



# Impact of heterogeneous uptake of nitrogen dioxide on the conversion of acetaldehyde on gamma-alumina in the absence and presence of simulated solar irradiation

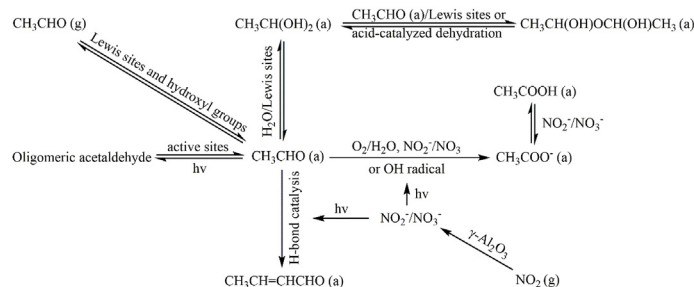


Chengtian Du<sup>a</sup>, Lingdong Kong<sup>a,b,\*</sup>, Assiya Zhanzakova<sup>a</sup>, Songying Tong<sup>a</sup>, Xin Yang<sup>a</sup>, Lin Wang<sup>a</sup>, Hongbo Fu<sup>a</sup>, Tiantao Cheng<sup>a,b</sup>, Jianmin Chen<sup>a,b,\*\*</sup>, Shicheng Zhang<sup>a</sup>

<sup>a</sup> Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Institute of Atmospheric Sciences, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China

<sup>b</sup> Shanghai Institute of Eco-Chongming (SIEC), No.3663 Northern Zhongshan Road, Shanghai 200062, China

## GRAPHICAL ABSTRACT



## ABSTRACT

Heterogeneous reactions of various atmospheric gaseous pollutants on particle surfaces are important pathways for the formation of secondary aerosols. However, these heterogeneous reactions are inevitably affected by each other in the real atmosphere. In this study, the impacts of the heterogeneous uptake of  $\text{NO}_2$  on the conversion of acetaldehyde on the particle surfaces in the absence and presence of simulated solar irradiation were investigated by using diffuse reflectance infrared spectroscopy (DRIFTS) at 298 K. It is found that in the absence of simulated solar irradiation the hydration reaction and subsequent polyoligomeric reaction as well as oligomeric reaction of  $\text{CH}_3\text{CHO}$  are promoted by the pre-adsorption of  $\text{NO}_2$  for a short reaction time, but these reactions are significantly hindered, accompanied with the slightly enhanced formation of crotonaldehyde and adsorbed acetate by the pre-adsorption of  $\text{NO}_2$  for a longer time. In the presence of simulated solar irradiation, the occurrence of the aldol condensation and the oxidation of  $\text{CH}_3\text{CHO}$  are promoted by the combined impacts of illumination, hydrogen bond (H-bond) catalysis, the enhanced surface acidity and the formed nitrite and nitrate, especially, the photolysis of the formed nitrite and nitrate, whereas the hydration reaction and subsequent polyoligomeric reaction as well as oligomeric reaction of  $\text{CH}_3\text{CHO}$  molecules are suppressed. Meanwhile, the

\* Corresponding author. Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Institute of Atmospheric Sciences, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China.

\*\* Corresponding author. Shanghai Institute of Eco-Chongming (SIEC), No.3663 Northern Zhongshan Road, Shanghai 200062, China.

E-mail addresses: [ldkong@fudan.edu.cn](mailto:ldkong@fudan.edu.cn) (L. Kong), [jmchen@fudan.edu.cn](mailto:jmchen@fudan.edu.cn) (J. Chen).

hydrogen bond catalysis for aldol condensation is significantly enhanced by light irradiation, showing a combined result of hydrogen bond catalysis and illumination. The heterogeneous reaction mechanism is proposed, and atmospheric implications based on these results are discussed in this study.

## 1. Introduction

In recent years, rapid urbanization and industrialization have resulted in serious air pollution in many cities and regions in China, and haze episodes have occurred frequently. In the haze episodes, nitrate pollution presents increasing trend due to SO<sub>2</sub> emission control strategies of China and rapid increase of NO<sub>x</sub> emitted from dramatically increased vehicle population. As an important component of atmospheric pollutants and an important precursor of atmospheric secondary nitrate and ozone, NO<sub>2</sub> mainly originates from anthropogenic emissions and can undergo various reaction processes (Goodman et al., 1998). Heterogeneous processes of NO<sub>2</sub> have received increasing attention because it accounts for the enhanced formation and accumulation of nitrate aerosol in haze events (Han et al., 2016; Liu et al., 2012; Wu et al., 2013). The studies of heterogeneous reactions of NO<sub>2</sub> on various particle surfaces have proved that NO<sub>2</sub> is easily adsorbed on sea salt, black carbon, mineral oxides and other particles, and converted into adsorbed products such as adsorbed nitric acid, nitrates and nitrites (Laskin et al., 2002; Thevenet et al., 2015; Usher et al., 2003; Zhang et al., 2012). As a more effective oxidant compared with oxygen, NO<sub>2</sub> can oxidize SO<sub>2</sub> into sulfate after capturing SO<sub>2</sub> into aerosol particles through the synergistic effects of NO<sub>2</sub> and SO<sub>2</sub> on different particle surfaces (Liu et al., 2012), and thus lead to the aggravation of severe haze pollution (Cheng et al., 2016). In addition, as one of the most common components of secondary aerosols (Dentener et al., 1996), the formed nitrate can enhance hygroscopic properties of original particulates and result in the change of physicochemical properties (Hoffman et al., 2004). For example, Kong et al. reported that nitrate can accelerate the formation of sulfate during the heterogeneous reaction of SO<sub>2</sub> (Kong et al., 2014). Furthermore, surface formed nitrate can also undergo photolysis to produce OH radical and O (<sup>3</sup>P) (Goldstein and Rabani, 2007; Schuttlefield et al., 2008). These active species are important oxidants for the oxidation and removal of other atmospheric trace gases including gas-phase inorganic and organic pollutants (Budiman et al., 2016; Ma et al., 2013). However, the research on the impacts of the pre-adsorption of NO<sub>2</sub> on the heterogeneous reactions of other atmospheric pollutants in the absence and presence of light irradiation is still limited.

Acetaldehyde is a typical volatile organic compound, and it can be produced from atmospheric photochemistry of VOCs (Wang et al., 2015; Yang et al., 2018). Acetaldehyde is also a precursor in the photochemical formation of tropospheric ozone (Duan et al., 2008). It can be adsorbed on the particle surfaces through the interaction of carbonyl group with surface hydroxyl group and Lewis acid site, and be converted into surface acetate and other organic species via various heterogeneous reactions (Guil et al., 2005; Li et al., 2001; Natal-Santiago et al., 1999; Rasko and Kiss, 2005; Wu et al., 1998). CH<sub>3</sub>CHO can be weakly and reversibly physisorbed on SiO<sub>2</sub> particle surfaces through hydrogen-bonding interaction between carbonyl group and surface hydroxyl group (Kydd et al., 2009; Li et al., 2001; Natal-Santiago et al., 1999; Rasko and Kiss, 2005), while on α-Al<sub>2</sub>O<sub>3</sub>, CaO, and TiO<sub>2</sub> surfaces CH<sub>3</sub>CHO can undergo heterogeneous reactions to yield irreversibly adsorbed unsaturated carbonyl compounds with higher molecular weight. For example, two acetaldehyde molecules on these particle surfaces can undergo aldol condensation reaction to produce 2-butenal via the intermediate product 3-hydroxy-butanal (Batault et al., 2015; Duan et al., 2008; Kydd et al., 2009; Rasko and Kiss, 2005). Theoretical studies also indicated that silicate, SiO<sub>2</sub> and TiO<sub>2</sub> are good sinks for various aldehyde including CH<sub>3</sub>CHO (Juga et al., 2010; Ji et al., 2015; Yao et al., 2017), and CH<sub>3</sub>CHO can be trapped on silicate and TiO<sub>2</sub>

surfaces through different surface atoms (Juga et al., 2010; Yao et al., 2017), especially, its adsorption complex structure on silicate can determine the subsequent path of its reaction with ·OH radicals (Juga et al., 2010). In addition, in the presence of H<sub>2</sub>O, CH<sub>3</sub>CHO can undergo heterogeneous uptake to form gem-diol and its dimer through the interaction of CH<sub>3</sub>CHO with Lewis acid, and the pre-adsorbed SO<sub>2</sub> significantly hinders oxidation of acetaldehyde to acetate (Zhao et al., 2015). Up to now, few studies have been carried out on the heterogeneous reaction of acetaldehyde, and the impacts of the heterogeneous reaction of NO<sub>2</sub> and its products on the conversion of acetaldehyde remain unclear.

Mineral aerosol is one of the important components of atmospheric aerosols (Xu et al., 2011). They play a significant role in atmospheric heterogeneous processes and new particle formation (Liu et al., 2012; Ma et al., 2008; Nie et al., 2014; Palacios et al., 2016; Shen et al., 2016), and therefore the significant influence of mineral aerosol on tropospheric chemistry has attracted great attention (Bauer et al., 2004; George et al., 2007; Usher et al., 2002, 2003). For instance, the new particle formation and growth rates in the real atmosphere can be enhanced during the dust episodes due to the influence of photo-induced, dust surface-mediated reactions (Nie et al., 2014). Some studies have begun to focus on the impact of pre-adsorption of one trace gas on the subsequent uptake and reaction processes of other gaseous pollutants on the mineral aerosols. For example, the study of synergistic reaction mechanism between SO<sub>2</sub> and NO<sub>2</sub> revealed that the heterogeneous reaction pathway of NO<sub>2</sub> adsorbed on alumina can be altered in the presence of SO<sub>2</sub>, while the presence of NO<sub>2</sub> also promotes the oxidation of SO<sub>2</sub> (Ma et al., 2008). In addition, the pre-adsorption of SO<sub>2</sub> on α-Fe<sub>2</sub>O<sub>3</sub> can hinder the heterogeneous oxidation of CH<sub>3</sub>CHO to acetate, while the pre-adsorption of CH<sub>3</sub>CHO has significant effects on the heterogeneous reaction of SO<sub>2</sub> (Zhao et al., 2015). Meanwhile, inhibition of heterogeneous reaction between SO<sub>2</sub> and HCOOH was demonstrated in previous study (Tong et al., 2010; Wu et al., 2011). However, the studies on these aspects remain limited, and the research in this field still needs further exploration. Alumina is a major component of mineral aerosol. As one type of alumina, γ-Al<sub>2</sub>O<sub>3</sub> is frequently used as a model for mineral aerosol to obtain useful spectral information about various heterogeneous reactions due to its superior reactivity and high surface area (Baltrusaitis et al., 2007; Börensén et al., 2000). Therefore, it is interesting to study the complex heterogeneous reactions of atmospheric trace gases by using γ-Al<sub>2</sub>O<sub>3</sub> as the model compound.

