no clear bands at 1580 and 1550 cm^{-1} are observed, indicating that no formation of acetate occurs on γ-Al_2O_3.

The results mentioned above clearly indicate that acetaldehyde molecules can be transformed into many other species on the surface of γ-Al_2O_3 particles and reveal that the adsorption of acetaldehyde on γ-Al_2O_3 surface is rather complicated.

3.2 Uptake of glyoxal on the surface of γ-Al_2O_3 particles.

As the simplest and one of the most abundant dialdehydes found in the atmosphere, glyoxal is produced largely via photochemical oxidation of volatile organic compounds (VOCs).[21-24] The heterogeneous reaction of glyoxal on the surface of γ-Al_2O_3 particles is also discussed. The DRIFTS spectra during the OHC-CHO (79 ppm) pre-adsorption process are shown in Figure 1b. It is interesting to find that two major bands (including a broad band from 3630 to 2780 cm^{-1} and another band at 1661 cm^{-1}) and a negative band at 3735 cm^{-1} are observed during the uptake of glyoxal on the surface of humid γ-Al_2O_3 particles. The broad band from 3630 to 2780 cm^{-1} reflects the OH groups of $CH(OH)_2CHO$.[59] The band appearing at 1661 cm^{-1} is due to ν(C=O) stretching vibration,[59, 60] indicating the coordination of glyoxal molecules with Lewis sites through the carbonyl oxygen. The observed species indicates that the gaseous glyoxal is easily converted to other surface species, which is consistent with the previous studies that have demonstrated that OHC-CHO can react with surface adsorbed water to form $CH(OH)_2CHO$.[33, 59] No OH groups which is coordinated with two aluminum atoms is consumed, only a few isolated OH groups are lost. The band at 1661 cm^{-1} is quickly saturated at 10 min, and then decreases with the reaction time. The explanation may be that with the introduction of glyoxal onto the humid γ-Al_2O_3 particles, the O atom of C=O group of OHC-CHO, with highly polar, is trapped in a hydrogen atom of the surface isolated hydroxyl group or a possible Lewis acid site to form adsorbed OHC-CHO, which makes the carbonyl carbon more electrophilic and easier to be attacked by an oxygen atom of the adjacent hydroxyl group or water molecules, resulting in the quick formation of $CH(OH)_2CHO$ and the consumption of the surface hydroxyls on the surface of humid γ-Al_2O_3 particles.[51, 61, 62] In addition, water molecules preferentially take up Al^{3+} active sites (i.e. Lewis acid sites) by non-dissociative adsorption on the humid surface of γ-Al_2O_3, and some of these water molecules can make part of the Lewis acid sites be converted into surface hydroxyl groups by its dissociative chemisorption.[63] These would result in a decrease of Lewis acid sites available for the adsorption of OHC-CHO and suppress the interaction of OHC-CHO with Al^{3+}, and thus inhibit the subsequent heterogeneous oxidation of the adsorbed glyoxal (combining with unsaturated Al^{3+}) by active oxygen species.[61] In addition, the presence of water on the humid surface of γ-Al_2O_3 would also shift the hydration equilibrium of glyoxal from the unhydrated carbonyl form to the hydrated form, which also suppress the heterogeneous oxidation of the adsorbed glyoxal. Therefore, no band assigned to ν(C=O) of carboxylic acid or carboxylate is observed on the humid γ-Al_2O_3. While the fact that the band at 1661 cm^{-1} decreases with the reaction time after saturation may suggest the further hydration of another aldehyde group in the product $CH(OH)_2CHO$.

