Interactive comment on "Heterogeneous chemistry of monocarboxylic acids on α–Al_2O_3 at ambient condition" by S. R. Tong et al.

We are grateful to the Referee #1 for the comments and the constructive suggestions to improve our manuscript. We have implemented all the comments and suggestions in the revised manuscript. Our point-to-point responses to the individual comments are as follows, we repeat the specific points raised by the reviewer in bold font, followed by our responses in italic font.

General Comments: The authors report on the identity of surface species resulting from exposure of formic, acetic and propanoic acid to α–Al_2O_3, both in the absence and the presence of water vapor, using Diffuse Reflectance FTIR spectroscopy (DRIFTS). In addition, uptake coefficients (gamma's) are calculated from the exposure of the acids to the ceramic substrate after quantitive desorption/elution of the adsorbates using ion chromatorgraphy and the rate law for the uptake of the acids was determined. The paper is longish and conveys rather little quantitative information, mostly collected in Table 1 and Figure 7. In the end, the results, essentially three uptake coefficients and information on spectra of adsorbed organic acids on a model substrate for mineral dust, do not justify the lengthy, and at times irrelevant discussion as well as the long list of references. On the other hand, certain quantitative aspects are not well reported such as the calibration of the surface concentration of the formate, acetate and propionate, and some data are outright missing such as the elements for constructing the log-log plots for the determination of the rate law for uptake of the acids (data displayed in Figure 5). The English is borderline at times (e.g. the use of plurals) and leaves the reader guessing at what the authors really meant to say (e.g. pg. 3955, lines 19 to 30 that leave me clueless).

Respond: *We greatly thank the reviewer #1.*

Firstly, according the referee suggestions, we have deleted some irrelevant sentences and references:

Page 3939 line 13: "It has been proposed in several modeling studies that mineral dust may provide reactive surfaces for trace atmospheric gases (Dentener et al., *1996)." was deleted in revised paper.*

Page 3940 line 26-28 was revised to be more simply: "Despite the results of field observations, few studies have been devoted on the heterogeneous chemistry of organic acids with various types of minerals. Most of them have been done at low pressure. In the previous studies,"

Page 3945 line 6-11 was revised as: "Fundamental vibrations of α-Al_2O_3 *are localized in the low frequency region around 1100* cm^{-1} *of the IR spectrum. Therefore, the spectral range extending from 1200-3900* cm^{-1} *was selected for all the spectra below."*

Page 3945 line 22-25 was revised as: "The band at 1378 cm^{-1} *and the shoulder at 1393* cm^{-1} *was associated with C–H in-plane bend and symmetric stretching mode (*$v_s(OCO)$*), respectively, in line with the assignment on other* Al_2O_3 *surfaces (Amenomiya, 1979; Chauvin et al., 1990)."*

Page 3946 line 9-10 was revised as: "We assigned the two peaks at 1343 cm^{-1} *and 1424* cm^{-1} *to C–H deformation (Chen and Bruce, 1995; Walmsley et al., 1981)."*

*Page 3947 line 1-10: "As seen from Fig. 3, a strong intensity band 2980*cm^{-1} *in the 2500–3000* cm^{-1} *region could be assigned to the antisymmetric* CH_3 *stretching modes (Kakihana and Akiyama, 1987). The band at 2946* cm^{-1} *can be related to the antisymmetric and symmetric* CH_2 *stretching modes. The remaining symmetric* CH_3 *stretching fundamental is observed only as a shoulder band at 2946* cm^{-1}*. The band at 1383* cm^{-1} *is assigned to symmetric* CH_3*–deformational mode. The band around 1475* cm^{-1} *is assigned to two antisymmetric* CH_3 *deformational overlap with one* CH_2 *scissoring vibrations. The band observed at 1303* cm^{-1} *is assigned to an in–plane* CH_2 *wagging mode, and the 1259* cm^{-1} *shoulder band is assigned to an out–of–phase* CH_2 *twisting mode." was revised to "The assignment of the other bands are shown in Table 1S."*

Page 3949 line 15-17: "As discussed in the Experimental section, calculated vibrational frequencies were scaled by the appropriate scaling factor of 0.9726." was deleted in revised paper.