In this study, the effect of NO<sub>2</sub> pre-adsorption on the heterogeneous reaction of acetaldehyde on the surface of γ-Al<sub>2</sub>O<sub>3</sub> was explored by using diffuse reflectance infrared spectroscopy (DRIFTS). This study facilitates a better understanding of the heterogeneous reactivity of atmospheric trace gases and of the formation mechanisms and processes of aerosol surface products in real atmosphere, and thus sheds light on topics of secondary aerosol formation, air pollution, atmospheric chemical modelling and pollution control strategy.

## 2. Experimental section

### 2.1. Chemicals

In this study, commercially available γ-Al<sub>2</sub>O<sub>3</sub> powders (99.997% purity, surface area: 50 m<sup>2</sup>/g) purchased from Alfa Aesar were used for acquirement of spectral information. The humid γ-Al<sub>2</sub>O<sub>3</sub> powders were prepared as before (Sun et al., 2016). In brief, the dried γ-Al<sub>2</sub>O<sub>3</sub> particles were kept in a desiccator for 48 h where the sample powder was equilibrated at 68% relative humidity. The relative humidity was

controlled with a saturated solution of potassium iodide (Sigma-Aldrich). The humid sample was still loose, fine powder after the equilibration, and this treatment caused some adsorbed water molecules to be present on the humid sample. CH<sub>3</sub>CHO (100 ppm, CH<sub>3</sub>CHO /N<sub>2</sub>) (Shanghai Qingkuan Chemical Co., Ltd) was used as reactant gas. NO<sub>2</sub> (200 ppm, NO<sub>2</sub>/N<sub>2</sub>) was used as influence gas of CH<sub>3</sub>CHO. O<sub>2</sub> (99.999% purity, Shanghai Qingkuan Chemical Co., Ltd) and N<sub>2</sub> (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 reaction of CH<sub>3</sub>CHO with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has been studied by using in situ DRIFTS as before (Sun et al., 2016; Zhao et al., 2015). The DRIFTS spectra were recorded on 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<sub>2</sub>.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders were placed into the ceramic crucible in the chamber and controlled temperature by using an automatic temperature controller. The synthetic air (21% O<sub>2</sub> and 79% N<sub>2</sub>) at a total flow rate of 100 mL/min was introduced for 60 min to purge the reaction chamber and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders. After the purge by synthetic air, a mixture of NO<sub>2</sub> ( $1.12 \times 10^{15}$  molecules cm<sup>-3</sup>), O<sub>2</sub> (21% v/v), and N<sub>2</sub> (79% v/v) was introduced into the chamber to react with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for different reaction times, and then synthetic air was used to purge the chamber for 60 min again. A background spectrum was recorded. After collecting the background spectrum, a mixture of gases [(CH<sub>3</sub>CHO) (79 mL/min) with O<sub>2</sub> (21 mL/min)] was introduced into the chamber at a total flow rate of 100 mL/min for 60 min, and the spectrum was collected automatically every 10 min during the reaction processes. All the IR spectra were recorded with a resolution of 4 cm<sup>-1</sup> for 100 scans. The data accuracy was ensured by repeated measurements. Simulated solar irradiation was provided by a 250 W xenon lamp coupled with an optical fiber (model CEL-TCX250, Beijing Jin Yuan Science and Technology Co., Ltd.).

## 3. Results and discussion

To investigate the impact of heterogeneous uptake of NO<sub>2</sub> on the heterogeneous reaction of acetaldehyde in the absence and presence of simulated solar irradiation, the following aspects were studied: 1) Investigation of heterogeneous process of NO<sub>2</sub>; 2) Investigation of heterogeneous conversion of acetaldehyde on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles pre-adsorbed by NO<sub>2</sub> for different times in the absence and presence of simulated solar irradiation.

### 3.1. Uptake of NO<sub>2</sub> on the surface of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles

Fig. 1a shows the surface reaction products formed during the heterogeneous reaction of NO<sub>2</sub> on the surface of humid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the absence of simulated solar irradiation. There are many positive peaks appeared, most of these peaks are increased with the reaction time. According to the peak assignments of previous studies, the main products of heterogeneous reaction of NO<sub>2</sub> on the surface of humid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are nitrite and nitrate (Sun et al., 2016). The peaks at 1343, 1404, 1504, 1540, and 1616 cm<sup>-1</sup> are assigned to adsorbed nitrate. The peak at 1540 cm<sup>-1</sup> represents the monodentate nitrate, the peaks at 1343 and 1404 cm<sup>-1</sup> represent the water-solvated nitrate, the peaks at 1504 and 1616 cm<sup>-1</sup> are assigned to bridging nitrate (Goodman et al., 1998; Wu et al., 2013). The peak at 1242 cm<sup>-1</sup> is attributed to nitrite, which increases at the beginning of reaction and then gradually disappears. This peak reaches maximum after the introduction of NO<sub>2</sub> for 30 min, and disappears after the introduction of NO<sub>2</sub> for 90 min, indicating nitrite is an intermediate during the introduction of NO<sub>2</sub>.

Many studies demonstrated that the adsorption of NO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces can result in the formation of both adsorbed nitrate and nitrite

(Börensén et al., 2000; Ma et al., 2008; Underwood et al., 1999; Wu et al., 2013; Szanyi et al., 2007), and the formed nitrite is usually considered to be an intermediate in the oxidation of NO<sub>2</sub> to surface nitrate species (Ma et al., 2008; Wu et al., 2013). For example, Börensén et al. (2000) investigated the reaction of NO<sub>2</sub> with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and found that the nitrite peak grows fast in the beginning of the reaction, reaches a maximum, and decreases in intensity as the reaction proceeds. They also found that the reaction time after which the nitrite peak has reached its maximum integrated absorbance strongly depends on the NO<sub>2</sub> concentration; at high NO<sub>2</sub> concentrations, the maximum is reached within a short time, and then subsequent decay of nitrite has been observed. Underwood et al. (1999) found that gas-phase NO<sub>2</sub> can react on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particle surfaces to yield surface nitrite, and they suggested a two-step mechanism in which NO<sub>2</sub>(g) is initially adsorbed as a nitrite species which subsequently reacts with another surface nitrite or additional NO<sub>2</sub> (g) to form surface nitrate and gas-phase NO. Wu et al. (2013) found that nitrite is an intermediate product and it exists as bidentate nitrite during the heterogeneous reaction of NO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particle surfaces. They suggested that surface bidentate nitrite begin to be oxidized to bidentate nitrate by gas-phase NO<sub>2</sub> when most of the surface reactive sites are taken up by surface nitrite and nitrate. In their study, gas-phase NO during the oxidation of nitrite is not observed because it is oxidized to NO<sub>2</sub> quickly in the presence of excess O<sub>2</sub>. In our

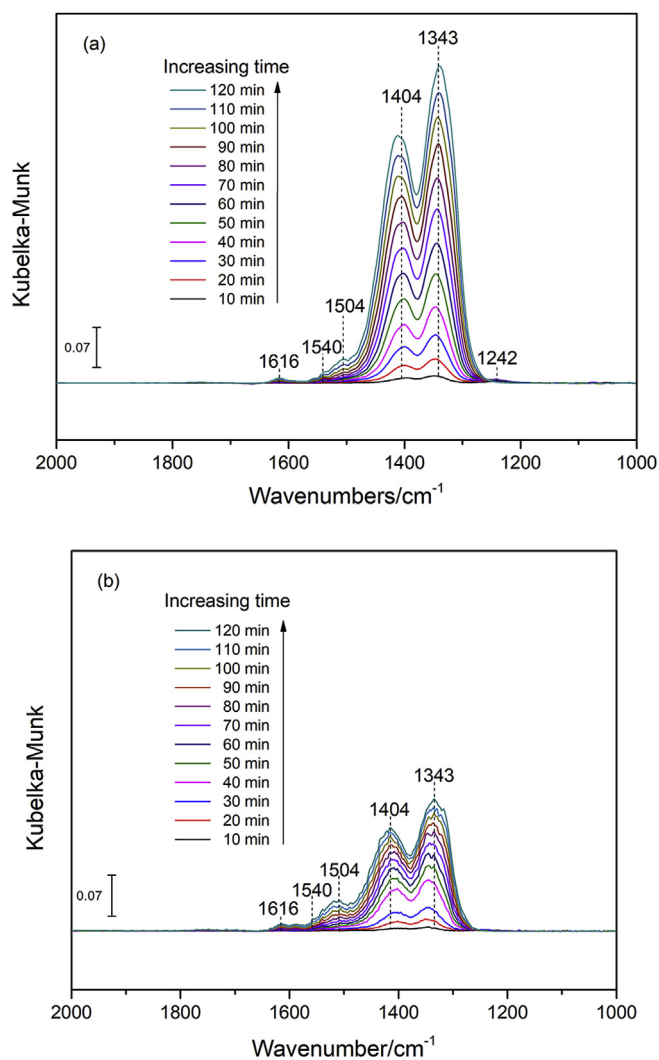
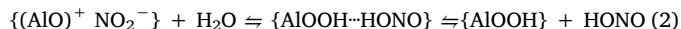
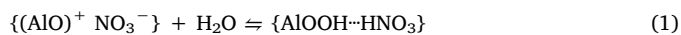


Fig. 1. DRIFTS spectra of surface products as a function of reaction time during the reaction of humid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with NO<sub>2</sub> in the absence of simulated solar irradiation (a) and in the presence of simulated solar irradiation (b).

study, surface nitrite is also found to be an intermediate product during the heterogeneous reaction of  $\text{NO}_2$  on the surface of humid  $\gamma\text{-Al}_2\text{O}_3$  in the absence of simulated solar irradiation. This result is consistent with previous studies (Börensén et al., 2000; Ma et al., 2008; Underwood et al., 1999; Wu et al., 2013; Szanyi et al., 2007). It should be pointed out that the mechanism of  $\text{NO}_2$  adsorption on  $\gamma\text{-Al}_2\text{O}_3$  surfaces postulated by Underwood et al., (1999) suggested that  $\text{NO}_2$  can react directly on  $\gamma\text{-Al}_2\text{O}_3$  particle surfaces to yield surface nitrite followed by oxidation to nitrate. In fact, the peaks of both nitrite and nitrate species are observed in the early spectra (Fig. 1a), which implies that nitrite and nitrate species should be yielded synchronously. Therefore, in the absence of simulated solar irradiation, the likely reaction mechanism for the heterogeneous reaction of  $\text{NO}_2$  on humid  $\gamma\text{-Al}_2\text{O}_3$  is as follows.