3.3 Uptake of acetic acid on the surface of γ-Al_2O_3 particles.

As an important component of organic acids in the troposphere and the oxidation product of acetaldehyde, the uptake of acetic acid on the surface of γ-Al_2O_3 particles at room temperature is investigated in this study. Figure 1c shows the DRIFTS spectra during the uptake of acetic acid on the surface of the humid γ-Al_2O_3 particles. There are several major bands at 1701, 1580, 1462, 1426, 1337 and 1288 cm^{-1}. The band at 1701 cm^{-1} is assigned to ν(C=O) in molecularly adsorbed acetic acid, and the molecularly adsorbed acetic acid is considered to be bonded to Lewis acid sites (Al^{3+}) through the oxygen lone-pair electrons of the carbonyl group.[56, 64] The two bands at 1580 and 1462 cm^{-1} reflect asymmetric and symmetric ν(COO) modes of surface-coordinated acetate, respectively,[56, 64, 65] the surface-coordinated acetate is derived from the dissociation of acetic acid on Al_2O_3. No band at 1550 cm^{-1} is observed with increasing exposure, indicating no formation of acetate ions on the humid surface.[65] The two bands at 1426 and 1337 cm^{-1} reflect δ(CH_3) modes of acetate and acetic acid respectively.[56, 65] The band at 1288 cm^{-1} is due to the molecularly adsorbed acetic acid.[56, 64, 65] The negative band at 3705 cm^{-1} is assigned to the OH groups which are coordinated with two aluminum atoms.[19]

Detailed assignments of the bands formed during the uptake of pre-adsorbed species are summarized in Table 1.

Table 1. Main Absorption Bands Observed during the Reaction of Pre-adsorption

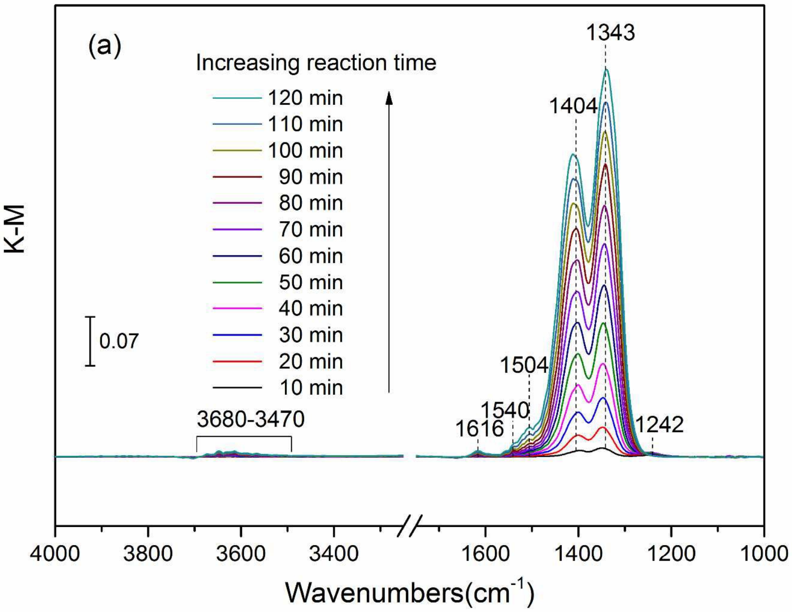
wavenumber/cm^{-1}	vibration type/functional groups
3735	Isolated OH[18]
3705	OH groups[66] (coordinated with two aluminum atoms)
3630-2780	OH[59] $CH_2(OH)CHO$

