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**Heterogeneous  
chemistry of  
monocarboxylic  
acids on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>**

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# Heterogeneous chemistry of monocarboxylic acids on $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at ambient condition

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## Abstract

A study of the atmospheric heterogeneous reactions of formic acid, acetic acid, and propionic acid on dust particles ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) was performed at ambient condition by using a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reactor. From the analysis of the spectral features, observations of carboxylates formation provide strong evidence for an efficient reactive uptake process. Comparison of the calculated and experimental vibrational frequencies of adsorbed carboxylates establishes the bridging coordinated structures on the surface. The uptake coefficients of formic acid, acetic acid, and propionic acid on  $\alpha$ - $\text{Al}_2\text{O}_3$  particles are  $(2.07 \pm 0.26) \times 10^{-3}$ ,  $(5.00 \pm 0.69) \times 10^{-3}$ , and  $(3.04 \pm 0.63) \times 10^{-3}$ , respectively (using geometric area). Besides, the effect of various relative humid (RH) on this heterogeneous reactions was studied. The uptake coefficients of monocarboxylic acids on  $\alpha$ - $\text{Al}_2\text{O}_3$  particles increase initially (RH < 20%) and then decrease with the increased RH (RH > 20%) which was due to the effect of water on carboxylic acids solvation, particles surface hydroxylation, and competition on reactive site. On the basis of the results of experimental simulation, the mechanism of heterogeneous reaction of dust with carboxylic acids at ambient condition was discussed. The loss of atmospheric monocarboxylic acids due to reactive uptake on available mineral dust particles can be competitive with homogeneous loss pathways, especially in dusty urban and desertified environments.

## 1 Introduction

About 33% of the earth's land surface is arid and a potential source region for atmospheric mineral aerosol (Tegen and Fung, 1994). Mineral aerosol is a general expression for fine particles of crustal origin that is generated by wind erosion. It can be uplifted into the atmosphere by strong surface winds that travel behind cold frontal systems (Carmichael et al., 1996). Currently, annual dust emissions are estimated in the range of 1000–3000 Tg/yr (Li et al., 1996; Prospero, 1999). Particles smaller than

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10  $\mu\text{m}$  have atmospheric lifetimes of weeks (Propero, 1999). Mineral aerosol may be transported over thousands of kilometers (Duce et al., 1980; Savoie and Prospero, 1982) and are therefore found far away from their sources resulting in a global distribution of this kind of atmospheric aerosols (Husar et al., 2001). The impact of mineral dust particles on the Earth's atmosphere is manifold. They can absorb and scatter solar and terrestrial radiation and they are of suitability as cloud condensation nuclei (Cziczo et al., 2004). Moreover, recent modeling studies (Dentener et al., 1996; Zhang et al., 1994) have predicted that mineral aerosol could also have a significant influence on atmospheric chemistry by promoting heterogeneous reactions. There is also strong experimental evidence that indicates an important role for mineral dust in modifying atmospheric trace gas distributions. The role of heterogeneous reactions on particulate matter present in the Earth's atmosphere remains an important subject in tropospheric chemistry. It has been proposed in several modeling studies that mineral dust may provide reactive surfaces for trace atmospheric gases (Dentener et al., 1996). Laboratory studies can be quantitatively assessed in atmospheric chemistry models.

Carboxylic acids are one class of oxygenated volatile organic compounds (OVOCs). They are from biomass and fuel burning (Kawamura et al., 1985; Talbot et al., 1987) and have received increasing attention in the literature in the past decade. They are a large fraction (25%) of the nonmethane hydrocarbon loading and are prevalent in both urban and remote atmospheres (Chebbi and Carlier, 1996; Khare and Kumari, 1999). Carboxylic acids are responsible for a significant portion of the free acidity in rainwater: up to 35% in North America (Keene and Galloway, 1984) and up to 64% in more remote regions (Keene et al., 1983). Formic acid is the most prevalent carboxylic acid in the gas phase, followed by acetic acid, which is also very abundant in the troposphere with reported concentrations from 0.05–16 ppbv gas-phase (Chebbi and Carlier, 1996). In some regions, the mixing ratio of formic acid can exceed those of  $\text{HNO}_3$  and  $\text{HCl}$  (Nolte et al., 1997). The level of propanoic acid is lower but still significant, in the range 300–700 ppt (Nolte et al., 1999; Satsumabayashi et al., 1989). These oxygenated organic molecules influence the oxidative capacity of the atmosphere through interaction with

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photochemical HO<sub>x</sub> and NO<sub>x</sub> cycles, which, in turn, regulate tropospheric O<sub>3</sub> production (Finlayson-Pitts and Pitts, 1997; Kley, 1997); they are also believed to be important sink for OH radicals in cloudwater, and, as such, they influence oxidation of other important atmospheric species such as SO<sub>2</sub> (Jacob, 1986). In fact, HO<sub>x</sub> production from the photolysis of acetone, peroxides, and carboxylic acids, can be more important than HO<sub>x</sub> production from the reaction of O(<sup>1</sup>D) with H<sub>2</sub>O in the upper troposphere (Jacob, 1986; Wennberg et al., 1998). Besides, the carboxylic acids are more polar and more surface active as they contain both a double-bonded oxygen and a single-bonded oxygen. However, atmospheric sources and sinks of carboxylic acids are not yet well-known, and their concentrations are not well reproduced in most models (von Kuhlmann et al., 2003). Therefore, it is important to understand the processes that control the gas-phase concentrations of these molecules.

Carboxylic acids in the atmosphere have been correlated with mineral aerosol in field studies. During the Atlanta SuperSite Project, Lee and co-workers (2002) analyzed 380 000 spectra of single aerosol particles in the 0.35–2.5 μm size range using laser mass spectrometry instrument. Approximately 40% of the particles analyzed contained fragments associated with organic acids, such as formic and acetic acid. Another study by Russell et al. (2002) using single particle X-ray spectroscopy has observed correlations between large calcium containing particles and fragments indicative of carboxylic acids. Carboxylic acids can increase both the rate of dissolution and solubility of minerals similar to the inorganic acids. Thus, naturally occurring organic acids in dust can affect kinetics and thermodynamics of weathering and diagenesis (Kubicki et al., 1997). Chelation reactions between organic acids and cations in aerosols can drive dissolution of the fine-grained particles comprising the aerosol and enhance the stability of ions in cloud droplets (Ere et al., 1993).

Despite the results of field observations, there have not been many laboratory experiments that investigate the heterogeneous reactivity of carboxylic acids on mineral aerosol. A few laboratory studies have begun to explore the heterogeneous chemistry of organic acids with various types of minerals. In the previous studies, the

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heterogeneous uptake kinetics of acetic acid on Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> (Carlos-Cuellar et al., 2003) and formic acid on CaCO<sub>3</sub> (Al-Hosney et al., 2005) have been measured with a Knudsen cell reactor. Al-Hosney et al. (2005) observed that under humidified conditions, adsorbed water on the surface of the particles participates in the surface reactivity of the particles, which results in the enhanced uptake kinetics as well as extent of this heterogeneous reaction and opens up several new reaction pathways. Hatch et al. (2007) investigated the heterogeneous uptake of the C<sub>1</sub> to C<sub>4</sub> organic acids on a swelling clay mineral under typical upper tropospheric temperatures and atmospherically relevant RH values. Prince et al. (2008) investigated heterogeneous reaction between calcite aerosol with both nitric and acetic acids in the presence of water vapor which indicated that calcium rich mineral dust may be an important sink for simple organic acids.

Based on the previous studies for mineral dust, the organic acid uptake is sufficiently large that dust may be a significant sink for them in the atmosphere. The uptake coefficient can be expected to be larger under higher RH conditions typical of the ambient troposphere. However, large uncertainties remain concerning the analysis of species formed on the surface and the reaction mechanism at ambient condition. Therefore, the heterogeneous reaction between dust and carboxylic acids should be studied in depth.

Alumina has a defined chemical composition and is widely used as model oxides for the study of trace gases heterogeneous reactions. In the present study, the uptake of formic acid, acetic acid, and propionic acid on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles have been investigated at 300 K, 1 atm synthetic air using a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reactor. Quantum chemical calculations were performed in order to better understand the mechanism of these reactions and study the modes of surface coordinate species on molecular level. Furthermore, the effect of various relative humid (RH) on these heterogeneous reactions were studied.