Initially, gas-phase  $\text{NO}_2$  is adsorbed onto the surface of  $\gamma\text{-Al}_2\text{O}_3$  through interaction between  $\text{NO}_2$  and surface OH group of the  $\gamma\text{-Al}_2\text{O}_3$ . In the next reaction step a disproportionation of two adsorbed  $\text{NO}_2$  molecules results in surface-coordinated nitrate and nitrite species (Börensén et al., 2000; Wu et al., 2013). The formed nitrate and nitrite species are coordinated to the surface in several different ways, such as monodentate, bidentate, and bridging. The intermediate nitrite exists as bidentate nitrite. As the reaction proceeds, the formed surface nitrite can then react with either; another surface nitrite in a Langmuir-Hinshelwood type mechanism, or the introduced  $\text{NO}_2$  (g) in an Eley-Rideal type mechanism. In either case the result is the decay of surface nitrite and the formation of surface nitrate and gas-phase NO formation (Börensén et al., 2000; Underwood et al., 1999; Wu et al., 2013), though gas-phase NO is not observed in our experiments due to the presence of  $\text{O}_2$  and the detection limit of DRIFTS technique. However, it was indeed observed by Underwood et al., (1999). These reactions finally lead to the disappearance of the peak assigned to adsorbed nitrite.

In addition, during the reactions of humid  $\gamma\text{-Al}_2\text{O}_3$  with  $\text{NO}_2$  in the absence of simulated solar irradiation, a weak broad absorption peak extending from 3700 to 2600  $\text{cm}^{-1}$  slowly increases in intensity with the increase of reaction time. This broad peak is primarily associated with O–H vibrations of hydrogen-bonded OH groups of acid (Börensén et al., 2000; Goodman et al., 1999; Ramazan et al., 2006; Finlayson-Pitts et al., 2003). That is, the observed acidic OH vibrations are caused by adsorbed  $\text{HNO}_3$  or  $\text{HONO}$ , which are in equilibrium (1, 2) with nitrate and nitrite ions and surface-adsorbed water (Börensén et al., 2000):



It should be pointed out that the adsorbed  $\text{HNO}_3$  and  $\text{HONO}$  can also be formed from the reaction of  $\text{NO}_2$  with surface adsorbed water due to the presence of adsorbed water on humid  $\gamma\text{-Al}_2\text{O}_3$  (Jenkin et al., 1988; Kleffmann et al., 1998; Langer et al., 1997), and they also participate in the equilibrium (1, 2). Therefore, an alternate mechanism involving the decrease of the initially observed nitrite peak and the formation of surface nitrate is based on that proposed by Börensén et al. (2000). That is, this phenomenon can be explained by a change in pH at the surface caused by the loss of surface OH groups. During the course of the reaction the number density of  $\{\text{AlOOH}\}$  sites decreases and consequently equilibrium (2) is shifted to the right side with associated release of  $\text{HONO}$  to the gas phase. In contrast, the “sticky” nitric acid that is formed in equilibrium (1) remains at the surface. Moreover, further reactions of nitrous acid are also possible, that is, disproportionation to nitric acid and nitric oxide (NO) (Börensén et al., 2000). These reactions also lead to the disappearance of adsorbed nitrite.

As described in the introduction, the reaction pathway of  $\text{NO}_2$  adsorbed on  $\gamma\text{-Al}_2\text{O}_3$  can be altered by the presence of  $\text{SO}_2$ , and in the absence of  $\text{SO}_2$ , nitrite is found to be an intermediate in the oxidation of  $\text{NO}_2$  to surface nitrate species, while in the presence of  $\text{SO}_2$ , the formation of nitrite is inhibited and  $\text{N}_2\text{O}_4$  becomes a new intermediate in the process of the adsorbed nitrate formation (Ma et al., 2008).

Therefore, no peak at 1300  $\text{cm}^{-1}$  indicates no formation of  $\text{N}_2\text{O}_4$  in our study because our experiment was carried out in the absence of  $\text{SO}_2$ . This result is consistent with that reported by Ma et al. (2008), implying that the oxidation reaction from  $\text{N}_2\text{O}_4$  can be excluded in our following study.

Fig. 1b shows the surface reaction products formed during the heterogeneous reaction of  $\text{NO}_2$  on the surface of humid  $\gamma\text{-Al}_2\text{O}_3$  in the presence of simulated solar irradiation. The peaks appeared at 1343, 1404, 1504, 1540, and 1616  $\text{cm}^{-1}$  are assigned to adsorbed nitrate. These peaks increase with the reaction time. However, different from the heterogeneous reaction of  $\text{NO}_2$  on the surface of humid  $\gamma\text{-Al}_2\text{O}_3$  in the absence of simulated solar irradiation, the peak at 1242  $\text{cm}^{-1}$  does not appear, indicating that there is no adsorbed nitrite formed in the presence of simulated solar irradiation. In addition, under the same reaction conditions, the formation of nitrate in the presence of simulated solar irradiation is less than that in the absence of simulated solar irradiation. One possible explanation is that the photolysis of the formed nitrite and nitrate reduces the yield of surface nitrite and nitrate, and results in the disappearance of nitrite.

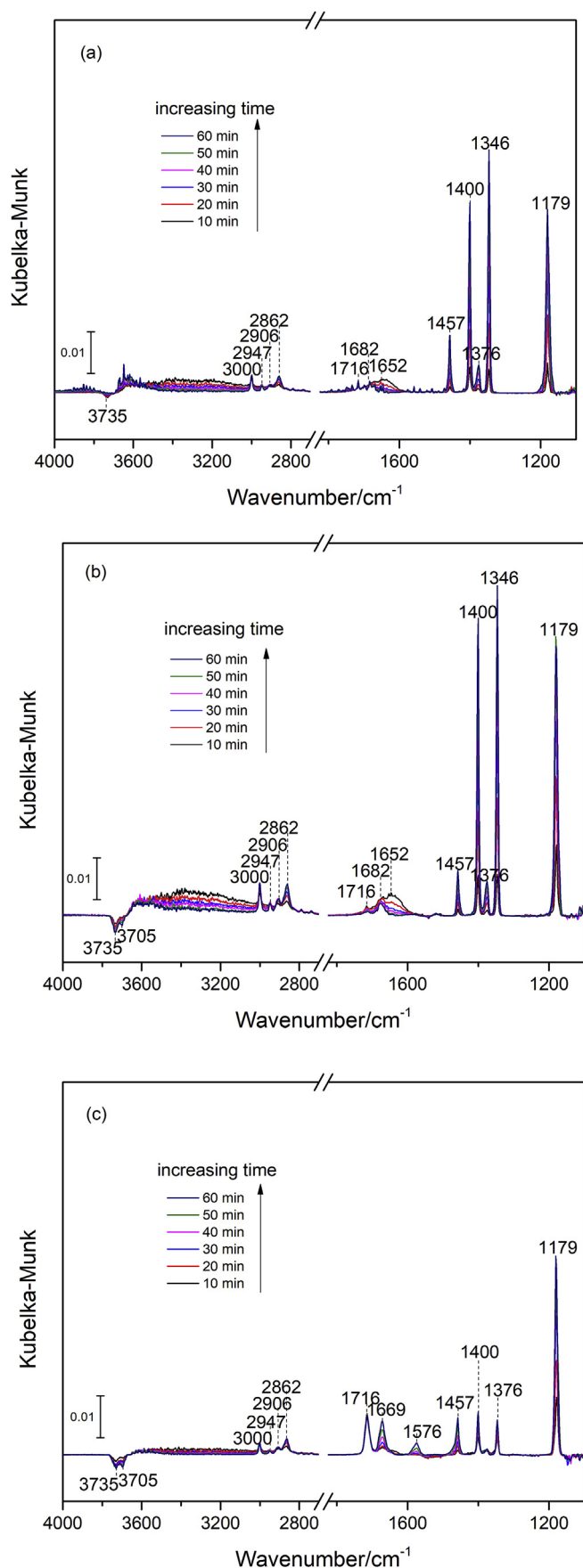
Therefore, in this study,  $\text{NO}_2$  pre-adsorption was mainly used to provide surface adsorbed nitrite and nitrate, and after the pre-adsorption of  $\text{NO}_2$ , the sample was purged with synthetic air for 1 h to exclude the influence of physical adsorbed  $\text{NO}_2$ . According to the results mentioned above, in the absence of simulated solar irradiation, the heterogeneous reaction of  $\text{NO}_2$  on the particle surfaces for 30 min is a source of co-adsorbed nitrite and nitrate, and the introduction of  $\text{NO}_2$  for 90 min is used to ensure that the formed nitrite on the surfaces of particles has been transformed into nitrate completely.

In addition, it should be pointed out that the consumption of OH groups is observed because that only one negative peak at 3705  $\text{cm}^{-1}$  increases with increasing reaction time. This peak is assigned to the OH groups coordinated with two aluminum atoms (Sun et al., 2016). No consumption of isolated OH groups is observed during the heterogeneous reaction, which is featured by the peak at 3735  $\text{cm}^{-1}$ .