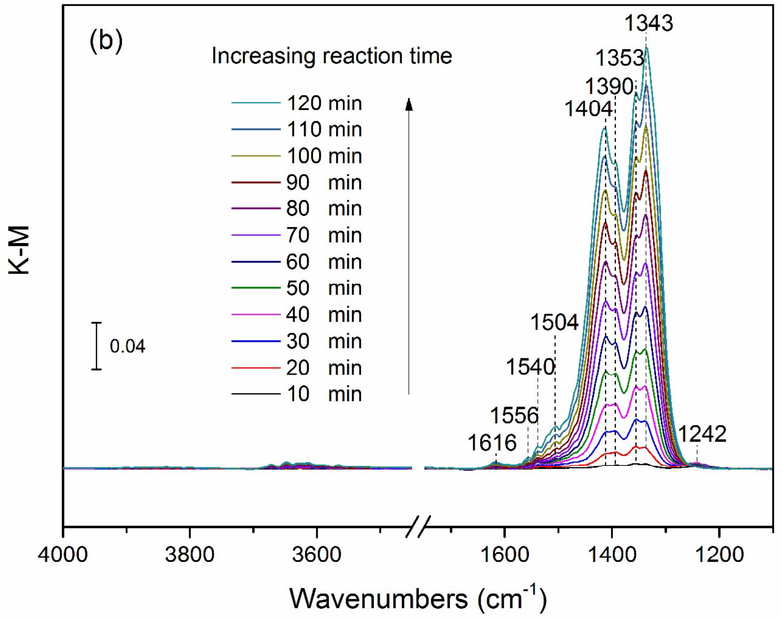
3000	$\nu_{as}(CH_3)$[53]
2947	$\nu_{as}(CH_3)$[46]
2906	C-H[1]
2862	ν (CH)[11, 19]
1716	ν(C=O) physisorbed CH_3CHO[11,53]
1701	ν(C=O) [56, 64] CH_3COOH
1682	ν(C=O) chemisorbed CH_3CHO[11]
1661	ν(C=O)[59, 60] $CH(OH)_2CHO$
1652	ν(C=O) chemisorbed crotonaldehyde[11]
1641	ν(C=C)[46, 49-51]
1622	ν(C=C) [46, 49-51]
1580	Asymmetric ν(COO)[56, 64]
1462	symmetric ν(COO)[56, 64]
1457	$\delta_{as}(CH_3)$[11, 19]
1426	$\delta(CH_3)$[65]
1400	$\delta_s(CH_3)$[46]
1376	$\delta_s(CH_3)$ [11, 19, 53]
1346	$\delta_s(CH_3)$ [19, 53]
1337	$\delta(CH_3)$[56, 65]
1288	Molecularly adsorbed acetic acid[56, 64, 65]
1179	ν (C–O-C)[20]

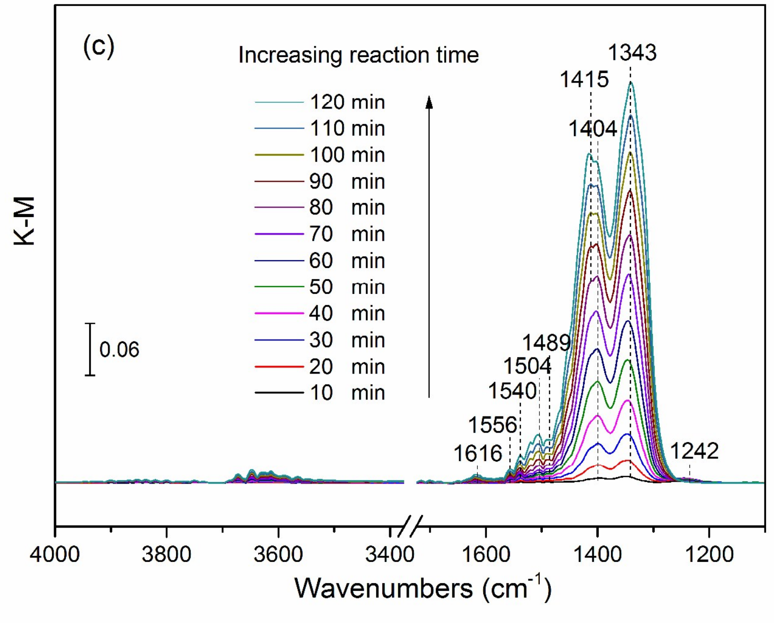
As can be seen from Figure 1, the heterogeneous uptake of acetaldehyde, glyoxal and acetic acid occurs on the humid γ-Al_2O_3 particles respectively, which would potentially change the properties of the particles and further affect the subsequent heterogeneous reactions of the other species on the coating particles. This study will provide significant information for atmospheric chemistry studies.

3.4 Uptake of NO_2 on the surface of γ-Al_2O_3 particles with different pre-adsorbed species.

In this study, the heterogeneous reactions of NO_2 on the surface of γ-Al_2O_3 particles with and without preadsorption of acetaldehyde, glyoxal and acetic acid are discussed in details. In uptake experiments, the DRIFTS spectra are collected as difference spectra with the unreacted γ-Al_2O_3 sample as the background, and thus, surface reaction products formed during the uptake can be observed through the positive absorption bands, whereas negative bands indicate the losses of surface species. The DRIFTS spectra of humid γ-Al_2O_3 with and without preadsorption exposed to NO_2 as a function of time are shown in Figure 2.