Page 3950 line 15-17: "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." was deleted in revised paper.*

Page 3951 line 4-12 was revised as: "The surface products of the carboxylic acids react on α-Al_2O_3 *particles in this study were followed using the integrated absorbance–reaction behavior instead of K–M method which is known give rise to unacceptable uncertainty levels in quantitative experiments (Samuels et al., 2006). The carboxylate concentrations:"*

Also, we have revised some sentences and deleted some references in the revised paper, some of them will be stated in the following comments.

Secondly, there are some quantitative aspects are not well reported according to the referee. In our revised paper, we added the calibration of the surface concentration of three carboxylates on page 3951 line 9:"The surface products of the carboxylic acids react on α-Al_2O_3 *particles in this study were followed using the integrated absorbance–reaction behavior..., and the carboxylate concentrations:*

$$\text{(integrated absorbance)} \times f = \{RCOO^-\} \tag{1}$$

f was the conversion factor, and the calculated values for formate, acetate, and propionate are 2.58×10^{18} *ions/int.abs,* 2.94×10^{18} *ions/int.abs, and* 3.13×10^{18} *ions/int.abs, respectively."*

We also added three tables about the elements for constructing the log-log plots for the determination of the rate law for uptake of the acids in supplement:

Table S5 Summary of kinetic results from the reaction HCOOH and α-Al_2O_3

No.	[HCOOH]^a	R^b	R{$HCOO^-$}^{c}
1	0.77	0.0024	0.10
2	1.54	0.0047	0.20
3	2.46	0.0087	0.37
4	6.15	0.022	0.99
5	8.20	0.032	1.39
6	12.3	0.048	2.08

7	16.4	0.055	2.38
8	24.6	0.092	3.96

[a] In units of 10^{13} molecules cm^{-3};

[b] Observed rate (integrated absorbance units min^{-1}) of formate formation obtained from the integrated area of all absorptions in the region 1250-1450 cm^{-1}.

[c] Rate of formate in 10^{15} ions s^{-1} calculated from the integrated infrared absorption in the region 1250-1450 cm^{-1} the calibrated by ion chromatography analysis of the formate as described in the text.

Table S6 Summary of kinetic results from the reaction CH_3COOH and α-Al_2O_3

No.	$[CH_3COOH]^a$	R^b	$R\{CH_3COO^-\}^c$
1	0.77	0.0057	0.28
2	1.54	0.0098	0.48
3	2.46	0.015	0.74
4	3.08	0.020	0.98
5	4.67	0.033	1.60
6	6.15	0.035	1.70
7	12.3	0.073	3.56
8	24.6	0.150	7.49

[a] In units of 10^{13} molecules cm^{-3};

[b] Observed rate (integrated absorbance units min^{-1}) of acetate formation obtained from the integrated area of all absorptions in the region 1360-1510 cm^{-1}.

[c] Rate of acetate in 10^{15} ions s^{-1} calculated from the integrated infrared absorption in the region 1360-1510 cm^{-1} the calibrated by ion chromatography analysis of the acetate as described in the text.

Table S7 Summary of kinetic results from the reaction CH_3CH_2COOH and α-Al_2O_3

No.	$[CH_3CH_2COOH]^a$	R^b	$R\{CH_3CH_2COO^-\}^c$
1	0.51	0.0014	0.072
2	1.03	0.0031	0.16
3	1.64	0.0044	0.23
4	2.95	0.0078	0.41
5	4.1	0.012	0.62
6	8.2	0.028	1.45
7	12.3	0.042	2.19
8	16.4	0.067	3.47

[a] In units of 10^{13} molecules cm^{-3};

[b] Observed rate (integrated absorbance units min^{-1}) of propionate formation obtained from the integrated area of all absorptions in the region 1330-1510 cm^{-1}.