### 3.2. Heterogeneous reaction of acetaldehyde on humid $\gamma\text{-Al}_2\text{O}_3$ in the absence of irradiation

The DRIFTS spectra during the heterogeneous reaction of  $\text{CH}_3\text{CHO}$  (79 ppm) on humid  $\gamma\text{-Al}_2\text{O}_3$  are shown in Fig. 2a. The peaks at 3735, 3000, 2947, 2906, 2862, 1716, 1682, 1652, 1457, 1400, 1376, 1346 and 1179  $\text{cm}^{-1}$  are observed, and most of the peaks increases with the reaction time except for the peak at 1652  $\text{cm}^{-1}$ . The peak at 1652  $\text{cm}^{-1}$  decreases with the reaction time. These results are consistent with previous studies (Chang et al., 2008; Ordonsky et al., 2010; Yang et al., 2017). Based on the previous studies, the negative peak at 3735  $\text{cm}^{-1}$  is assigned to isolated surface OH groups. The peaks at 3000  $\text{cm}^{-1}$  ( $\nu_{\text{as}}(\text{CH}_3)$ ), 2947  $\text{cm}^{-1}$  ( $\nu_{\text{as}}(\text{CH}_3)$ ), 2906  $\text{cm}^{-1}$  ( $\nu(\text{CH})$ ), 2862  $\text{cm}^{-1}$  ( $\nu(\text{CH})$ ) are assigned to paraldehyde or metaldehyde produced through the oligomeric reaction of acetaldehyde (Chang et al., 2008; Ordonsky et al., 2010; Yang et al., 2017). All the peaks at 1716, 1682 and 1652  $\text{cm}^{-1}$  are attributed to  $\nu(\text{C}=\text{O})$ , indicating the formation of physisorbed  $\text{CH}_3\text{CHO}$ , chemisorbed  $\text{CH}_3\text{COOH}$  and chemisorbed  $\text{CH}_3\text{CHO}$ , respectively (Zhao et al., 2015). The peaks at 1400  $\text{cm}^{-1}$ , 1376  $\text{cm}^{-1}$ , 1346  $\text{cm}^{-1}$  are assigned to  $\delta_{\text{s}}(\text{CH}_3)$ , which are due to the formation of oligomeric products of acetaldehyde (Ordonsky et al., 2010). The peaks at 1457  $\text{cm}^{-1}$  and 1179  $\text{cm}^{-1}$  are assigned to  $\delta_{\text{as}}(\text{CH}_3)$  and  $\nu(\text{C}-\text{O}-\text{C})$ , respectively, representing the formation of small amounts of gem-diol [ $\text{CH}_3\text{CH}(\text{OH})_2$ ] and dimer [ $\text{CH}_3\text{CH}(\text{OH})-\text{OCH}(\text{OH})\text{CH}_3$ ], indicating the occurrences of the hydration of  $\text{CH}_3\text{CHO}$  and subsequent polymerization reaction of hydration product under the catalysis of Lewis acid sites (Ordonsky et al., 2010). The decrease of the peak at 1652  $\text{cm}^{-1}$  demonstrates the conversion of chemisorbed  $\text{CH}_3\text{CHO}$  into other species with increasing reaction time. Meanwhile, this result also suggests that the formation rate of chemisorbed  $\text{CH}_3\text{CHO}$  is faster than the consumption rate of chemisorbed  $\text{CH}_3\text{CHO}$  at the





**Fig. 2.** DRIFTS spectra of surface products as a function of reaction time during the reaction of acetaldehyde with humid  $\gamma$ - $\text{Al}_2\text{O}_3$  in the absence of irradiation. (a)  $\gamma$ - $\text{Al}_2\text{O}_3$ , (b)  $\gamma$ - $\text{Al}_2\text{O}_3$  pre-adsorbed by  $\text{NO}_2$  for 30 min, (c)  $\gamma$ - $\text{Al}_2\text{O}_3$  pre-adsorbed by  $\text{NO}_2$  for 90 min.

initial stage of reaction, which leads to the presence of surface chemisorbed  $\text{CH}_3\text{CHO}$ . However, as the reaction proceeds, the rate of the latter is much faster than the rate of the former, though more physisorbed  $\text{CH}_3\text{CHO}$  is formed with the increase of reaction time. This leads to a decrease in the number of chemisorbed  $\text{CH}_3\text{CHO}$  molecules. In short, the appearance of these positive peaks demonstrates that complicated heterogeneous reactions occur when acetaldehyde is introduced, leading to the formation of various products on the particle surfaces, such as physically and chemically adsorbed acetaldehyde, hydrated acetaldehyde, dimerization glyoxylic, and metaldehyde.

Fig. 2b shows the DRIFTS spectra during the heterogeneous reaction of  $\text{CH}_3\text{CHO}$  on the humid  $\gamma$ - $\text{Al}_2\text{O}_3$  surfaces pre-adsorbed by  $\text{NO}_2$  for 30 min. Compared to those peaks in Fig. 2a, the positive peaks at 1400, 1346 and  $1179\text{ cm}^{-1}$  increases greatly, which indicates the production of more gem-diol, dimer and oligomer of acetaldehyde (Ordonsky et al., 2010). This result demonstrates that the hydration reaction and subsequent polyoligomeric reaction as well as oligomeric reaction of  $\text{CH}_3\text{CHO}$  are promoted by the pre-adsorption of  $\text{NO}_2$  for a short reaction time.

However, obvious differences are observed when  $\text{NO}_2$  is introduced for 90 min (Fig. 2c). Compared to Fig. 2a and b, physisorbed  $\text{CH}_3\text{CHO}$  shown by the peak at  $1716\text{ cm}^{-1}$  presents a marked increase and then gradually keeps steady with increasing reaction time, while the peak at  $1652\text{ cm}^{-1}$  which is assigned to chemisorbed  $\text{CH}_3\text{CHO}$  disappears. The results may imply that physisorbed  $\text{CH}_3\text{CHO}$  can be hindered to convert into chemisorbed  $\text{CH}_3\text{CHO}$  or rapid secondary reaction of chemisorbed  $\text{CH}_3\text{CHO}$  occurs with the continuous introduction of  $\text{CH}_3\text{CHO}$  on the humid  $\gamma$ - $\text{Al}_2\text{O}_3$  pre-adsorbed by  $\text{NO}_2$  for 90 min, suggesting that the heterogeneous reaction of  $\text{NO}_2$  and the formed nitrate may greatly influence the formation of chemisorbed  $\text{CH}_3\text{CHO}$ . New peak at  $1669\text{ cm}^{-1}$  is observed clearly, this peak is assigned to the carbonyl of crotonaldehyde, indicating the occurrence of aldol condensation (Ordonsky et al., 2010; Singh et al., 2008; Stefanov et al., 2014). Previous studies indicated the aldol condensation of acetaldehyde proceeds via acidic mechanism initiated on the surface of  $\gamma$ - $\text{Al}_2\text{O}_3$  (Ordonsky et al., 2010). In this study, the  $\gamma$ - $\text{Al}_2\text{O}_3$  surface acidity can be enhanced by pre-adsorption of  $\text{NO}_2$ , which may promote the formation of crotonaldehyde by the pre-adsorption of  $\text{NO}_2$ . In addition, another new peak at  $1576\text{ cm}^{-1}$  is also observed, which is assigned to  $\nu_{\text{as}}(\text{COO})$ , indicating the formation of adsorbed acetate (Lee and Condrate, 1999). Compared to the Fig. 2a and b, this result indicates that the formed nitrate through the heterogeneous uptake of  $\text{NO}_2$  on the  $\gamma$ - $\text{Al}_2\text{O}_3$  surface can enhance the surface oxidation ability and promote the formation of adsorbed acetate. The intensities of the peaks at 1457, 1400, 1376 and  $1179\text{ cm}^{-1}$  obviously decreases compared to those in Fig. 2a and b, indicating the oligomeric reactions of  $\text{CH}_3\text{CHO}$ , the hydration of  $\text{CH}_3\text{CHO}$  and subsequent polymerization reaction of hydration product are hindered after the introduction of  $\text{NO}_2$  for 90 min. As is well known, the oligomeric reactions of  $\text{CH}_3\text{CHO}$  and the hydration of  $\text{CH}_3\text{CHO}$  and subsequent polymerization reaction of hydration product are acid-catalyzed (Ordonsky et al., 2010), while the surface acidity increases with the introduction of  $\text{NO}_2$ . However, these reactions have been suppressed as shown in Fig. 2c. A possible explanation for the decrease of these peaks is that the active sites for oligomeric reaction, hydration reaction and subsequent polymerization reaction on the surface of particles are reduced greatly by the pre-adsorbed  $\text{NO}_2$  for a longer reaction time. The absorbed  $\text{NO}_2$  not only consumes a portion of absorbed water but also consumes active sites including surface hydroxyl groups and Lewis acid sites in the process of pre-absorption (Jenkin et al., 1988; Zhao et al., 2015).

In addition, compared the blank experiment (experiment involving no  $\text{NO}_2$  pre-adsorption, see Fig. 2a) with the control experiments (experiment involving  $\text{NO}_2$  pre-adsorption, see Fig. 2b and c), the consumption of surface hydroxyl has an obvious difference among the three experiments. Generally, acetaldehyde can interact with surface adsorbed  $\text{H}_2\text{O}$ , surface OH groups and Lewis acid sites during its heterogeneous reaction, while  $\text{NO}_2$  can also consume surface adsorbed  $\text{H}_2\text{O}$  and OH groups as shown in Fig. 1a (Ordonsky et al., 2010; Rasko and Kiss, 2005). During the blank experiment, only one negative peak at  $3735\text{ cm}^{-1}$  is observed in Fig. 2a, indicating that acetaldehyde is inclined to be adsorbed onto  $\gamma\text{-Al}_2\text{O}_3$  via the isolated surface hydroxyl groups, consistent with previous studies (Li et al., 2001; Ordonsky et al., 2010; Sun et al., 2016). However, besides the peak at  $3735\text{ cm}^{-1}$ , a new negative peak at  $3705\text{ cm}^{-1}$  is detected in the control experiment for 30 min (Fig. 2b), while this negative peak is more obvious when  $\gamma\text{-Al}_2\text{O}_3$  is pre-adsorbed by  $\text{NO}_2$  for 90 min (Fig. 2c). As discussed above, the major active sites for the heterogeneous conversion of  $\text{NO}_2$  on the surface of  $\gamma\text{-Al}_2\text{O}_3$  are isolated OH groups (Sun et al., 2016). Therefore, these results indicate that the isolated OH groups is not completely exhausted during the pre-adsorption of  $\text{NO}_2$  for 30 min and 90 min, while the pre-adsorption of  $\text{NO}_2$  promotes the consumption of the hydroxyl coordinated with two aluminum atoms. In conclusion, all the results mentioned above indicates that the pre-adsorption of  $\text{NO}_2$  and the formed different products have complicated and significant impacts on the subsequent heterogeneous reaction processes of  $\text{CH}_3\text{CHO}$  and its products, showing the complexity of the heterogeneous reaction of  $\text{CH}_3\text{CHO}$  on mineral aerosols. This study only takes into consideration the impact of pre-adsorption of  $\text{NO}_2$  on the heterogeneous conversion of  $\text{CH}_3\text{CHO}$  on  $\gamma\text{-Al}_2\text{O}_3$ , and it is found that the heterogeneous reaction pathways and reaction products of  $\text{CH}_3\text{CHO}$  are greatly affected by the pre-adsorption of  $\text{NO}_2$ , irradiation and humidity. However, complex gas- and particle-phase compositions and variable meteorological conditions in the real atmosphere can provide more impact factors and thus lead to a wide variety of effects on the heterogeneous reaction processes of  $\text{CH}_3\text{CHO}$ . Therefore, the results of this study also suggest the complicated heterogeneous reaction processes of  $\text{CH}_3\text{CHO}$  in the real atmosphere.