(b)
Increasing reaction time
120 min
110 min
100 min
90 min
80 min
70 min
60 min
50 min
40 min
30 min
20 min
10 min
0.04
1343
1353
1390
1404
1504
1540
1556
1616
1242
K-M
4000
3800
3600
1600
1400
1200
Wavenumbers (cm^{-1})


(c)
Increasing reaction time
120 min
110 min
100 min
90 min
80 min
70 min
60 min
50 min
40 min
30 min
20 min
10 min
0.06
1343
1415
1404
1489
1504
1540
1556
1616
1242
K-M
4000
3800
3600
3400
1600
1400
1200
Wavenumbers (cm^{-1})

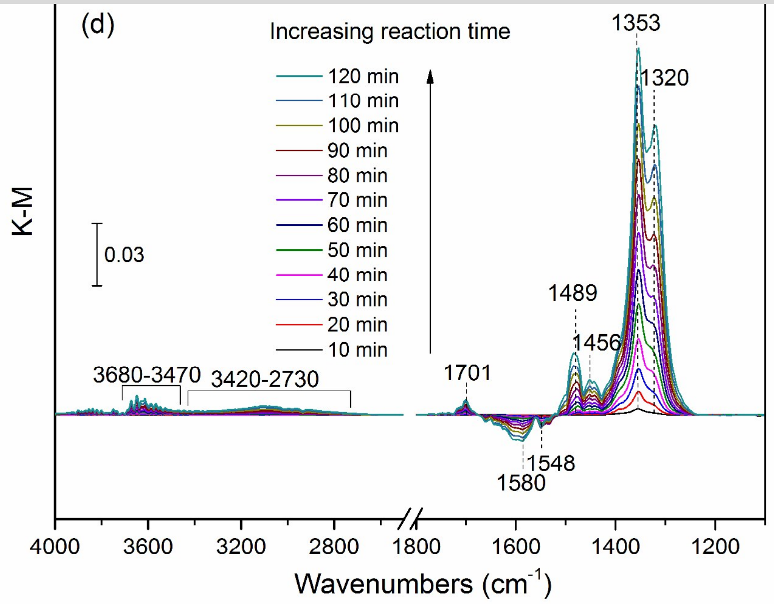


Figure 2. DRIFTS spectra of surface products during the reaction of humid γ-Al_2O_3 with NO_2 as a function of reaction time, the particles have been preadsorbed by (a) none, (b) acetaldehyde (2.21× 10^{15} molecules cm^{-3}), (c) glyoxal (2.21× 10^{15} molecules cm^{-3}), (d) acetic acid (2.21× 10^{15} molecules cm^{-3}) for 30 min, respectively.

As a control group, Figure 2a shows the reaction products formed during the heterogeneous reaction of NO_2 on the surface of humid γ-Al_2O_3 without preadsorption. It is found that once NO_2 is adsorbed on the humid γ-Al_2O_3 particles, several new absorption bands appear and grow with the increasing reaction time. The absorption bands in the region from 1250 to 1670 cm^{-1} are mainly assigned to the degenerate ν_3 mode of nitrate ions coordinated to the surface.[1, 8] In this study, the adsorption bands are consistent with previous studies.[8,66] According to the previous studies, the band at 1242 cm^{-1} is assigned to bidentate nitrite species which grows in the early stage of the reaction and then gradually disappears, the band at