The aim of this work was to reveal some of the kinetics and mechanism of the reaction between alumina and carboxylic acids at ambient condition and to study whether

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the loss of atmospheric organic acids due to these reactions can be competitive with homogeneous reactions. The DRIFTS reactor has been employed to probe the heterogeneous chemistry on particle surfaces (Finlayson-Pitts, 2000; Vogt and Finlayson-Pitts, 1994; Roscoe and Abbatt, 2005; Zhang et al., 2006) and it can be used to measure in situ spectra of the reaction products without interrupting the reaction processes (Finlayson-Pitts, 2000). DRIFTS can provide mechanistic details not available through other methods. Kinetic data can also be obtained (Vogt and Finlayson-Pitts, 1994) as the uptake coefficient by calibrating the infrared absorbance with ion chromatographic analysis of reacted samples. Probing the chemistry and measuring the rates of these reactions under atmospheric conditions will provide essential information for developing an accurate computer model of our atmosphere. Characterizing heterogeneous reactions in our atmosphere is one of the first steps gaining a more complete understanding of the earth-atmosphere system and humanity's role in climate change.

## 2 Experimental

### 2.1 Sources of powders and gases

Commercially available  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles purchased from Alfa Aesar (with a stated minimum purity of 99%) were used for the spectroscopic measurements. The Brunauer-Emmett-Teller (BET) surface area of the particles is measured to be 11.9 m<sup>2</sup> g<sup>-1</sup> (Autosorb-1-MP automatic equipment, Quanta Chrome Instrument Co.). HCOOH (>97%, Alfa Aesar), CH<sub>3</sub>COOH (>99.7%, Alfa Aesar), and CH<sub>3</sub>CH<sub>2</sub>COOH (>99%, Alfa Aesar) were diluted and mixed with N<sub>2</sub> (>99.999%, Beijing Tailong Electronics Co., Ltd) before used. O<sub>2</sub> (>99.998%, Orient Center Gas Science & Technology Co., Ltd) was used to simulate the ambient air. Distilled water (Barnstead Easypure II D7411, Thermo Scientific) was degassed prior to use.

## 2.2 Measurement

Infrared spectra were recorded in the spectral range from 4000 to 650  $\text{cm}^{-1}$  with a Nicolet FTIR Spectrometer 6700 equipped with a liquid-nitrogen-cooled narrow band mercury-cadmium-telluride (MCT) detector and DRIFTS optics (Model CHC-CHA-3, Harrick Scientific Corp.). The spectra were recorded at a resolution of 4  $\text{cm}^{-1}$ , and 100 scans were usually averaged for each spectrum corresponding to a time resolution of 40 s. The flow cell in DRIFTS optics has been described in detail elsewhere (Li et al., 2006).

To obtain reproducible packing of the DRIFTS sampling cup, the powder (60 mg) was pressed into the cup (10 mm diameter, 0.5 mm depth). The sample could be heated and the temperature of the sample cup measured by a thermocouple located directly underneath. The outer walls of the reaction chamber were maintained at room temperature by circulating cooled water through a jacket surrounding the cell.

The gas supply system was composed of four inlet lines. The first line supplied diluted organic acids; the second line provided  $\text{O}_2$ ; the third line supplied water vapor mixed in nitrogen gas, and the fourth line provided  $\text{N}_2$ . All gases were mixed together before entering the reactor chamber, resulting in a total flow of 400 sccm synthetic air (21%  $\text{O}_2$  and 79%  $\text{N}_2$ ). The active gas flow was forced through the powder. To investigate the adsorption behavior of water on the particles, the infrared spectra and adsorptive isothermal curves of water and carboxylic acids on  $\text{Al}_2\text{O}_3$  were measured using DRIFTS. Pretreated samples were exposed to wet air with different RH at 300 K for 20 min to establish adsorption equilibrium. The infrared spectra at equilibrium were collected.

The integrated absorption bands of the products were calibrated absolutely by analyzing the sample by ion chromatography after reaction. The reacted particles were sonicated for 20 min in 1.5 mL of distilled water. The filtered solution was analyzed using a Dionex ICS 900 system, which was equipped with a Dionex AS 14A analytical column and a conductivity detector (DS5). The number of carboxylate ions found in

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the samples was linearly correlated to the integrated absorbance of the corresponding absorption bands. Using this calibration the formation rate of carboxylate ions and thus the uptake coefficients for products formation on mineral dust could be calculated.

## 2.3 Theoretical calculation

5 IR bands, and adsorption energies of the surface carboxylate species on  $\text{Al}_2\text{O}_3$  were calculated using the Gaussian 03 program package (Frisch et al., 2003). To calculate the vibrational frequencies of the carboxylate ions, tetrahedrally coordinated binuclear cluster models of the formula  $[\text{Al}_2(\text{OH}_4)(\mu\text{-OH})(\text{RCOO})]$  (Baltrusaitis et al., 2007; Grassian, 2008) were used. The structure parameter of the coordinated carboxylate species were optimized with DFT method. The Becke-three-parameter Lee-Yang-Parr functional (B3LYP) with the 6-311++G(3df,3pd) basis set was used throughout this work. A vibrational analysis was performed for the optimized structure to compare with the IR spectra obtained experimentally. The structure, vibrational frequencies and intensities for the calculated models by the Gaussian 03 program were analyzed by the Gaussview 3.07 program package. Generally, theoretical harmonic frequencies overestimate experimental values due to incomplete descriptions of electron correlations and neglecting mechanical anharmonicity. To compensate for this problem, a uniform scaling factor of 0.9726 was used on calculated frequencies obtained at the B3LYP level of theory (Halls et al., 2001). As reported by Irikura et al. (2005), the scaling factor depends only weakly on the basis set, thus it can be used for the majority of basis sets under the same level of theory as used in these calculations.

## 3 Result and discussion

### 3.1 Observed products

25 Prior to initiation of the heterogeneous reactions, the reaction chamber was evacuated and then flushed with carrier gas while the sample was kept at 573 K for 3 h by dry

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synthetic air before the experiment was started. This treatment gives stable conditions and also removes adsorbed species such as loosely bonded water, from the surface. After the system was cooled to 300 K, a background spectrum of the unreacted particles was recorded. Spectra were collected as different spectra with the unreacted particles as the background and surface products were shown as positive bands while losses of surface species were shown as negative bands.

Fundamental vibrations of Al<sub>2</sub>O<sub>3</sub> are localized in the low frequency region around 1100 cm<sup>-1</sup> of the IR spectrum. In fact, the intensity of these vibrational modes is so high that they represent a virtually complete spectral cut-off for the solid, even when very thin pellets or thin-layer deposition samples are used. Therefore, the spectral range extending from 1200–3900 cm<sup>-1</sup> was selected for all the spectra below.

Figures 1–3 shows DRIFTS spectra (absorbance units) of three carboxylic acids adsorbed on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at room temperature under dry conditions (RH<1%). The spectra were recorded in the presence of the gas phase at a concentration of 1.23×10<sup>14</sup> molecules cm<sup>-3</sup>. Assignments of the absorbance bands were facilitated by examination of spectra in the literature that involved the reactions of carboxylic acids on solids.

When formic acid was introduced to the flow system several absorption bands were observed: 1600 cm<sup>-1</sup>, 1378 cm<sup>-1</sup>, 2866 cm<sup>-1</sup>, a broad band around 3450 cm<sup>-1</sup>, a negative band at 3730 cm<sup>-1</sup>. A shoulder at 1393 cm<sup>-1</sup> can also be observed. These results are present in Table S1 (see supplement: <http://www.atmos-chem-phys-discuss.net/10/3937/2010/acpd-10-3937-2010-supplement.pdf>). The band at 1378 cm<sup>-1</sup> we associate with C–H in-plane bend and the shoulder at 1393 cm<sup>-1</sup> was associated with symmetric stretching mode ( $\nu_s(\text{OCO})$ ), in line with the assignment on other Al<sub>2</sub>O<sub>3</sub> surfaces (Amenomiya, 1979; Chauvin et al., 1990). The negative band indicates loss of surface species which we will discuss later. Reaction of the acid on the surface to give the formate anion is suggested by the absence of the C=O stretch mode at 1780 cm<sup>-1</sup> and the C–OH stretch mode at ~1100 cm<sup>-1</sup> (Klein, 1973). Instead we see clearly the broad OCO antisymmetric stretch mode ( $\nu_{as}(\text{OCO})$ ) of the

formate anion at  $1600\text{ cm}^{-1}$  (Table S1: <http://www.atmos-chem-phys-discuss.net/10/3937/2010/acpd-10-3937-2010-supplement.pdf>).