### 3.3. Heterogeneous reaction of acetaldehyde on humid $\gamma\text{-Al}_2\text{O}_3$ in the presence of irradiation

Considering that the photolysis of the formed nitrite and nitrate can produce active species such as OH radical and reactive oxygen species, and these species may play important roles in the heterogeneous reaction processes of  $\text{CH}_3\text{CHO}$  and the formation of products, the heterogeneous reactions of acetaldehyde on  $\gamma\text{-Al}_2\text{O}_3$  pre-adsorbed by  $\text{NO}_2$  under simulated solar irradiation were investigated. Fig. 3 shows DRIFTS spectra of surface products during the heterogeneous reactions of  $\text{CH}_3\text{CHO}$  on the surface of  $\gamma\text{-Al}_2\text{O}_3$  under illumination. For the heterogeneous reaction of acetaldehyde on  $\gamma\text{-Al}_2\text{O}_3$  untreated by  $\text{NO}_2$ , a main peak at  $1669\text{ cm}^{-1}$  and several weak peaks at  $1716$ ,  $1576$ ,  $1457$ ,  $1400$  and  $1346\text{ cm}^{-1}$  are observed in Fig. 3a, indicating the formation of crotonaldehyde, physisorbed  $\text{CH}_3\text{CHO}$ , chemisorbed acetate and oligomeric acetaldehyde, respectively. Compared to those in Fig. 2a, no obvious peaks at  $1179\text{ cm}^{-1}$  but a new peak at  $1576\text{ cm}^{-1}$  are observed, and the intensities of peaks at  $1457$ ,  $1400$ ,  $1376$  and  $1346\text{ cm}^{-1}$  are weakened. The results indicate that the simulated solar irradiation promotes the occurrence of the aldol condensation and the oxidation of  $\text{CH}_3\text{CHO}$ , but suppresses the hydration reaction of  $\text{CH}_3\text{CHO}$  and subsequent polyoligomeric reaction of hydration product as well as oligomeric reaction among  $\text{CH}_3\text{CHO}$  molecules, resulting in the formation of more crotonaldehyde and acetate.

Previous study demonstrated that hydrogen bonding plays a crucial role in various organic chemical reactions including aldol condensation reaction by orienting the substrate molecules and lowering barriers to reactions (Gondi et al., 2005; Han et al., 2014; Jenkin et al., 1988; Niu

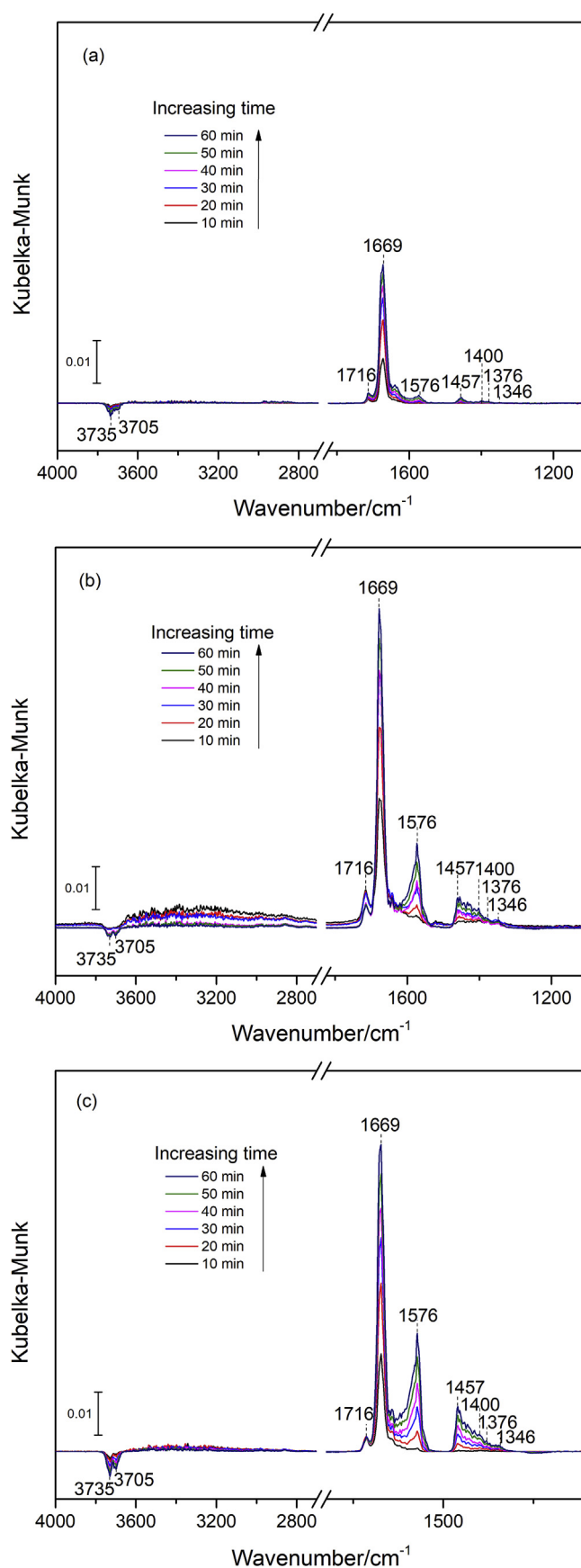


Fig. 3. DRIFTS spectra of surface products as a function of reaction time during the heterogeneous reaction of acetaldehyde on humid  $\gamma\text{-Al}_2\text{O}_3$  under simulated solar irradiation. (a)  $\gamma\text{-Al}_2\text{O}_3$ , (b)  $\gamma\text{-Al}_2\text{O}_3$  pre-adsorbed by  $\text{NO}_2$  for 30 min, (c)  $\gamma\text{-Al}_2\text{O}_3$  pre-adsorbed by  $\text{NO}_2$  for 90 min.

et al., 2010; Pihko, 2004), and thus hydrogen bond (H-bond) catalysis has been used as a typical organocatalysis to accelerate organic reactions and stabilize reaction intermediates and transition states (Doyle and Jacobsen, 2007), while the H-bond catalytic activities can be significantly enhanced with light irradiation (Han et al., 2014). Although the photocatalytic activity of the particles is excluded since  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is not a photocatalytic material,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> possesses abundant surface hydroxyl groups, these hydroxyl groups not only can act as active sites for the adsorption of organics but also act as heterogeneous organocatalyst for hydrogen bonding reactions (Han et al., 2014; Niu et al., 2008). Therefore, the enhanced formation of crotonaldehyde under irradiation in this study has demonstrated the roles of the H-bond and irradiation. This result may show a combined result of illumination and H-bond catalysis in aldol condensation (Han et al., 2014).

The peaks at 1716, 1669, 1576, 1457, 1400, 1346 cm<sup>-1</sup> are observed in Fig. 3b, which are the same as those in Fig. 3a, indicating the formation of same products. However, the intensities of the peaks at 1669 and 1576 cm<sup>-1</sup> are greatly enhanced, indicating that the formation of crotonaldehyde and acetate are greatly promoted. This result not only demonstrates the combined effects of H-bond catalysis and illumination, but also verifies the significant impacts of the photolysis of the formed nitrate and nitrite on the heterogeneous reaction of CH<sub>3</sub>CHO. Higher yields of crotonaldehyde, acetate, and oligomeric acetaldehyde are observed compared to Fig. 3a, indicating that the formed nitrate and nitrite by the heterogeneous uptake of NO<sub>2</sub> can also promote the heterogeneous conversions of CH<sub>3</sub>CHO on the surface of humid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under illumination, especially the aldol condensation and the oxidation conversion of CH<sub>3</sub>CHO. A possible explanation is that the simulated solar irradiation greatly promotes H-bond catalytic activity for the aldol condensation, resulting in the inhibition of hydration reaction and subsequent polyoligomeric reaction as well as oligomeric reaction of CH<sub>3</sub>CHO. While the photolysis of the formed nitrite and nitrate may produce OH radicals (Gankanda and Grassian, 2014; Mack and Bolton, 1999; Roca et al., 2008; Schuttelfield et al., 2008), which promotes the oxidation of CH<sub>3</sub>CHO into acetate. Similar phenomena are shown in Fig. 3c, however, higher yield of acetate demonstrates the pre-adsorption of NO<sub>2</sub> for 90 min has more significant promoting effect on the generation of acetate due to more OH radicals produced under irradiation. It should be pointed out that the consumption of nitrate is not observed because its peaks at 1599, 1587 and 1567 cm<sup>-1</sup> happens to be covered by the products of aldol condensation and oxidation of CH<sub>3</sub>CHO (Kong et al., 2014).

The detailed assignments of the peaks of surface species during the heterogeneous processes are summarized in Table 1.

### 3.4. Heterogeneous reaction mechanisms of acetaldehyde on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles in the absence and presence of simulated solar irradiation

Based on the experimental observations mentioned above, possible reaction mechanisms for the conversions of CH<sub>3</sub>CHO on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles are proposed. Gaseous CH<sub>3</sub>CHO can be readily adsorbed on the humid particle surfaces by the interaction of carbonyl oxygen with hydroxyl group or Lewis acid site to form physisorbed and chemisorbed CH<sub>3</sub>CHO (Zhao et al., 2015). In the absence of simulated solar irradiation, adsorbed CH<sub>3</sub>CHO is easily transformed to gem-diol through the hydration reaction, and then produces the dimer through subsequent polymerization reaction between the hydroxyl group of gem-diol and adsorbed CH<sub>3</sub>CHO or dehydration between gem-diol molecules, and these reactions may be mainly catalyzed by Lewis acid sites (Iraci and Tolbert, 1997; Jang and Kamens, 2001). Meanwhile, a small amount of adsorbed CH<sub>3</sub>CHO is transformed to adsorbed oligomeric acetaldehyde, acetate and CH<sub>3</sub>COOH as the reaction proceeds.