1540 cm^{-1} is assigned to the monodentate nitrate species, the bands at 1343 and 1404 cm^{-1} reflect the formation of adsorbed water-solvated nitrate species, and the two absorption bands at 1616 and 1504 cm^{-1} are assigned to the bridging nitrate species. The broad absorption band extending from 3680 to 3470 cm^{-1} slowly increases in intensity with the increase of reaction time, which is primarily associated with O-H vibration of hydrogen-bonded OH groups.[8, 66-70] Figure 2b and Figure 2c show the reaction products formed during the heterogeneous reactions of NO_2 on the surfaces of humid γ-Al_2O_3 with acetaldehyde and glyoxal preadsorption for 30 min, respectively. Compared with Figure 2a, there are several new bands at 1556, 1489, 1415, 1390 and 1353 cm^{-1}. The bands at 1353, 1390 and 1415 cm^{-1} are still assigned to adsorbed water-solvated nitrate species, which is in agreement with previous study that have shown that inner-sphere and outer-sphere nitrate coordination exist in the presence of co-adsorbed water.[43] The presence of co-adsorbed water can affect the local bonding of the nitrate ion on the surface, as well as the geometry and vibrational frequencies of the adsorbed nitrate.[43] The band at 1556 cm^{-1} is assigned to monodentate nitrate species, and the weak band at 1489 cm^{-1} is assigned to monodentate nitrito NO_2^-.[8, 71] Figure 2d shows the in situ DRIFTS spectra of surface species produced and consumed during the heterogeneous reaction of NO_2 on the surface of humid γ-Al_2O_3 with the pre-adsorption of acetic acid for 30 min. Several new positive bands at 1701, 1489, 1456, 1353 and 1320 cm^{-1} and two negative bands around 1580 and 1548 cm^{-1} are observed. Most of the bands are different from those in Figure 2a, but the major species are still nitrate and nitrite species according to previous studies.[8, 66, 71, 72] The broad absorption band extending from 3680 to 3470 cm^{-1} is primarily associated with O-H vibration of H-O-H.[8, 66-70] The broad band from 3420 to 2730 cm^{-1} is primarily assigned to O-H vibration of hydrogen-bonded OH groups, but it is associated with the acetic acid species. The band at 1701 cm^{-1} is assigned to ν(C=O) of acetic acid.[56, 64] The band at 1489 cm^{-1} is assigned to monodentate nitrite.[67, 71] The bands at 1456 and 1320 cm^{-1} reflect bridging nitrite species. [71, 72] The band at 1353 cm^{-1} is attributed to water-solvated nitrate.[8, 67] The two increased negative bands around 1580 and 1548 cm^{-1} are assigned to the asymmetric stretching modes of COO in acetate [ν_a(COO)].[56, 64] The former can be assigned to the surface-coordinated acetate and the latter can be assigned to the acetate ions, [56, 64] indicating the consumption of acetate on the surface of γ-Al_2O_3 particles during the reaction. From previous studies,[10, 73] it can be known that, with the NO_2 introduced, the acidity of the surface of γ-Al_2O_3 particles would increase through the disproportionation reaction between NO_2 and surface-adsorbed water, resulting in the loss of acetate species and the formation of acetic acid species.

It is worth noting that the trends in changes in the amounts of nitrite species shown in Figure 2b and Figure 2c have almost no change comparing with the control experiment shown in Figure 2a, and all the amounts of nitrite shown in Figure 2a, 2b and 2c increase at first, then decrease gradually and finally disappear with the increase of reaction time. But the trend in change in the amount of nitrite shown in Figure 2d has completely changed, the amount of nitrite is always increasing, and it does not disappear during the reaction. In addition, Figure 2a, 2b, 2c and 2d all have shown a slightly loss of OH groups at the bands of 3705, 3714, 3727 and 3735 cm^{-1}, indicating that these OH groups are still the active sites for the heterogeneous reaction of NO_2 on the surface of γ-Al_2O_3 particles, which is consistent with previous studies.[10, 66]

The assignments of bands of adsorbed nitrate and nitrite during the heterogeneous reaction of NO_2 on γ-Al_2O_3 with different pre-adsorbed species are summarized in Table 2.