Adsorption and surface reaction of acetic acid were monitored on  $\alpha\text{-Al}_2\text{O}_3$  particles. The absence of a peak characteristic of the C=O stretch of acetic acid in the region  $1690\text{--}1790\text{ cm}^{-1}$  clearly indicates that the physisorbed acetic acid is inexistent (Bertie and Michaelian, 1982; Pei and Ponec, 1996). Upon adsorption of  $\text{CH}_3\text{COOH}$  on the surface of  $\alpha\text{-Al}_2\text{O}_3$ , several prominent bands are seen to grow. Bands at  $1343$ ,  $1424$ ,  $1468$ ,  $1578$ ,  $2935$ ,  $2986$ , and  $3016\text{ cm}^{-1}$  are shown to increase in intensity as the times of gas phase acetic acid were increased. We assigned the two peaks at  $1343\text{ cm}^{-1}$  and  $1424\text{ cm}^{-1}$  to C–H deformation which are in accordance with the references (Chen and Bruce, 1995; Walmsley et al., 1981). The peaks of  $1578$  and  $1468\text{ cm}^{-1}$  are correlated to two C–O stretching vibrations of the OCO group of acetate (Dobson and McQuillan, 1999; Gao et al., 2008; Pei and Ponec, 1996). Further confidence in the assignment of the  $1468$  and  $1424\text{ cm}^{-1}$  bands comes from the spectra of  $\text{CD}_3\text{COO}^-$  and  $\text{CF}_3\text{COO}^-$  adsorbates on aluminium oxide (Brown et al., 1979). The  $1424\text{ cm}^{-1}$  is entirely absent from both as would be expected if it is due to a  $\text{CH}_3$  mode. Superimposed on  $\nu_{\text{sym}}(\text{OCO})$  is the symmetric methyl bending mode,  $\delta_{\text{s}}(\text{CH}_3)$ , which is located at  $1343\text{ cm}^{-1}$ . This peak is significantly smaller than the carboxylate stretching modes, but still sharp and distinct. These bands indicate the acetate forms on the surface.

Figure 3 shows the typical time series monitored during the exposure of  $\text{CH}_3\text{CH}_2\text{COOH}$  to  $\alpha\text{-Al}_2\text{O}_3$ . In comparison with the vibrational features of the liquid-phase (Jakobsen et al., 1971) and gas-phase  $\text{CH}_3\text{CH}_2\text{COOH}$ , the absence of the  $\nu(\text{OH})$  and  $\nu(\text{C}=\text{O})$  indicates that the physisorbed propionic acid is inexistent. Similar to the vibrational features of  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$ , the product of heterogeneous reaction between propionic acid and  $\text{Al}_2\text{O}_3$  is propionate. The peaks at  $1568$ ,  $1478$  and  $1424\text{ cm}^{-1}$  are assigned to  $\nu_{\text{as}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  of OCO group, respectively. Due to CH group of  $\text{CH}_3\text{CH}_2\text{COOH}$ , more bands are appeared at the region between  $1200\text{--}1500\text{ cm}^{-1}$ . The peaks at  $1259$ ,  $1303$ ,  $1383$ ,  $1424$ , and  $1478\text{ cm}^{-1}$  are all assigned to

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the vibrational features of C–H of CH<sub>3</sub> and CH<sub>2</sub> groups (Yang et al., 2006). As seen from Fig. 3, a strong intensity band 2981 cm<sup>-1</sup> in the 2500–3000 cm<sup>-1</sup> region could be assigned to the antisymmetric CH<sub>3</sub> stretching modes (Kakihana and Akiyama, 1987). The band at 2946 cm<sup>-1</sup> can be related to the antisymmetric and symmetric CH<sub>2</sub> stretching modes. The remaining symmetric CH<sub>3</sub> stretching fundamental is observed only as a shoulder band at 2946 cm<sup>-1</sup>. The band at 1383 cm<sup>-1</sup> is assigned to symmetric CH<sub>3</sub>-deformational mode. The band around 1478 cm<sup>-1</sup> is assigned to two antisymmetric CH<sub>3</sub> deformational overlap with one CH<sub>2</sub> scissoring vibrations. The band observed at 1303 cm<sup>-1</sup> is assigned to an in-plane CH<sub>2</sub> wagging mode, and the 1259 cm<sup>-1</sup> shoulder band is assigned to an out-of-phase CH<sub>2</sub> twisting mode.

Comparing the three carboxylic acids, we note that the peak ( $\nu_{\text{as}}(\text{COO})$  1600–1550 cm<sup>-1</sup>) red shifts by  $\sim 15$  cm<sup>-1</sup> for each additional CH<sub>2</sub> unit added to the molecule. Formate is unique, lacking any C–C bond, and has a much higher  $\nu_{\text{as}}$  than the other compounds. The  $\nu_{\text{as}}$  frequency decreases as the number of carbon atoms increases from 1–3, finally reaching a minimum at 1568 cm<sup>-1</sup> for propionate. Spectral features indicative of carboxylates are present from the spectra (Max and Chapados, 2004).

For the heterogeneous reactions of three carboxylic acids, an interesting observation is the decrease in absorption of a peak centered at 3730 cm<sup>-1</sup>. This band has been described before (Börensén et al., 2000; Morerra and Magnacca, 1996) and is attributed to a loss of OH surface species. Negative features of this band indicate either loss of hydroxyl groups from the surface or that the hydroxyl groups are involved in hydrogen bonding. These groups may present reactive sites for adsorption organic acids and are ubiquitous on alumina which can be replaced by nucleophilic reagents. The OH band at around 3690–3800 cm<sup>-1</sup> was identified as being coordinated to an tetrahedral Al site and termed the I-a group by Knözinger and Ratnasamy (1978), and it is generally ascribed to the basic hydroxyl group (Morterra and Magnacca, 1996). Datka et al. (1994) reported that higher frequency OH bands (above 3700 cm<sup>-1</sup>) were consumed during carboxylate formation on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and concluded that the formation of

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carboxylate is related to the basic hydroxyl groups. On the other hand, Boehm (1971) studied the adsorption of NO<sub>2</sub> on  $\eta$ -Al<sub>2</sub>O<sub>3</sub> and suggested that formation of nitrate is related to the basic OH groups. From the above mentioned, it is suggested that the basic OH group is reactive and removed or exchanged upon formation of carboxylates, resulting in coordination of carboxylates on the Al–O site with an anion vacancy.

The band observed at 1640 cm<sup>-1</sup> at initial stage and the broad band around 3450 cm<sup>-1</sup> were assigned as the frequency of H<sub>2</sub>O which was the byproduct of the heterogeneous reaction. When water from the vapor phase condenses onto an inert surface, the asymmetric and symmetric stretching modes at 3756 and 3657 cm<sup>-1</sup>, respectively, collapse into a broad, irregularly shaped band with a principal maximum near 3400 cm<sup>-1</sup> with a full width at half height of 400 cm<sup>-1</sup> in the infrared spectrum. This band is primarily associated with O–H stretching modes with some contribution from the first overtone of the H–O–H bending mode (Downing and Williams, 1975; Luck, 1974; Eisenberg and Kauzmann, 1969; Goodman et al., 2000). The occurrence of strongly hydrogen bonded water may be explained by the fact that protons react with hydroxyl groups to form adsorbed water during the reaction of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with organic acids and remains attached to the surface.