In the presence of simulated solar irradiation, aldol condensation is promoted by the combined impacts of illumination, H-bond catalysis, the enhanced surface acidity and the formed nitrate and nitrite (Chang et al., 2008; Han et al., 2014; Yang et al., 2017). Meanwhile, the

photolysis of the formed nitrite and nitrate produces OH radical and O (<sup>3</sup>P) species (Goldstein and Rabani, 2007; Schuttelfield et al., 2008), which enhances the surface oxidation activity, resulting in the formation of acetate. The proposed mechanisms of the heterogeneous conversions of CH<sub>3</sub>CHO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pre-adsorbed by NO<sub>2</sub> are shown in Scheme 1.

## 4. Conclusion

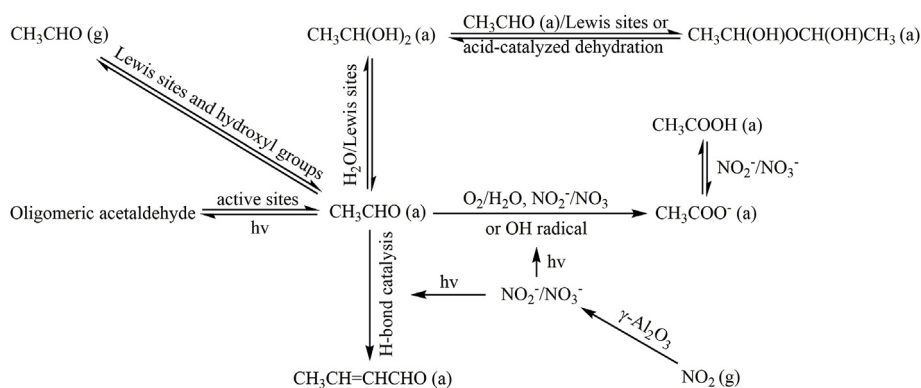
In this study, the impact of heterogeneous uptake of NO<sub>2</sub> on the conversion processes of CH<sub>3</sub>CHO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particle surfaces in the absence and presence of simulated solar irradiation at 298 K was investigated. The main results are as following.

- (1) In the absence of simulated solar irradiation, complicated heterogeneous reactions occur when CH<sub>3</sub>CHO is introduced alone, leading to the formation of various products on the particle surfaces, including physically and chemically adsorbed CH<sub>3</sub>CHO, crotonaldehyde, hydrated CH<sub>3</sub>CHO, dimerization glyoxylic, and metaldehyde. However, different pre-adsorption times of NO<sub>2</sub> have different effects on heterogeneous reactions of CH<sub>3</sub>CHO on the surface of the humid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The hydration reaction and subsequent polyoligomeric reaction as well as oligomeric reaction of CH<sub>3</sub>CHO are promoted by the introduction of NO<sub>2</sub> for a short pre-adsorption time. However, the heterogeneous reaction of NO<sub>2</sub> and the formed nitrate from a longer pre-adsorption time greatly influence the formation of chemisorbed CH<sub>3</sub>CHO. Meanwhile, the formation of crotonaldehyde and adsorbed acetate are promoted slightly, due to the enhanced surface acidity and surface oxidation ability from the heterogeneous uptake of NO<sub>2</sub> on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
- (2) In the presence of simulated solar irradiation, the occurrence of the aldol condensation and the oxidation of CH<sub>3</sub>CHO are promoted by the combined impacts of illumination, H-bond catalysis, the enhanced surface acidity and the formed nitrite and nitrate, especially, the enhanced H-bond catalytic activity and the photolysis of the formed nitrite and nitrate under illumination, whereas the hydration reaction and subsequent polyoligomeric reaction as well as oligomeric reaction of CH<sub>3</sub>CHO molecules are suppressed.
- (3) The heterogeneous uptake of NO<sub>2</sub> and the heterogeneous conversion of CH<sub>3</sub>CHO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> not only consume adsorbed water but also consume active sites including surface hydroxyl groups and Lewis acid sites. The pre-adsorption of NO<sub>2</sub> promotes the consumption of the hydroxyl coordinated with two aluminum atoms by

**Table 1**  
Infrared vibrational assignments for surface species during the heterogeneous reactions in this study.

Wavenumber/cm <sup>-1</sup>	Vibration modes/ function groups	Surface species
3735	isolated OH	
3705	OH groups	coordinated with two aluminum atoms
3000, 2947	$\nu_{\text{as}}(\text{CH}_3)$	paraldehyde or metaldehyde
2906, 2862	$\nu(\text{CH})$	
1716	$\nu(\text{C}=\text{O})$	physisorbed CH <sub>3</sub> CHO
1682	$\nu(\text{C}=\text{O})$	chemisorbed CH <sub>3</sub> COOH
1669	$\nu(\text{C}=\text{O})$	crotonaldehyde
1652	$\nu(\text{C}=\text{O})$	chemisorbed CH <sub>3</sub> CHO
1616, 1504		bridging nitrate
1540		monodentate nitrate
1576	$\nu_{\text{as}}(\text{COO})$	adsorbed acetate
1457	$\delta_{\text{as}}(\text{CH}_3)$	gem-diol and its dimer, and oligomers
1400, 1376, 1346	$\delta_{\text{s}}(\text{CH}_3)$	oligomeric acetaldehyde
1404, 1343		water-solvated nitrate
1242		bidentate nitrite
1179	$\nu(\text{C}-\text{O}-\text{C})$	dimer





**Scheme 1.** Mechanism of the heterogeneous uptake of  $\text{CH}_3\text{CHO}$  on  $\gamma\text{-Al}_2\text{O}_3$ .

the heterogeneous conversion of  $\text{CH}_3\text{CHO}$ . It is found that surface hydroxyl groups not only can act as active sites for the adsorption and uptake of  $\text{CH}_3\text{CHO}$  but also act as heterogeneous catalyst for hydrogen bonding reactions of  $\text{CH}_3\text{CHO}$ , and the H-bond catalytic activity for aldol condensation can be significantly enhanced under light irradiation, revealing a combined result of illumination and H-bond catalysis.

Results from this study have important atmospheric implications. Firstly, the results reveal that the heterogeneous conversion of  $\text{CH}_3\text{CHO}$  can be affected by RH, solar light and the availability of nitrate and mineral oxide, and they further emphasize the complexity of the reaction of  $\text{CH}_3\text{CHO}$  on mineral oxides. This chemistry may occur on surfaces of airborne dust particles and play a role in the chemistry of the troposphere because the coexistence of  $\text{NO}_2$ ,  $\text{CH}_3\text{CHO}$  and dust particles in the atmosphere, especially in the atmospheric environment with high emission, high gaseous pollutant concentration and high particulate pollution level. Meanwhile, complex gas- and particle-phase compositions and variable meteorological conditions in the real atmosphere can provide more impact factors and thus lead to a wide variety of effects on the heterogeneous reaction processes of  $\text{CH}_3\text{CHO}$ . The results of this study also imply the complicated heterogeneous reaction processes of  $\text{CH}_3\text{CHO}$  in the real atmosphere. Secondly, the revealed impacts of RH, light and the pre-adsorption of  $\text{NO}_2$  on the heterogeneous reaction of  $\text{CH}_3\text{CHO}$  suggest that the heterogeneous reaction products of  $\text{CH}_3\text{CHO}$  in the real atmosphere may have some differences between daytime and nighttime, which would affect the physicochemical properties of atmospheric particle surfaces, and further affect subsequent heterogeneous reactions of other gaseous inorganic and organic species on these particles, leading to different cloud condensation nucleation ability and optical properties of these particles. Meanwhile, the results of this study demonstrated that the roles of the photolysis of the formed nitrite and nitrate, H-bond catalysis and the enhanced H-bond catalytic activity by light in the heterogeneous reaction products of  $\text{CH}_3\text{CHO}$  on mineral oxides in the presence of simulated solar irradiation. These may happen on surfaces of atmospheric dust particles when the heterogeneous reactions of some other organic pollutants occur under illumination, which would affect the conversion of atmospheric organic species and the formation of secondary organic aerosols, and further affect the nucleation and growth of atmospheric particles. Finally, this study not only reveals the complex heterogeneous reaction mechanisms and processes of  $\text{CH}_3\text{CHO}$  on  $\gamma\text{-Al}_2\text{O}_3$  pre-adsorbed by  $\text{NO}_2$  in the absence and presence of simulated solar irradiation, but also reveals the inevitable interactions between the heterogeneous conversion processes of atmospheric trace gases, facilitating a better understanding of the complexities of atmospheric heterogeneous reactions of inorganic and organic pollutants, the formation of atmospheric aerosols and air pollution. And also, these will provide significant information for atmospheric chemistry research and atmospheric chemistry modelling.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2018.05.067>.