Table 2. Assignment of the vibrational frequencies (cm^{-1}) for adsorbed nitrate and nitrite following exposure of γ-Al_2O_3 particle surfaces to NO_2 in this study.

wavenumber/cm^{-1}	Vibration type/functional groups
1616, 1504	bridging nitrate[8, 66]
1556, 1540, 1489	monodentate nitrate[8, 66, 71]
1456, 1320	bridging nitrite[72, 73]
1404, 1390, 1353, 1343	water-solvated nitrate[8, 66, 67]
1242	bidentate nitrite[8, 66]

3.5 The effect of pre-adsorbed species on the formation of nitrate.

In the experiments, the formation of nitrate on the surface of γ-Al_2O_3 with different preadsorbed species under the same concentration of NO_2 is investigated as a function of reaction time. As shown in Figure 3, the pre-adsorption of the organic species can clearly suppress the formation of nitrate to different extents. The pre-adsorption of glyoxal only has a little contribution to the suppression of the formation of nitrate, while the pre-adsorption of acetic acid contributes a lot. It should be pointed out that no surface adsorbed nitro compounds are formed in the process of the heterogeneous reaction of NO_2 on the surface of γ-Al_2O_3 with different pre-adsorption during the DRIFTS experiments, which is also verified by Ion Chromatography (IC). This result may mean that there are no direct interactions between the pre-adsorbed species (acetaldehyde, glyoxal and acetic acid) and NO_2 to form any adsorbed nitrogen-containing products. This is consistent with the previous study that has demonstrated that NO_2 cannot react with acetaldehyde in the room temperature.[74]

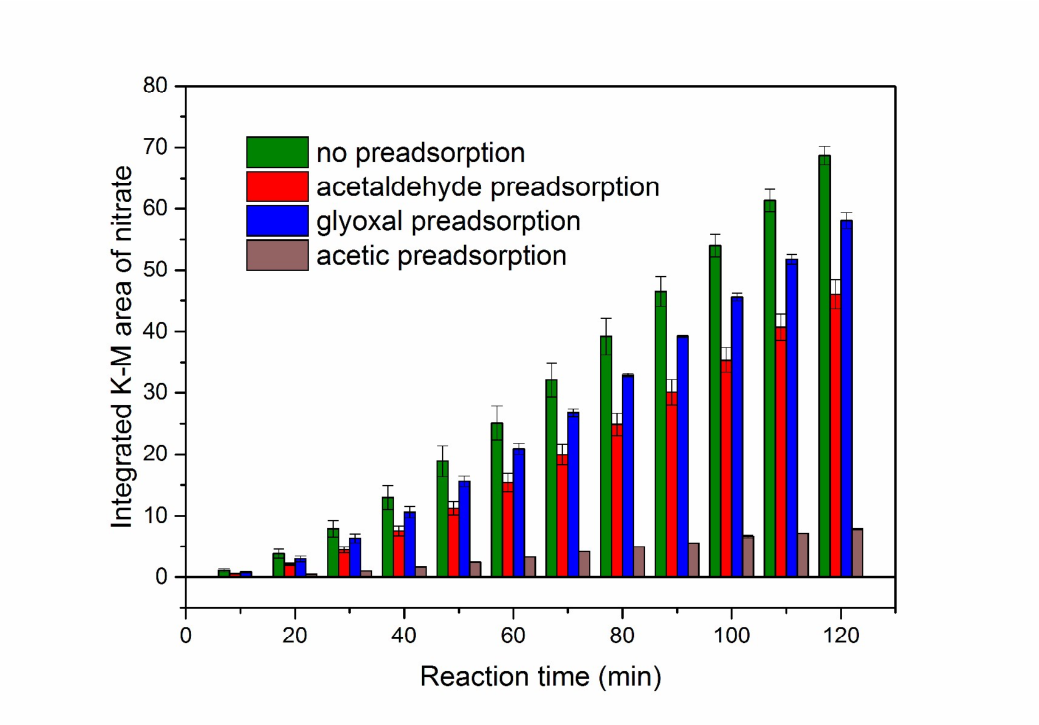


Figure 3. Integrated K-M areas of the nitrate absorption bands for different pre-adsorbed reactant species. The error bars represent one standard deviation from repeated experiments.