### 3.2 Conformational analysis of carboxylates generated on $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface by DFT calculations

It has been shown that mainly carboxylate species were formed on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface. The vibrational frequency at which the OCO band is formed, can give us information about the way it coordinates to the surface. Since the OCO stretching band is most sensitive to its interaction with the metal, the relationship between this frequency and arrangement of the carboxylates on the surface has been studied by several investigators (Gao et al., 2008; Hedberg et al., 2009; Rachmady and Vannice, 2002). There may exist three coordination modes: a monodentate mode where one carboxylate oxygen is coordinated to a surface Al atom (model I), a bidentate mode involving

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a deprotonated molecule where the two carboxylate oxygens are bonded to the same Al atom (model II), and a bridging mode similar to above but where the two oxygens of carboxylate are coordinated to two different surface Al atoms (model III) (Alcock et al., 1976; Dobson and McQuillan, 1999; Mehrotra and Bohra, 1983; Popova et al., 2007).

In recent years, in addition to the conventional spectroscopic techniques, quantum chemistry has been applied to state of adsorbed species and the structure of the adsorption sites in gas adsorption on particles (Baltrusaitis et al., 2007; Gao et al., 2008; Grassian, 2008; Yang et al., 2006). To understand the exact structures of adsorbed carboxylates and assignment of carboxylate species on the particles surface clearly, we tried to compare the adsorption energies and frequencies of the IR bands of carboxylates adsorbed on the respective sites with the values evaluated from the calculation method utilizing the DFT method.

Vibrational frequencies were then calculated for adsorbed formate corresponding to different modes of bonding to the surface. The optimized geometry of three different modes for these carboxylic acids are shown in Fig. 4. As discussed in the Experimental section, calculated vibrational frequencies were scaled by the appropriate scaling factor of 0.9726. Only frequencies in 1300–1610 cm<sup>-1</sup> region are given to investigate the characteristic OCO and C–H vibrations. Tables S2–S4 give the structural parameters including bond lengths and bond angles, as well as the calculated vibrational frequencies for the calculated models I–III.

The calculated vibrational modes  $\nu_{as}(\text{COO})$  for the models I–III are 1651, 1513, and 1606 cm<sup>-1</sup>, respectively. In comparison with the same experimental frequency of 1600 cm<sup>-1</sup>, the calculated frequency of bridging mode with the least error (6 cm<sup>-1</sup>) is relatively good match of the band 1600 cm<sup>-1</sup> in the experimental spectrum (Fig. 1). The calculated vibrational modes  $\nu_s(\text{COO})$  for the calculated models I–III are 1268, 1362, and 1393 cm<sup>-1</sup>, respectively. For the same experimental frequency of 1393 cm<sup>-1</sup>, the calculated frequency of bridging mode is good match of this band in the experimental spectrum (Fig. 1). Similarly, the calculated frequency of bridging mode with the least error (5 cm<sup>-1</sup>) is also good match of  $\delta(\text{CH})$  with 1378 cm<sup>-1</sup> band in the experimental

spectrum (Fig. 1). Therefore, the spectra of bridging mode simulated by DFT evidently best match the experimental counterparts for the three calculated models.

The calculated  $\nu_{\text{as}}(\text{OCO})$ ,  $\nu_{\text{s}}(\text{OCO})$ , and  $\delta(\text{CH})$  vibrational modes of bridging mode acetate are also good matches of the experimental spectrum with the errors  $-6$ ,  $4$ , and  $6 \text{ cm}^{-1}$ , respectively. Similarly, the most possible conformation for propionate is bridging mode.

Therefore, the spectra of bridging mode simulated by DFT evidently best match the experimental counterparts for the three carboxylic acids and the substitution of the H atom with the  $\text{CH}_3$  group and  $\text{CH}_3\text{CH}_2$  group does not considerably influence the adsorption mode of the acid.

### 3.3 Uptake coefficient and kinetics

Combined with ion chromatography, kinetic data can be deduced from the DRIFTS experiments. In the inset in Figs. 1–3, the integrated absorbance of  $1250\text{--}1450 \text{ cm}^{-1}$ ,  $1360\text{--}1510 \text{ cm}^{-1}$ , and  $1330\text{--}1510 \text{ cm}^{-1}$  for formate, acetate, and propionate, respectively, formed during the reaction as functions of reaction time are shown. From the slope of that curve and the calibration factor derived by ion chromatography, the rate of carboxylates formation on the surface can be calculated. As can be seen from Figs. 1–3, the integrated absorbance increases linearly with time after an induction of the carboxylic acids. Whereas the linear region of this increase corresponds to a constant formation rate of carboxylate ions on the surface, at reaction times longer than 50 min the integrated absorbance starts to level off indicating that the formation rate slows down. In addition, the absolute values of the integrated absorption band due to surface OH-groups ( $3600\text{--}3800 \text{ cm}^{-1}$ ) are shown in the inset of Figs. 1–3. The intensity of the negative band at  $3730 \text{ cm}^{-1}$  due to the basic OH group increased with time on stream in a flow of carboxylic acids, which is likely to coincide with an increase of the carboxylate bands. This result suggests again the coordination of carboxylates on the Al–O site.

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The amount of carboxylate ions on the sample was determined by ion chromatography in order to quantify the carboxylate ions formation rate  $d[\text{RCOO}^-]/dt$  in terms of the reactive uptake coefficient. The formation rate was translated from absorption units  $\text{s}^{-1}$  to  $\text{RCOO}^- \text{s}^{-1}$  by a conversion factor obtained from a calibration plot. Both the absorbance (Vogt and Finlayson-Pitts, 1994; Ullerstam et al., 2002) and Kubelka–Munk (K–M) function (Averet and Griffiths, 2006; Tsai and Kuo, 2006) integrated can be used to quantify the surface products. The K–M method is known to vary with baseline position error that give rise to unacceptable uncertainty levels in quantitative experiments (Samuels et al., 2006). Hence, the surface products of the carboxylic acids react on Al<sub>2</sub>O<sub>3</sub> particles in this study were followed using the integrated absorbance–reaction behavior. The reactive uptake coefficient ( $\gamma$ ) is defined as the rate of carboxylate ions formation on the surface divided by the total number of surface collisions per unit time ( $Z$ ):

$$\gamma = \frac{d\{\text{RCOO}^-\}/dt}{Z} \quad (1)$$

$$Z = \frac{1}{4} \times A_S \times [\text{RCOOH}] \times \sqrt{\frac{8RT}{\pi M_{\text{RCOOH}}}} \quad (2)$$

Where  $\{\text{RCOO}^-\}$  is surface concentrations of the carboxylate ions (where  $\{\}$  have been used to distinguish surface concentrations from gas-phase concentrations),  $[\text{RCOOH}]$  is the gas-phase concentration,  $A_S$  is the effective sample surface,  $R$  is the gas constant,  $T$  is the temperature, and  $M_{\text{RCOOH}}$  is the molecular weight of carboxylic acids. Two extreme cases of effective sample surface need to be considered (Li et al., 2006; Ullerstam et al., 2002). The uptake coefficients of three carboxylic acids on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are shown in Table 1, both BET surface area and geometric surface area of the sample are used. For the same heterogeneous reaction, the uptake coefficients can differ by about four orders of magnitude depending on the choice of the effective surface area (geometric or BET area). The use of the BET area introduces a larger correction factor

than may be necessary as the BET area is measured using molecular nitrogen as the adsorbent. Since molecular nitrogen is of smaller dimensions than carboxylic acids, the surface area accessible to molecular nitrogen may not be accessible to carboxylic acids. The BET area may overestimate the surface area of the particles and thus underestimate the uptake coefficient (Goodman and Grassian, 2000). Therefore, the uptake coefficient for formic, acetic, and propionic acids are  $2.07 \times 10^{-3}$ ,  $5.00 \times 10^{-3}$ , and  $3.04 \times 10^{-3}$  if the geometric surface area is used and  $2.37 \times 10^{-7}$ ,  $5.99 \times 10^{-7}$ , and  $3.03 \times 10^{-7}$  if the BET surface area is applied.