## References

- Baltrusaitis, J., Schuttlefield, J., Jensen, J.H., Grassian, V.H., 2007. FTIR spectroscopy combined with quantum chemical calculations to investigate adsorbed nitrate on aluminium oxide surfaces in the presence and absence of co-adsorbed nitrate. *Phys. Chem. Chem. Phys.* 9, 4970–4980. <http://dx.doi.org/10.1039/B705189A>.
- Batault, F., Thevenet, F., Hequet, V., Rillard, C., Le Coq, L., Locoge, N., 2015. Acetaldehyde and acetic acid adsorption on  $\text{TiO}_2$  under dry and humid conditions. *Chem. Eng. J.* 264, 197–210. <http://dx.doi.org/10.1016/j.cej.2014.10.089>.
- Bauer, S.E., Balkanski, Y., Schulz, M., Hauglustaine, D.A., Dentener, F., 2004. Global modeling of heterogeneous chemistry on mineral aerosol surfaces: influence on tropospheric ozone chemistry and comparison to observations. *J. Geophys. Res. Atmos.* 109. <http://dx.doi.org/10.1029/2003jd003868>.
- Börensén, C., Kirchner, U., Scheer, V., Vogt, R., Zellner, R., 2000. Mechanism and kinetics of the reactions of  $\text{NO}_2$  or  $\text{HNO}_3$  with alumina as a mineral dust model compound. *J. Phys. Chem. A* 104, 5036–5045. <http://dx.doi.org/10.1021/jp994170d>.
- Budiman, A.W., Nam, J.S., Park, J.H., Mukti, R.I., Chang, T.S., Bae, J.W., Choi, M.J., 2016. Review of acetic acid synthesis from various feedstocks through different catalytic processes. *Catal. Surv. Asia* 20, 173–193. <http://dx.doi.org/10.1007/s10563-016-9215-9>.
- Chang, C.-A., Ray, B., Paul, D.K., Demydov, D., Klabunde, K.J., 2008. Photocatalytic reaction of acetaldehyde over  $\text{SrTiO}_3$  nanoparticles. *J. Mol. Catal. Chem.* 281, 99–106. <http://dx.doi.org/10.1016/j.molcata.2007.08.014>.
- Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Poschl, U., Su, H., 2016. Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. *Sci. Adv.* 2. <http://dx.doi.org/10.1126/sciadv.1601530>.
- Dentener, F.J., Carmichael, G.R., Zhang, Y., Lelieveld, J., Crutzen, P.J., 1996. Role of mineral aerosol as a reactive surface in the global troposphere. *J. Geophys. Res.* Atmos. 101, 22869–22889. <http://dx.doi.org/10.1029/96jd01818>.
- Doyle, A.G., Jacobsen, E.N., 2007. Small-molecule H-bond donors in asymmetric catalysis. *Chem. Rev.* 107, 5713–5743. <http://dx.doi.org/10.1021/cr068373r>.
- Duan, J., Tan, J., Yang, L., Wu, S., Hao, J., 2008. Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing. *Atmos. Res.* 88, 25–35. <http://dx.doi.org/10.1016/j.atmosres.2007.09.004>.
- Finlayson-Pitts, B.J., Wingen, L.M., Sumner, A.L., Syomin, D., Ramazan, K.A., 2003. The heterogeneous hydrolysis of  $\text{NO}_2$  in laboratory systems and in outdoor and indoor atmospheres: an integrated mechanism. *Phys. Chem. Chem. Phys.* 5, 223–242. <http://dx.doi.org/10.1039/B208564J>.
- Gankanda, A., Grassian, V.H., 2014. Nitrate photochemistry on laboratory proxies of mineral dust aerosol: wavelength dependence and action spectra. *J. Phys. Chem. C* 118, 29117–29125. <http://dx.doi.org/10.1021/jp312247m>.
- George, C., Ndour, M., Balkanski, Y., Ka, O., 2007. Photoenhanced uptake of  $\text{NO}_2$  on mineral dust. In: Mellouki, A., Ravishankara, A.R. (Eds.), *Regional Climate Variability and its Impacts in the Mediterranean Area*, pp. 219–233. DOI: 978-1-4020-6427-2.
- Goldstein, S., Rabani, J., 2007. Mechanism of nitrite formation by nitrate photolysis in aqueous solutions: the role of peroxyxynitrite, nitrogen dioxide, and hydroxyl radical. *J. Am. Chem. Soc.* 129, 10597–10601. <http://dx.doi.org/10.1021/ja073609>.
- Gondi, V.B., Gravel, M., Rawal, V.H., 2005. Hydrogen bond catalyzed enantioselective