[c] Rate of propionate in 10^{15} ions s^{-1} calculated from the integrated infrared absorption in the region 1330-1510 cm^{-1} the calibrated by ion chromatography analysis of the propionate as described in the text.

Also, we added some explanation of these tables before page 3953 line 1: "Tables S5-7 summarizes the results of experiments carried out with carboxylic acids concentrations ranging from 7.7×10^{12} *to* 2.46×10^{14}*,* 7.7×10^{12} *to* 2.46×10^{14}*, and* 5.1×10^{12} *to* 1.64×10^{14} *for formic, acetic, and propionic acid, respectively. The rates, R, shown in Tables S5-7 are calculated from the linear initial rate of formation of carboxylates."*

Finally, we have revised some sentences may confuse the authors according the suggestion of referee on pages 3955 line 19-28: "The result in this paper is a little different from that of heterogeneous reactions between $CaCO_3$ *and carboxylic acid (Al-Hosney et al., 2005) at wet condition.* $CaCO_3$ *are reactive soluble particles (Goodman et al., 2001). And the heterogeneous reaction of acids on* $CaCO_3$ *is not* *limited to the surface, the bulk oxygen atoms participate in the reaction as well as the surface oxygen atoms, this participation is enhanced in the presence of water vapor. Nevertheless,* α-Al_2O_3 *are reactive insoluble particles. The uptake coefficients of carboxylic acids on* α-Al_2O_3 *decreased above 20% RH which suggest the bulk oxygen doesn't participate in the reaction and the reactions happen only on the surface. The similar phenomenon was observed in the study of* HNO_3 *adsorption on oxide particles at wet condition (Goodman et al., 2000; Goodman et al., 2001)."*

Comment 1: Under "Experimental": what is the gas-flow lifetime in the DRIFTS cell? What are the partial pressures or densities of the acids? What dose "dry" mean in terms of partial pressure of water vapor? Which tests did the authors perform to ensure complete elution of the adsorbed acids form the substrate? Did they perform a second elutin/sonication?

Respond: *We greatly thank the referee on the detailed information we should show in "Experimental".*

1. *Average residence time of gases inside the DRIFTS cell was approximately 2.5 s. A typical experiment lasted 180 min with continuous active gases in same concentration.*
2. *The organic acids were diluted by* N_2 *in a glass bottle and the partial pressures were monitored by a pressure transducer. The diluted system was connected all by Teflon tube. Then mass flow controllers were used to adjust the flux of diluted organic acids and* N_2 *to an expected concentration.*
3. N_2 *and* O_2 *were dehumidified by silica gel and molecular sieve before they flow in the system and the RH was less than 1% which was called dry condition.*
4. *For ensuring complete elution of the adsorbed acids form the substrate, we obtained the same mass of* α-Al_2O_3 *particles with same adsorbed organic acids, and then they were sonicated in 1.5 mL distilled water for 10 min, 20min, 30min, 40min, and 60 min, respectively. The filtered solution was analyzed using ion chromatography and the result showed that the adsorbed acids form on the surface can be completely elution in 20 min. The mass of the substrate are small (60 mg) and the solution of carboxylate is well which lead to the elution easily.*

In our revised paper, we added these information according to the suggestions of referee on page 3943 line 18: "All gases were mixed together before entering the reactor chamber, resulting in a total flow of 400 sccm synthetic air (21% O_2 and 79% N_2). N_2 and O_2 were dehumidified by silica gel and molecular sieve before they flow in the system, and the RH was less than 1% which was called dry condition. The organic acids were diluted by N_2 in a glass bottle and the partial pressures were monitored by absolute pressure transducer (MKS 627B range 0 to 1000 torr). Then mass flow controllers (Beijing Sevenstar electronics Co., LTD) were used to adjust the flux of diluted organic acids and N_2 to an expected concentration. Average residence time of gases inside the DRIFTS cell was approximately 2.5 s. A typical experiment lasted 180 min. And the DRIFTS cell is connected with other parts through Teflon tube."