There are several studies concerning the uptake of organic acid on different surfaces or materials, and most of them were deduced from experimental results using Knudsen Cell reactors and IR reactors. The uptake coefficients were of the order of  $10^{-3}$ – $10^{-4}$  (Al-Hosney et al., 2005; Carlos-Cuellar et al., 2003), which is close to our value using the geometric surface area, but significantly higher than the value obtained with the BET surface area. Ullerstam et al. (2003) studied the uptake coefficients for  $\text{SO}_2$  in the presence of  $\text{NO}_2$  using the two different techniques, and found the difference between them are by a factor of around  $2 \times 10^4$  (BET ratios). The Knudsen cell studies were done at much lower pressures on the order of a factor of  $10^6$  lower. Thus, saturation effects are minimized in the Knudsen cell experiments. The assumption of a uniform site distribution might not be valid, and the most reactive sites may be probed at the lower pressures. Moreover, the uptake coefficient obtained using the two techniques are fundamentally different. The Knudsen cell measures the loss rate of gaseous species during exposure, while the DRIFTS technique determines the rate of the formation of products on the surface. Besides, the difference in uptake coefficient from our work compared to coefficients found in the literature is also likely due to a difference in substances and experimental conditions. For instance, Hatch et al. (2007) used Namontmorillonite clay at 212 K; Al-Hosney et al. (2005) used  $\text{CaCO}_3$  sample with a BET surface area of  $1.4 \text{ m}^2 \text{ g}^{-1}$ , and both of their experimental conditions were at lower pressure.

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Equation (1) shows that the uptake coefficient of unreacted surface is expected to be inversely dependent on the reactant concentration in the case of zero-order kinetics and independent on concentration under first-order conditions. In Fig. 5, the formation rate derived from the linear temporal increase of the integrated absorbance of experiments performed at different RCOOH<sub>(g)</sub> concentration has been plotted against the corresponding RCOOH concentration on a double-logarithmic scale. All the solid lines have a slope near to 1, indicating first-order rate laws for three carboxylic acids uptake on the surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the uptake coefficients are independent on the concentration of the reactive species.

### 3.4 Role of water in the reaction of carboxylic acids on Al<sub>2</sub>O<sub>3</sub> particles

Adsorption on mineral surfaces is mostly studied under dry conditions. However, for practical applications, e.g., in environmental chemistry, we are interested in the sorption properties of mineral surfaces for organic compounds under ambient conditions. Hence, it is necessary to consider the influence of humidity because hydrophilic mineral surfaces are partly or completely covered by one or more molecular layers of adsorbed water at ambient humidity. It is becoming increasingly clear through laboratory studies that surface adsorbed water plays a role in the heterogeneous chemistry of trace atmospheric gases (Al-Abadleh et al., 2005; Roscoe and Abbatt, 2005). Water is one of the reactants, and should have a fundamental effect on the reaction kinetics. Therefore, the reaction kinetics at different RH were studied using DRIFTS in the presence of the carboxylic acid gas phase at a concentration of  $1.23 \times 10^{14}$  molecules cm<sup>-3</sup>.

Figure 6 shows the spectra of three carboxylic acids adsorbed on Al<sub>2</sub>O<sub>3</sub> at humid condition. When carboxylic acids were introduced, the negative bands at 1670 cm<sup>-1</sup> and 3000–3600 cm<sup>-1</sup> region indicate water consumed in the formation of hydrated carboxylates or as a reactant. Besides, the bandwidths in the spectrum of the adsorbed carboxylate species are greater at dry condition than those of the wet condition. This band broadening with adsorption onto the sol-gel substrates is a general feature of the spectra of adsorbed carboxylic acid species and is probably due to a range of

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adsorption sites of slightly different energy. For formic acid, the addition of water vapor to the system caused the peak  $2864\text{ cm}^{-1}$  to shift to  $2811\text{ cm}^{-1}$ . This peak is assigned to the C–H stretch of formate ion. The C–H band is sensitive to the hydration state of formate. The presence of water red shifts this peak approximately  $50\text{ cm}^{-1}$ , as observed by both IR and Raman spectroscopy of bulk aqueous HCOONa (Bartholomew and Irish, 1993; Iro and Bernstein, 1956) and VSFS spectroscopy of exposure of ZnO/Zn to wet HCOOH (Hedberg et al., 2009). Thus the peak at  $2811\text{ cm}^{-1}$  on the Al<sub>2</sub>O<sub>3</sub> surface is attributed to the hydrated formate. During the  $\delta(\text{CH})$  and  $\nu_{\text{s}}(\text{OCO})$  regions, the appearance of the  $1362\text{ cm}^{-1}$  peak also red shifts after exposure in humid which may attribute to the formate ion (Spinner, 1985). Simultaneously, the peak at  $2856\text{ cm}^{-1}$ , which belongs to surface formate coordinate still exists. Therefore, the oxide coordinated and hydrated formate coexist at wet condition. For acetic and propionic acids adsorbed on Al<sub>2</sub>O<sub>3</sub> particle surface at wet condition, the similar phenomena are observed as that of formic acid. Similarly, for acetic and propionic acids, the bands of  $\delta(\text{CH}_3)$  and  $\nu_{\text{s}}(\text{OCO})$  regions also changed at wet condition, which may indicate the coexistence of hydrated carboxylate. These spectral changes may suggest that the environment of the carboxylate groups is different after exposure to adsorbed water.

The presence of water has two potential roles in this process: solvation of the carboxylate ion, and hydroxylation of the particles surface. Using crystal truncation rod (CTR) diffraction techniques, Eng et al. (2000) examined the structure of the hydrated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) surface. The fully hydrated surface is oxygen-terminated with a contracted aluminum layer underneath and is found to have a structure which is intermediate between  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al(OH)<sub>3</sub> with hydroxylation occurred. Al-Abadleh and Grassian (2003) also found that water adsorbed on the surface in an ordered fashion with the formation of a stable hydroxide layer at lower RH. Although a rather high initial sticking coefficient of 0.1 has been measured for H<sub>2</sub>O on Al<sub>2</sub>O<sub>3</sub> at 300 K, the sticking coefficient was found to decrease exponentially with increasing water coverage (Elam et al., 1998). After the surface is fully hydroxylated, additional water can only be physisorbed on the hydroxyl layer on Al<sub>2</sub>O<sub>3</sub> (Al-Abadleh and Grassian, 2003; Elam

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et al., 1998; Goodman et al., 2001; Liu et al., 2009). Because surface –OH is the reactive site for the heterogeneous reaction of carboxylic acids, the formation of surface –OH should promote the reaction while the molecular adsorption of water on surface –OH should suppress this reaction. Theoretically, the uptake coefficients on Al<sub>2</sub>O<sub>3</sub> should increase initially and then decrease with the increased RH. This turning point was observed in our experiment (Fig. 7).

Studies of water adsorption versus relative humidity on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder showed that approximately one monolayer formed at 20% relative humidity, two to three adsorbed water layers formed at 50% relative humidity, and three to four adsorbed water layers formed at 85% relative humidity (Eng et al., 2000; Goodman et al., 2001). Therefore, more –OH were formed which promote the reaction rate below 20% RH. Then competitive adsorption of water and carboxylic acids on surface –OH decrease the reaction rate after multilayer water formed. It should be noted that not all of the surface OH sites were consumed by adsorbed water from our results. There still exists some oxide coordinated carboxylates on the surface. Baltrusaitis et al. (2007) have found that there are adsorbed water islands. Water is not adsorbed according to the hypothetical monolayer, but rather in islands such that some surface adsorption sites are still available for reaction by carboxylic acids.

Our result is a little different from that of heterogeneous reactions between CaCO<sub>3</sub> and carboxylic acids (Al-Hosney et al., 2005). Al<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub> particles represent two defined classes of oxides, reactive insoluble, and reactive soluble, respectively (Goodman et al., 2001). This is important as it will show that the reactivity with CaCO<sub>3</sub> is not limited to the surface, the bulk oxygen atoms participate in the reaction as well as the surface oxygen atoms and that this participation is enhanced in the presence of water vapor. Whereas the uptake coefficients of carboxylic acids on Al<sub>2</sub>O<sub>3</sub> decreased above 20% RH which suggest the bulk oxygen doesn't participate in the reaction and the reactions happen on the surface. The similar phenomenon was observed in the study of HNO<sub>3</sub> adsorption on oxide particles at wet condition (Goodman et al., 2000, 2001).