The pre-adsorption of acetaldehyde and glyoxal suppresses the formation of nitrate slightly, and it can be known from the DRIFTS spectra that the major active sites for the adsorption of acetaldehyde and glyoxal on the surface of γ-Al_2O_3 are isolated OH groups. Although the isolated OH groups are also the active sites for the heterogeneous reaction of NO_2, the major active sites for the adsorption of NO_2 on the surface of γ-Al_2O_3 are the OH groups coordinated with two aluminum atoms, which gives the band at 3705 cm^{-1}. Therefore, the consumption of the isolated OH groups by preadsorbed species would suppress the heterogeneous reaction of NO_2 on γ-Al_2O_3 to some extent. In addition, as the water-solvated nitrate is the major product of the heterogeneous reaction of NO_2 in this study, and the presence of water is beneficial to the formation of surface OH groups, the pre-adsorption of acetaldehyde and glyoxal would also consume some surface adsorbed water, the loss of surface adsorbed water may be an influence factor for the suppression. For acetic acid, its pre-adsorption makes some of the OH groups giving the band at 3705 cm^{-1} be consumed, these OH groups are the major active sites for the heterogeneous reaction of NO_2 on the surface of γ-Al_2O_3 particles,[10, 66] and hence resulting in the decrease of the active sites and the subsequent suppression for the heterogeneous reaction of NO_2. Additionally, in this study, water molecules preferentially take up Al^{3+} active sites (i.e. Lewis acid sites) on the humid surface of γ-Al_2O_3, but the preadsorbed acetic acid will also be adsorbed on Lewis acid sites (Al^{3+}) through the oxygen lone-pair electrons of the carbonyl group.[56, 64] The competitive adsorption would decrease the chemisorbed water molecules, which may reduce the regeneration of surface active OH groups through the interaction of water molecule with Al^{3+} active site on the humid surface of γ-Al_2O_3,[75, 76] and further suppress the subsequent heterogeneous reaction of NO_2. In addition, nitrate generated during the subsequent heterogeneous reaction of NO_2 may also occupy the reaction active sites for the heterogeneous reaction of NO_2, which may be another reason for the suppression of nitrate formation. In conclusion, the formation of nitrate is suppressed by the pre-adsorbed organic species.

3.6 The effect of pre-adsorbed species on the formation of nitrite.

As one of the adsorbed products of the heterogeneous reaction of NO_2 on the surface of γ-Al_2O_3, nitrite species has important influence in the atmosphere, and the effect of pre-adsorbed species on the formation of nitrite is discussed in this study.

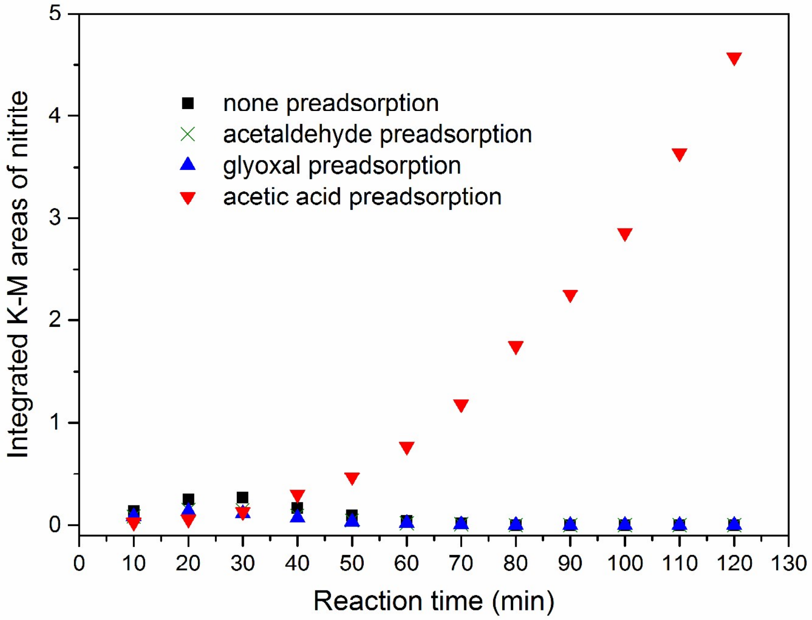


Figure 4. Integrated K-M areas of the nitrite absorption bands for different preadsorbed species.