- vinyllogous Mukaiyama aldol reaction. *Org. Lett.* 7, 5657–5660. <http://dx.doi.org/10.1021/ol052301p>.
- Goodman, A.L., Miller, T.M., Grassian, V.H., 1998. Heterogeneous reactions of NO<sub>2</sub> on NaCl and Al<sub>2</sub>O<sub>3</sub> particles. *J. Vac. Sci. Technol.*, A 16, 2585–2590. <http://dx.doi.org/10.1116/1.581386>.
- Goodman, A.L., Underwood, G.M., Grassian, V.H., 1999. A spectroscopic investigation of the heterogeneous reaction 2NO<sub>2</sub> + H<sub>2</sub>O (a) → HONO(g) + HNO<sub>3</sub> (a) on hydrated silica Particles: characterization of gas-phase and adsorbed products. *J. Phys. Chem. A* 103, 7217–7223. <http://dx.doi.org/10.1021/jp9910688>.
- Guil, J.M., Homs, N., Llorca, J., de la Piscina, P.R., 2005. Microcalorimetric and infrared studies of ethanol and acetaldehyde adsorption to investigate the ethanol steam reforming on supported cobalt catalysts. *J. Phys. Chem. B* 109, 10813–10819. <http://dx.doi.org/10.1021/jp050414k>.
- Han, C., Yang, W., Wu, Q., Yang, H., Xue, X., 2016. Key role of pH in the photochemical conversion of NO<sub>2</sub> to HONO on humic acid. *Atmos. Environ.* 142, 296–302. <http://dx.doi.org/10.1016/j.atmosenv.2016.07.053>.
- Han, Y.Z., Huang, H., Zhang, H.C., Liu, Y., Han, X., Liu, R.H., Li, H.T., Kang, Z.H., 2014. Carbon quantum dots with photoenhanced hydrogen-bond catalytic activity in aldol condensations. *ACS Catal.* 4, 781–787. <http://dx.doi.org/10.1021/cs401118x>.
- Hoffman, R.C., Laskin, A., Finlayson-Pitts, B.J., 2004. Sodium nitrate particles: physical and chemical properties during hydration and dehydration, and implications for aged sea salt aerosols. *J. Aerosol Sci.* 35, 869–887. <http://dx.doi.org/10.1016/j.jaerosci.2004.02.003>.
- Iraci, L.T., Tolbert, M.A., 1997. Heterogeneous interaction of formaldehyde with cold sulfuric acid: implications for the upper troposphere and lower stratosphere. *J. Geophys. Res.* Atmos 102, 16099–16107. <http://dx.doi.org/10.1029/97jd01259>.
- Iuga, C., Sainz-Díaz, I., Vivier-Bunge, A., 2010. On the OH initiated oxidation of C2-C5 aliphatic aldehydes in the presence of mineral aerosols. *Geochem. Cosmochim. Acta* 74, 3587–3597. <http://dx.doi.org/10.1016/j.gca.2010.01.034>.
- Jang, M.S., Kamens, R.M., 2001. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environ. Sci. Technol.* 35, 4758–4766. <http://dx.doi.org/10.1021/es010790s>.
- Jenkin, M.E., Cox, R.A., Williams, D.J., 1988. Laboratory studies of the kinetics of formation of nitrous-acid from the thermal-reaction of nitrogen-dioxide and water-vapor. *Atmos. Environ.* 22, 487–498. [http://dx.doi.org/10.1016/0004-6981\(88\)90194-1](http://dx.doi.org/10.1016/0004-6981(88)90194-1).
- Ji, Y., Wang, H., Li, G., An, T., 2015. Theoretical investigation on the role of mineral dust aerosol in atmospheric reaction: a case of the heterogeneous reaction of formaldehyde with NO<sub>2</sub> onto SiO<sub>2</sub> dust surface. *Atmos. Environ.* 103, 207–214. <http://dx.doi.org/10.1016/j.atmosenv.2014.12.044>.
- Kleffmann, J., Becker, K.H., Wiesen, P., 1998. Heterogeneous NO<sub>2</sub> conversion processes on acid surfaces: possible atmospheric implications. *Atmos. Environ.* 32, 2721–2729. [http://dx.doi.org/10.1016/S1352-2310\(98\)00065-X](http://dx.doi.org/10.1016/S1352-2310(98)00065-X).
- Kong, L.D., Zhao, X., Sun, Z.Y., Yang, Y.W., Fu, H.B., Zhang, S.C., Cheng, T.T., Yang, X., Wang, L., Chen, J.M., 2014. The effects of nitrate on the heterogeneous uptake of sulfur dioxide on hematite. *Atmos. Chem. Phys.* 14, 9451–9467. <http://dx.doi.org/10.5194/acp-14-9451-2014>.
- Kydd, R., Teoh, W.Y., Scott, J., Ferri, D., Amal, R., 2009. Probing surface properties and reaction intermediates during heterogeneous catalytic oxidation of acetaldehyde. *ChemCatChem* 1, 286–294. <http://dx.doi.org/10.1002/cctc.200900099>.
- Langer, S., Pemberton, R.S., Finlayson-Pitts, B.J., 1997. Diffuse reflectance infrared studies of the reaction of synthetic sea salt mixtures with NO<sub>2</sub>: a key role for hydrates in the kinetics and mechanism. *J. Phys. Chem. A* 101, 1277–1286. <http://dx.doi.org/10.1021/jp962122c>.
- Laskin, A., Iedema, M.J., Cowin, J.P., 2002. Quantitative time-resolved monitoring of nitrate formation in sea salt particles using a CSEM/EDX single particle analysis. *Environ. Sci. Technol.* 36, 4948–4955. <http://dx.doi.org/10.1021/es020551k>.
- Lee, D.H., Condrate, R.A., 1999. FTIR spectral characterization of thin film coatings of oleic acid on glasses: I. Coatings on glasses from ethyl alcohol. *J. Mater. Sci.* 34, 139–146. <http://dx.doi.org/10.1023/a:1004494331895>.
- Li, P., Perreault, K.A., Covington, E., Song, C.H., Carmichael, G.R., Grassian, V.H., 2001. Heterogeneous reactions of volatile organic compounds on oxide particles of the most abundant crustal elements: surface reactions of acetaldehyde, acetone, and propionaldehyde on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and CaO. *J. Geophys. Res.* Atmos 106, 5517–5529. <http://dx.doi.org/10.1029/2000jd900573>.
- Liu, C., Ma, Q.X., Liu, Y.C., Ma, J.Z., He, H., 2012. Synergistic reaction between SO<sub>2</sub> and NO<sub>2</sub> on mineral oxides: a potential formation pathway of sulfate aerosol. *Phys. Chem. Chem. Phys.* 14, 1668–1676. <http://dx.doi.org/10.1039/c1cp22217a>.
- Ma, J., Liu, Y., Han, C., Ma, Q., Liu, C., He, H., 2013. Review of heterogeneous photochemical reactions of NO<sub>y</sub> on aerosol - a possible daytime source of nitrous acid (HONO) in the atmosphere. *J. Environ. Sci.* 25, 326–334. [http://dx.doi.org/10.1016/s1001-0742\(12\)60093-x](http://dx.doi.org/10.1016/s1001-0742(12)60093-x).
- Ma, Q., Liu, Y., He, H., 2008. Synergistic effect between NO<sub>2</sub> and SO<sub>2</sub> in their adsorption and reaction on gamma-alumina. *J. Phys. Chem. A* 112, 6630–6635. <http://dx.doi.org/10.1021/jp802025z>.
- Mack, J., Bolton, J.R., 1999. Photochemistry of nitrite and nitrate in aqueous solution: a review. *J. Photochem. Photobiol.*, A 128, 1–13. [http://dx.doi.org/10.1016/s1010-6030\(99\)00155-0](http://dx.doi.org/10.1016/s1010-6030(99)00155-0).
- Natal-Santiago, M.A., Hill, J.M., Dumesic, J.A., 1999. Studies of the adsorption of acetaldehyde, methyl acetate, ethyl acetate, and methyl trifluoroacetate on silica. *J. Mol. Catal. A* 140, 199–214. [http://dx.doi.org/10.1016/s1381-1169\(98\)00231-3](http://dx.doi.org/10.1016/s1381-1169(98)00231-3).
- Nie, W., Ding, A., Wang, T., Kerminen, V.-M., George, C., Xue, L., Wang, W., Zhang, Q., Petaja, T., Qi, X., Gao, X., Wang, X., Yang, X., Fu, C., Kulmala, M., 2014. Polluted dust promotes new particle formation and growth. *Sci. Rep.* 4. <http://dx.doi.org/10.1038/srep06634>.
- Niu, F., Liu, C.C., Cui, Z.M., Zhai, J., Jiang, L., Song, W.G., 2008. Promotion of organic reactions by interfacial hydrogen bonds on hydroxyl group rich nano-solids. *Chem. Commun.* 2803–2805. <http://dx.doi.org/10.1039/b801361f>.
- Niu, F., Zhang, L., Luo, S.Z., Song, W.G., 2010. Room temperature aldol reactions using magnetic Fe<sub>3</sub>O<sub>4</sub>@Fe(OH)<sub>3</sub> composite microspheres in hydrogen bond catalysis. *Chem. Commun.* 46, 1109–1111. <http://dx.doi.org/10.1039/b920009f>.
- Ordonsky, V.V., Sushkevich, V.L., Ivanova, I.I., 2010. Study of acetaldehyde condensation chemistry over magnesia and zirconia supported on silica. *J. Mol. Catal. A* 333, 85–93. <http://dx.doi.org/10.1016/j.molcata.2010.10.001>.
- Palacios, L.G., Arroyo, P.C., Aregahegn, K.Z., Steimer, S.S., Bartels-Rausch, T., Noziere, B., George, C., Ammann, M., Volkamer, R., 2016. Heterogeneous photochemistry of imidazole-2-carboxaldehyde: HO<sub>2</sub> radical formation and aerosol growth. *Atmos. Chem. Phys.* 16, 11823–11836. <http://dx.doi.org/10.5194/acp-16-11823-2016>.
- Pihko, P.M., 2004. Activation of carbonyl compounds by double hydrogen bonding: an emerging tool in asymmetric catalysis. *Angew. Chem. Int. Ed.* 43, 2062–2064. <http://dx.doi.org/10.1002/anie.200301732>.
- Ramazan, K.A., Wingen, L.M., Miller, Y., Chaban, G.M., Gerber, R.B., Xanthas, S.S., Finlayson-Pitts, B.J., 2006. New experimental and theoretical approach to the heterogeneous hydrolysis of NO<sub>2</sub>: key role of molecular nitric acid and its complexes. *J. Phys. Chem. A* 110, 6886–6897. <http://dx.doi.org/10.1021/jp056426n>.
- Rasko, J., Kiss, J., 2005. Adsorption and surface reactions of acetaldehyde on TiO<sub>2</sub>, CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. *Appl. Catal. A-Gen* 287, 252–260. <http://dx.doi.org/10.1016/j.apcata.2005.04.003>.
- Roca, M., Zahardis, J., Bone, J., El-Maazawi, M., Grassian, V.H., 2008. 310 nm irradiation of atmospherically relevant concentrated aqueous nitrate solutions: nitrite production and quantum yields. *J. Phys. Chem. A* 112, 13275–13281. <http://dx.doi.org/10.1021/jp809017b>.
- Schuttlefield, J., Rubasinghe, G., El-Maazawi, M., Bone, J., Grassian, V.H., 2008. Photochemistry of adsorbed nitrate. *J. Am. Chem. Soc.* 130, 12210. <http://dx.doi.org/10.1021/ja802342m>.
- Shen, X., Wu, H., Zhao, Y., Huang, D., Huang, L., Chen, Z., 2016. Heterogeneous reactions of glyoxal on mineral particles: a new avenue for oligomers and organosulfate formation. *Atmos. Environ.* 131, 133–140. <http://dx.doi.org/10.1016/j.atmosenv.2016.01.048>.
- Singh, M., Zhou, N., Paul, D.K., Klabunde, K.J., 2008. IR spectral evidence of aldol condensation: acetaldehyde adsorption over TiO<sub>2</sub> surface. *J. Catal.* 260, 371–379. <http://dx.doi.org/10.1016/j.jcat.2008.07.020>.
- Stefanov, B.I., Topalian, Z., Granqvist, C.G., Osterlund, L., 2014. Acetaldehyde adsorption and condensation on anatase TiO<sub>2</sub>: influence of acetaldehyde dimerization. *J. Mol. Catal. A* 381, 77–88. <http://dx.doi.org/10.1016/j.molcata.2013.10.005>.
- Sun, Z.Y., Kong, L.D., Ding, X.X., Du, C.T., Zhao, X., Chen, J.M., Fu, H.B., Yang, X., Cheng, T.T., 2016. The effects of acetaldehyde, glyoxal and acetic acid on the heterogeneous reaction of nitrogen dioxide on gamma-alumina. *Phys. Chem. Chem. Phys.* 18, 9367–9376. <http://dx.doi.org/10.1039/c5cp05632b>.
- Szanyi, J., Kwak, J.H., Chimentao, R.J., Peden, C.H.F., 2007. Effect of H<sub>2</sub>O on the adsorption of NO<sub>2</sub> on γ-Al<sub>2</sub>O<sub>3</sub>: an in situ FTIR/MS study. *J. Phys. Chem. C* 111, 2661–2669. <http://dx.doi.org/10.1021/jp066326x>.
- Thevenet, F., Olivier, L., Batault, F., Sivachandiran, L., Locoge, N., 2015. Acetaldehyde adsorption on TiO<sub>2</sub>: influence of NO<sub>2</sub> preliminary adsorption. *Chem. Eng. J.* 281, 126–133. <http://dx.doi.org/10.1016/j.cej.2015.06.084>.
- Tong, S.R., Wu, L.Y., Ge, M.F., Wang, W.G., Pu, Z.F., 2010. Heterogeneous chemistry of monocarboxylic acids on alpha-Al<sub>2</sub>O<sub>3</sub> at different relative humidities. *Atmos. Chem. Phys.* 10, 7561–7574. <http://dx.doi.org/10.5194/acp-10-7561-2010>.
- Underwood, G.M., Miller, T.M., Grassian, V.H., 1999. Transmission FT-IR and Knudsen Cell study of the heterogeneous reactivity of gaseous nitrogen dioxide on mineral oxide particles. *J. Phys. Chem. A* 103, 6184–6190. <http://dx.doi.org/10.1021/jp991586i>.
- Usher, C.R., Al-Hosney, H., Carlos-Cuellar, S., Grassian, V.H., 2002. A laboratory study of the heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles. *J. Geophys. Res.* Atmos 107. <http://dx.doi.org/10.1029/2002jd002051>.
- Usher, C.R., Michel, A.E., Grassian, V.H., 2003. Reactions on mineral dust. *Chem. Rev.* 103, 4883–4939. <http://dx.doi.org/10.1021/cr020657y>.
- Wang, H.H., Ji, Y.M., Gao, Y.P., Li, G.Y., An, T.C., 2015. Theoretical model on the formation possibility of secondary organic aerosol from -OH initiated oxidation reaction of styrene in the presence of O<sub>2</sub>/NO. *Atmos. Environ.* 101, 1–9. <http://dx.doi.org/10.1016/j.atmosenv.2014.10.042>.
- Wu, L.Y., Tong, S.R., Ge, M.F., 2013. Heterogeneous reaction of NO<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub>: the effect of temperature on the nitrite and nitrate formation. *J. Phys. Chem. A* 117, 4937–4944. <http://dx.doi.org/10.1021/jp402773c>.
- Wu, L.Y., Tong, S.R., Wang, W.G., Ge, M.F., 2011. Effects of temperature on the heterogeneous oxidation of sulfur dioxide by ozone on calcium carbonate. *Atmos. Chem. Phys.* 11, 6593–6605. <http://dx.doi.org/10.5194/acp-11-6593-2011>.
- Wu, Y.S., Salmela, K.S., Lieber, C.S., 1998. Microsomal acetaldehyde oxidation is negligible in the presence of ethanol. *Alcohol Clin. Exp. Res.* 22, 1165–1169. <http://dx.doi.org/10.1097/0000374-199808000-00028>.
- Xu, B.Y., Shang, J., Zhu, T., Tang, X.Y., 2011. Heterogeneous reaction of formaldehyde on the surface of gamma-Al<sub>2</sub>O<sub>3</sub> particles. *Atmos. Environ.* 45, 3569–3575. <http://dx.doi.org/10.1016/j.atmosenv.2011.03.067>.
- Yang, X., Xue, L., Wang, T., Wang, X., Gao, J., Lee, S., Blake, D.R., Chai, F., Wang, W., 2018. Observations and explicit modeling of summertime carbonyl formation in Beijing: identification of key precursor species and their impact on atmospheric oxidation chemistry. *J. Geophys. Res.* Atmos. 123, 1426–1440. <http://dx.doi.org/10.1002/2017JD027403>.
- Yang, Y., Lin, F., Tran, H., Chin, Y.-H., 2017. Butanal condensation chemistry catalyzed by Bronsted acid sites on polyoxometalate clusters. *ChemCatChem* 9, 287–299. <http://dx.doi.org/10.1016/j.atmosenv.2011.03.067>.
- Yao, M., Ji, Y., Wang, H., Ao, Z., Li, G., An, T., 2017. Adsorption mechanisms of typical

- carbonyl-containing volatile organic compounds on anatase TiO<sub>2</sub> (001) surface: a DFT investigation. *J. Phys. Chem. C* 121, 13717–13722. <http://dx.doi.org/10.1021/acs.jpcc.7b02964>.
- Zhang, Z., Shang, J., Zhu, T., Li, H., Zhao, D., Liu, Y., Ye, C., 2012. Heterogeneous reaction of NO<sub>2</sub> on the surface of montmorillonite particles. *J. Environ. Sci.* 24, 1753–1758. [http://dx.doi.org/10.1016/S1001-0742\(11\)61014-0](http://dx.doi.org/10.1016/S1001-0742(11)61014-0).
- Zhao, X., Kong, L.D., Sun, Z.Y., Ding, X.X., Cheng, T.T., Yang, X., Chen, J.M., 2015. Interactions between heterogeneous uptake and adsorption of sulfur dioxide and acetaldehyde on hematite. *J. Phys. Chem. A* 119, 4001–4008. <http://dx.doi.org/10.1021/acs.jpca.5b01359>.