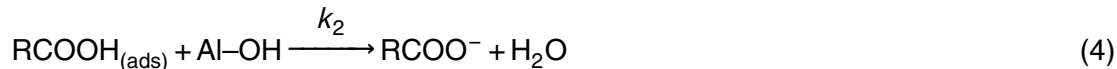
### 3.5 Mechanism

According to the analysis and the results of the experiments, there is a two step mechanism for the carboxylic acids –  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reaction.

In the first step (Eq. 3), RCOOH are physically adsorbed on the surface. It is unclear whether the adsorption involves a molecular precursor state, RCOOH<sub>(abs)</sub>, prior to the dissociation step in our experimental result as has been proposed for HNO<sub>3</sub> uptake on particles (Börensén et al., 2000).



In the second reaction step, adsorbed RCOOH and surface OH-groups form carboxylate and water, the latter partly adsorbed on the surface and the rest released into the gas phase.



The carboxylate ions and the loss of the proton reacts on the surface with surface hydroxyl groups to form adsorbed water which can be monitored by infrared spectroscopy.

Thus the reaction rate of carboxylate formation can be described by a general equation:

$$r = \frac{d[\text{HCOO}^-]}{dt} = k_2[\text{HCOOH}_{(ads)}] \quad (5)$$

When Al<sub>2</sub>O<sub>3</sub> was exposed to carboxylic acids, no obvious carboxylic acids were observed. This phenomenon implies that the carboxylic acids adsorbed on the surface is quickly transformed into carboxylates. Also according to the steady state approximation, for the intermediates adsorptive carboxylic acids on the surface, the generation

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rates are then equal to their consumption rate:

$$\frac{d[\text{RCOOH}_{(\text{ads})}]}{dt} = k_1[\text{RCOOH}_{(\text{g})}] - k_{-1}[\text{RCOOH}_{(\text{ads})}] - k_2[\text{RCOOH}_{(\text{ads})}] = 0 \quad (6)$$

Thus:

$$r = \frac{d[\text{RCOO}^-]}{dt} = \frac{k_1}{k_{-1} + k_2} [\text{RCOOH}_{(\text{g})}] = k[\text{RCOOH}_{(\text{g})}] \quad (7)$$

5 Where:

$$k = \frac{k_1}{k_{-1} + k_2} \quad (8)$$

Equation (7) shows that the reaction is first order. Therefore, the reaction order deduced from the proposed mechanism is well consistent with the experimental results shown in Fig. 5.

10 In the presence of adsorbed water, the adsorbed water layer provides another medium for the dissociation reaction and can be written as



#### 4 Conclusion and atmospheric implications

15 The reaction of three monocarboxylic acids on the surface of  $\alpha\text{-Al}_2\text{O}_3$  was investigated with DRIFTS. New absorption bands assigned to the formation of carboxylates were observed to grow when the surface was exposed to three carboxylic acids. The vibrational frequency at which the OCO band is formed, can give us information about the way it coordinates to the surface. Comparison of the calculated and experimental vibrational frequencies of adsorbed carboxylates establishes the bridging bidentate coordinated carboxylate structures. The uptake coefficients of organic acids on  $\alpha\text{-Al}_2\text{O}_3$  particles increase initially (RH < 20%) and then decrease with the increased

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RH (RH>20%), which was due to the effect of water on organic acids salvation, particles surface hydroxylation, and competition on reactive site. The loss of atmospheric organic acids due to reactive uptake on available mineral dust particles may be competitive with homogeneous loss pathways, especially in dusty urban and desertified environment.

The rate of removal of RCOOH by uptake onto mineral dust can be approximated in a simple model. We assume that the lifetime  $\tau$  for removal of RCOOH by dust is given by

$$\tau = \frac{4}{\gamma \bar{c} A} \quad (6)$$

where  $A$  is the dust surface area density in  $\text{cm}^2/\text{cm}^3$ ,  $\bar{c}$  is the mean molecular speed, and  $\gamma$  is the uptake coefficient. If we assume a conservatively low (i.e., background) dust loading of  $5 \mu\text{g}/\text{m}^3$  to a high dust loading of  $150 \mu\text{g}/\text{m}^3$  (Aymoz et al., 2004), we obtained  $A \approx 6 \times 10^{-7} \text{ cm}^2/\text{cm}^3$  to  $1.8 \times 10^{-5} \text{ cm}^2/\text{cm}^3$ . Our measured uptake coefficient are about  $2 \times 10^{-3}$ ,  $5 \times 10^{-3}$ , and  $3 \times 10^{-3}$ , for formic acid, acetic acid, and propionic acid, respectively, which lead to the corresponding lifetimes with respect to processing by dust of 50 min to 25 h, 23 min to 12 h, and 43 min to 21 h, respectively. The main removal mechanism for organic acid is thought to be rainout, as removal rates with respect to photolysis (Chebbim and Carrier, 1996) and reaction with OH (Butkovskaya et al., 2004; Singleton et al., 1989) are low. The lifetimes calculated from our result are shorter than the lifetimes of several days to weeks for removal by reaction with OH.

It can then be concluded from our experimental data and the calculated lifetimes that heterogeneous reactions of carboxylic acids on mineral dust should be included in atmospheric chemistry models if carboxylic acid levels are to be accurately predicted.

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**Table 1.** Summary of the reactive uptake coefficients obtained for the uptake of three organic acids on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles at  $T=300$  K using DRIFTS measurements.

Organic acid	$\gamma(\text{RCOOH})$ geometric	$\gamma(\text{RCOOH})$ BET	References
HCOOH	$(2.07 \pm 0.26) \times 10^{-3}$	$(2.37 \pm 0.30) \times 10^{-7}$	$(3 \pm 1) \times 10^{-3}$ <sup>a</sup> $1.7 \times 10^{-5}$ <sup>b</sup>
CH <sub>3</sub> COOH	$(5.00 \pm 0.69) \times 10^{-3}$	$(5.99 \pm 0.78) \times 10^{-7}$	$(2 \pm 1) \times 10^{-3}$ <sup>c</sup> $1.3 \times 10^{-5}$ <sup>b</sup>
CH <sub>3</sub> CH <sub>2</sub> COOH	$(3.04 \pm 0.63) \times 10^{-3}$	$(3.03 \pm 0.52) \times 10^{-7}$	$5.4 \times 10^{-5}$ <sup>b</sup>

<sup>a</sup> from Al-Hosney et al. (2005)

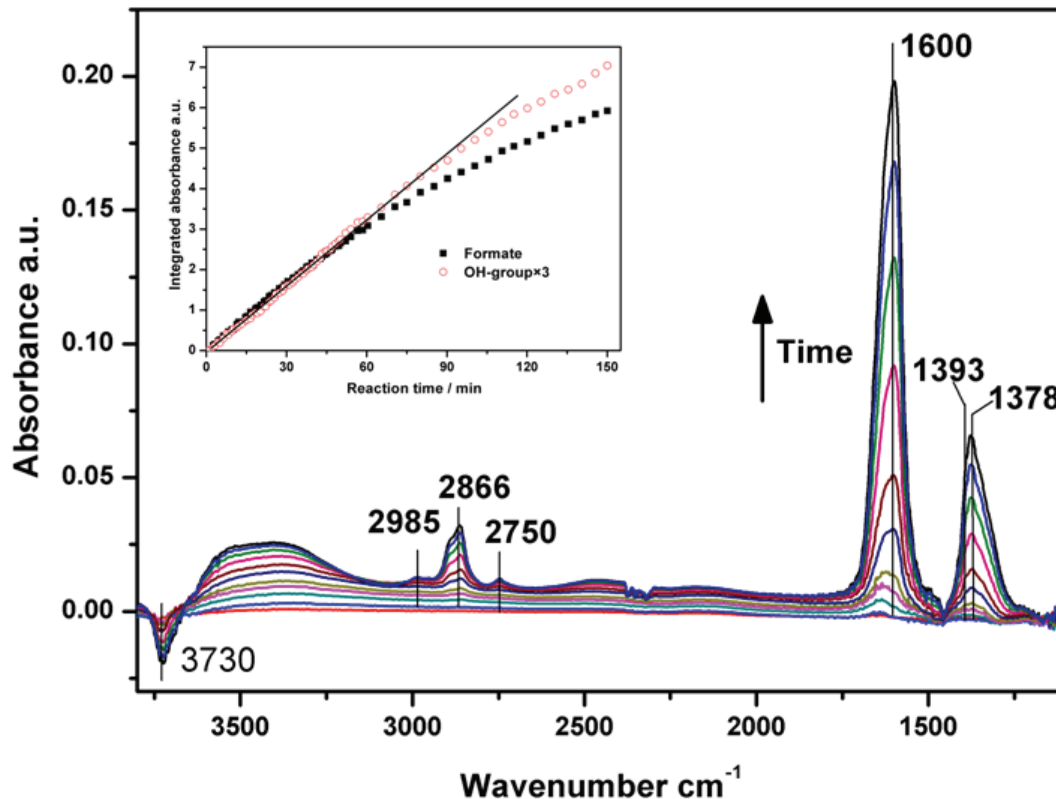
<sup>b</sup> from Carlos-Cuellar et al. (2003)