As shown in Figure 4, the pre-adsorption of acetaldehyde and glyoxal can suppress the formation of nitrite to a similar extent, the amounts of the formed nitrite species firstly increase and then decrease and finally disappear with the increase of reaction time. In this study, the nitrite species is an intermediate of the heterogeneous reaction of NO_2 on the surface of γ-Al_2O_3 particles with and without pre-adsorption of acetaldehyde and glyoxal, respectively. The nitrite species can be formed through a disproportionation of two adsorbed NO_2 molecules on the surface of γ-Al_2O_3 and a disproportionation reaction between NO_2 and surface-adsorbed water,[10, 66] and the formed nitrite species will be further oxidized to nitrate species by excess NO_2.[8, 66] This is in agreement with previous studies. However, it should be pointed out that, compared with no pre-adsorption of acetaldehyde and glyoxal, the presence of preadsorbed acetaldehyde and glyoxal neither obviously promotes the formation of nitrite nor clearly accelerates the decrease of nitrite.

It can also be seen from Figure 4 that the amount of nitrite formed on the surface of γ-Al_2O_3 with acetic acid pre-adsorption always increase with the reaction time, after the slow increase of nitrite species in the first 50 min of the reaction, the rate of the nitrite formation is greatly increased. Nitrite is identified as an intermediate in the previous studies and would disappear quickly when the high concentrations of NO_2 are continuously introduced.[65] But in this study, nitrite is a final product of the heterogeneous reaction of NO_2 on the surface of γ-Al_2O_3 with acetic acid pre-adsorption. One possible explanation is that the pre-adsorption of acetic acid consumes the major OH group active sites for the heterogeneous reaction of NO_2 and decreases the regeneration of surface OH groups on the surface of γ-Al_2O_3 particles, and finally suppresses the formation of nitrate and leads to the formation of nitrite. This may also suggest that the major OH group active sites giving the band at 3705 cm^{-1} play an important role in the formation of nitrate during the heterogeneous reaction of NO_2.

4. Conclusions

In the study the heterogeneous reactions of NO_2 with alumina with and without pre-adsorption of organic species (acetaldehyde, glyoxal and acetic acid) have been studied by using in situ DRIFT spectroscopy as surface-sensitive method. It is found that the pre-adsorbed species has a clear influence on the heterogeneous reaction of NO_2 on the surface of γ-Al_2O_3, the preadsorbed acetaldehyde, glyoxal and acetic acid have suppression effect on the formation of nitrate in different degrees respectively, and influence the formation of nitrite. Under the same experimental conditions, the extent of the suppression by pre-adsorption of acetic acid for the formation of nitrate is much stronger than that by pre-adsorption of acetaldehyde and glyoxal, and the influence of acetic acid on the heterogeneous reaction of NO_2 is different from that of acetaldehyde and glyoxal. Compared with the heterogeneous reactions of NO_2 on the humid γ-Al_2O_3 with and without the pre-adsorption of acetaldehyde and glyoxal, the preadsorbed acetic acid make nitrite species be the main product of the heterogeneous reaction of NO_2 on the surface of γ-Al_2O_3. Based on our experimental results, the influence mechanisms of the different pre-adsorbed species on the heterogeneous reaction of NO_2 have been studied and it is found that the surface OH groups which act as the reaction active sites for the heterogeneous reaction of NO_2 are the major influence factor of the product formation.

It has been already shown in a number of previous studies that the heterogeneous reaction of NO_2 with mineral dust particles and its chemical reactivity are of great importance in atmospheric chemistry,[3, 8-11] and many studies have discussed the heterogeneous reactions of the simple organic compunds existing in the atmosphere respectively, such as acetaldehyde, glyoxal and acetic acid.[13, 21-24, 38] But little attention is paid to the synergism effect between NO_2 and the organic species like acetaldehyde, glyoxal and acetic acid. The results from this study have important atmospheric implications. The results reveal a significant impact of acetaldehyde, glyoxal and acetic acid on the heterogeneous conversion of NO_2 and the formation of nitrite and nitrate in the atmosphere. This chemistry may occur on surfaces of airborne dust particles that are known to be transported and play a role in the chemistry of the troposphere, which would affect the level of particulate nitrate in the troposphere and the estimation of the amount of global atmospheric nitrate.

Notes

The authors declare no competing financial interest.

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