Comment 2: What is "loosely-bounded water" (adsorbed on α–Al_2O_3)? What sets it apart from "strongly bounded water" (pg. 3945, line 2)? What is the basis of that distinction?

Respond: *We are sorry for this confusion. In our opinion, "loosely-bounded water" means the water adsorbed on α–Al_2O_3 which can be removed by heat. To avoid this confusion, we revised it on page 3945 line 1-2: "This treatment gives stable conditions and also removes adsorbed species such as adsorbed water from the surface."*

Comment 3: Regarding the measurement of the uptake coefficient using integrated band areas (absorbance) the authors never justify their choice of the symmetric stretch υ_{sym}(OCO) + δ(CH) or δ(CH_3) as opposed to taking the strong isolated carboxylate band corresponding to υ_{sym}(OCO). I would have expected that this isolated band (υ_{as}) was a much better marker for the surface concentratin of adsorbed organic acids than υ_{sym}+ δ(CH). Where (or what) is the snag (pg. 3950, lines 13 and 14)?

Respond: *The referee is right that the isolated band (υ_{as}) is certainly stronger than υ_{sym}+ δ(CH)* as seen f*rom the IR spectra. However, there is a shoulder (1640 cm^{-1}) on the υ_{as}, which belongs to H_2O. Therefore, we choose the absorbance of υ_{sym}+ δ(CH) to avoid this error. We added some explanation about this comment on page 3950 for* *reader to better understand it: "In the inset in Figs. 1–3, the integrated absorbance of 1250–1450 cm^{-1}, 1360–1510 cm^{-1}, and 1330–1510 cm^{-1} for formate, acetate, and propionate, respectively, formed during the reaction as functions of reaction time are shown. The obvious peak of* v_{as}*(OCO) were not used to avoid the error which from the vibration of water (a shoulder at 1640 cm^{-1})."*

Comment 4: The peak positions mentioned in the text on pg. 3946, lines 25 and following, do not match with the ones displayed in Figures 1, 2 and 3. In addition, propanoic acid does not have a CH group (line 27).

Respond: *We thank the referee's suggestion and sorry for this error. We revised these in our paper on page 3946 line 25 to 3947 line 3, page 3947 line 8, and page 3947 line 14-16, respectively: "The peaks at 1566, 1475 and 1420 cm^{-1} are assigned to* v_{as} *(OCO) and* v_s *(OCO) of OCO group, respectively. Due to* CH_2 *and* CH_3 *group of* CH_3CH_2COOH*, more bands are appeared at the region in 1200–1500 cm^{-1}. The peaks at 1259, 1303, 1382, 1420, and 1475 cm^{-1} are all assigned to the vibrational features of* CH_3 *and* CH_2 *groups (Yang et al., 2006), respectively. As seen from Fig. 3, a strong intensity band 2980cm^{-1} in the 2500–3000 cm^{-1} region could be assigned to the antisymmetric* CH_3 *stretching modes (Kakihana and Akiyama, 1987).", "The band around 1475 cm^{-1} is assigned to two antisymmetric* CH_3 *deformational overlap with one* CH_2 *scissoring vibrations.", and "The* v_{as} *frequency decreases as the number of carbon atoms increases from 1–3, finally reaching a minimum at 1566 cm^{-1} for propionate."*

Comment 5: The DRIFTS spectra displayed in Figures 1, 2 and 3 seem to show an isosbestic point close to the isolated (basic) OH-group, yet the mechanistic consequences in terms of the surface kinetics involving adsorbed H_2O are never mentioned in the discussion of the role of water vapor and adsorbed H_2O. The existence of isosbestic points is a strong mechanistic hint that the authors should exploit. Figure 6 presumably also shows isosbestic points, but the drawings are too small to inspect. The behavior of H_2O vapor on dry α–Al_2O_3 is never presented although, as the author rightly point out, H_2O is a reaction product resulting from the interaction of organic acids on the α–Al_2O_3 substrate (pg. 3948,

lines 6 to 17). I understand that the authors are unable to determine the uptake coefficient of H_2O using ion chromatography, however, DRIFTS spectra should yield valuable information when referenced against dry samples.