<sup>c</sup> from Hatch et al. (2007)

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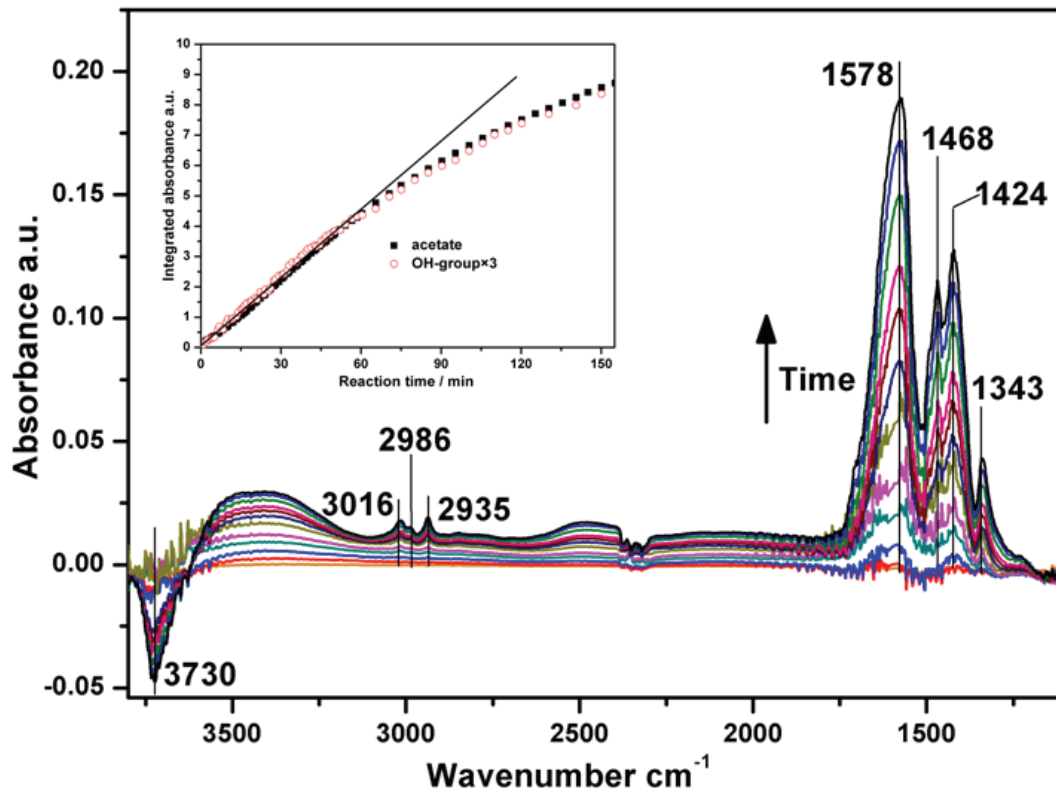
**Fig. 1.** Absorption spectra recorded during the reaction of HCOOH ( $[\text{HCOOH}]_0 = 1.23 \times 10^{14} \text{ molecules cm}^{-3}$ ) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles. The inset shows the temporal evolution of the integrated absorbance of the formate absorption band ( $1250\text{--}1450 \text{ cm}^{-1}$ ) and the OH absorption band ( $3600\text{--}3800 \text{ cm}^{-1}$ ).

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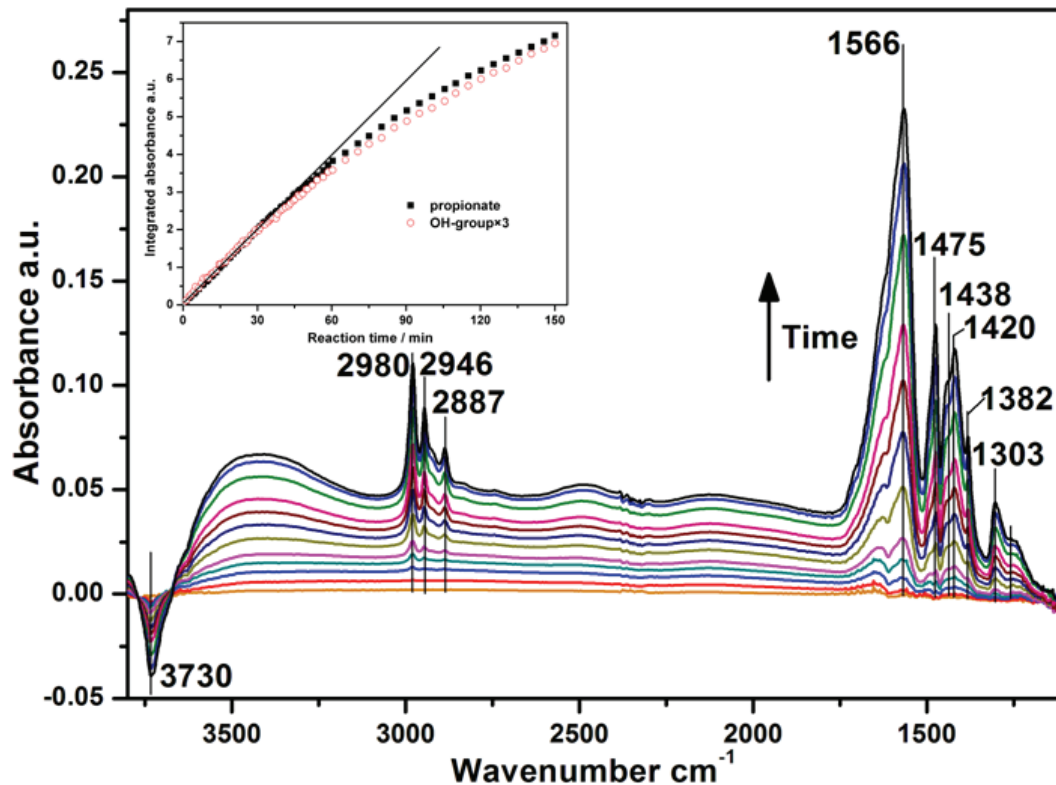


**Fig. 2.** Absorption spectra recorded during the reaction of  $\text{CH}_3\text{COOH}$  ( $[\text{CH}_3\text{COOH}]_0 = 1.23 \times 10^{14}$  molecules  $\text{cm}^{-3}$ ) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles. The inset shows the temporal evolution of the integrated absorbance of the acetate absorption band ( $1330$ – $1510$   $\text{cm}^{-1}$ ) and the OH absorption band ( $3600$ – $3800$   $\text{cm}^{-1}$ ).

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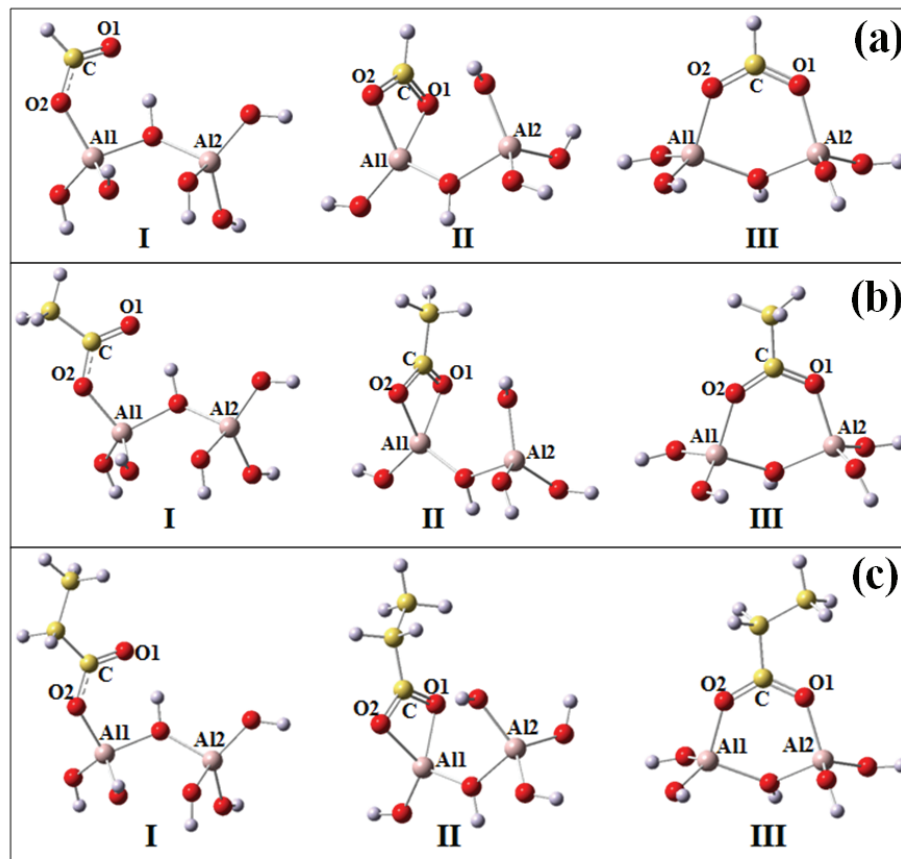


**Fig. 3.** Absorption spectra recorded during the reaction of  $\text{CH}_3\text{CH}_2\text{COOH}$  ( $[\text{CH}_3\text{COOH}]_0 = 1.23 \times 10^{14} \text{ molecules cm}^{-3}$ ) on  $\alpha\text{-Al}_2\text{O}_3$  particles. The inset shows the temporal evolution of the integrated absorbance of the propionate absorption band ( $1360\text{--}1510 \text{ cm}^{-1}$ ) and the OH absorption band ( $3600\text{--}3800 \text{ cm}^{-1}$ ).

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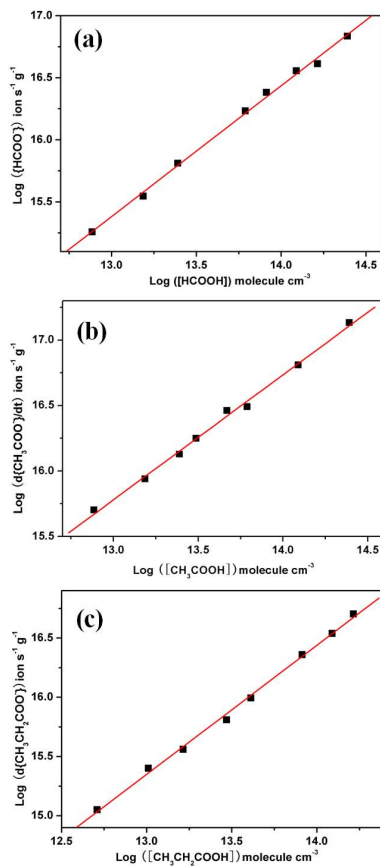


**Fig. 4.** Optimized structure of the computational models (I–III) for (a) formate, (b) acetate, and (c) propionate species on  $\alpha$ - $\text{Al}_2\text{O}_3$  surface. Red circles represent O atoms; yellow circles represent C atoms; pink circles represent Al atoms; gray circles represent H atoms.

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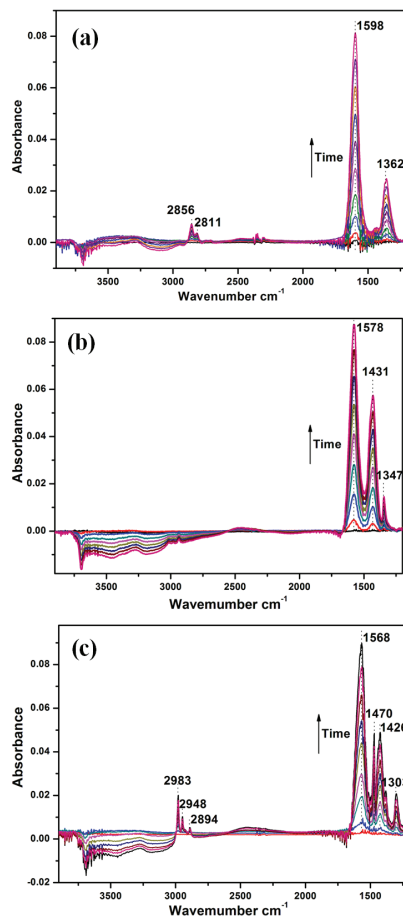


**Fig. 5.** Bilogarithmic plot of the rate of carboxylates formation as a function of the concentration of **(a)** HCOOH, **(b)** CH<sub>3</sub>COOH, and **(c)** CH<sub>3</sub>CH<sub>2</sub>COOH. The reaction order in HCOOH, CH<sub>3</sub>COOH, and CH<sub>3</sub>CH<sub>2</sub>COOH was determined from linear regression to be  $n=1.05\pm 0.02$ ,  $n=0.95\pm 0.03$ , and  $n=1.09\pm 0.02$ , respectively.

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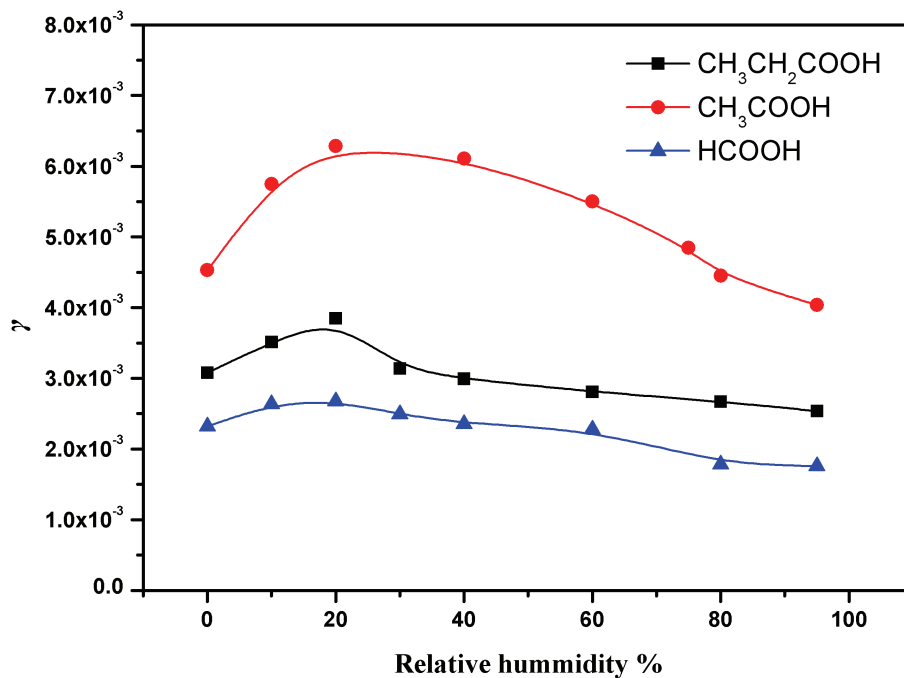


**Fig. 6.** Absorption spectra recorded during the reaction of (a) HCOOH, (b) CH<sub>3</sub>COOH and (c) CH<sub>3</sub>CH<sub>2</sub>COOH ( $[\text{RCOOH}]_0 = 1.23 \times 10^{14}$  molecules  $\text{cm}^{-3}$ ) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles at 30% RH.

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**Fig. 7.** Uptake coefficients for the reactions of alumina with carboxylic acids as a function of RH.

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