Respond: *We thank the referee's suggestion and added a figure in supplement:*

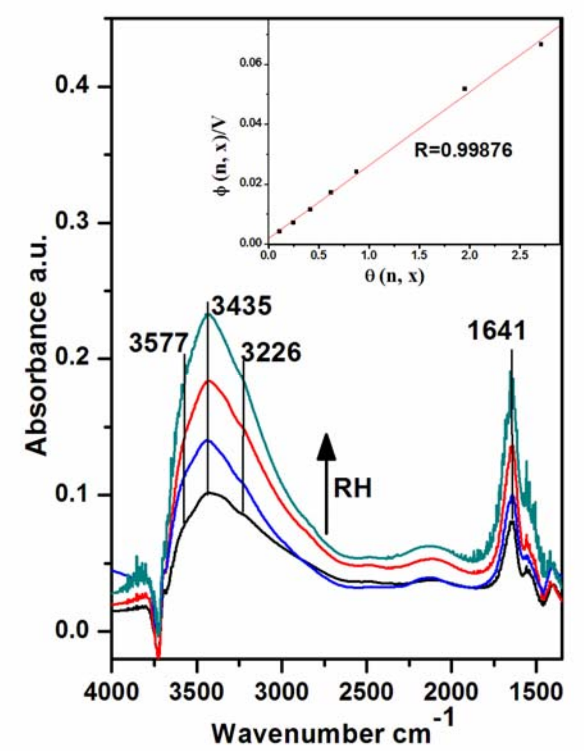


Figure S1 Absorption spectra for water vapour adsorption on dry α–Al_2O_3 powder at 300 K as a function of relative humidity 10%, 30%, 60%, and 80%, respectively. Each spectrum was referenced to the appropriate clean oxide spectrum prior to exposure to water vapour. The insets show the linearized BET fits for water adsorption on α–Al_2O_3 using the integrated absorbance of the OH stretch in 3000-3800 cm^{-1} region.

Also, we added some explanation of this figure on page 3955 line 7 before the paragraph: "The coverage of adsorbed water on α–Al_2O_3 *can be quantified by generating adsorption isotherm curves. The three parameter BET equation (Goodman, et al., 2001) was used to obtain a fit to the experimental data (Figure S1). The relative humidity, corresponding to one monolayers of water adsorbed on* α–Al_2O_3 *surface is calculated to be 19%. This result is similar to other investigations. Studies of water adsorption versus relative humidity on α–Al_2O_3 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). It can be also observed from Fig. S1 that there is a negative feature around 3730* cm^{-1}*. This feature is associated with the loss of OH groups on the surface due to hydrogen bonding to adsorbed water molecules (Al-Abadleh and Grassian, 2003). And there is a small peak at 3690* cm^{-1} *in low RH (10%) which may indicate the OH groups formed from water and* α*–*Al_2O_3*."*

Also, on page 3948 line 8: "heterogeneous reaction. This phenomenon is similar to water vapor adsorbed on dry α*–*Al_2O_3 *surface (Figure S1). When water from the vapor phase condenses onto an inert surface,"*

Comment 6: The authors are well advised to take the geometric surface rather than the BET area as the relevant surface parameter in the evaluation of the uptake coefficient (gamma, pg. 3951). Wagner et al. (Atmos. Chem. Phys. 8, 91-109 (2008)) have presented convincing arguments in their work for the use of the geometric rather than the BET or pore-diffusion corrected surface area. I take exception to the fact that the uptake coefficient measured by the disappearance of the trace gas on the one hand, and by accumulation on the substrate surface by adsorption, on the other hand, are fundamentally different (pg. 3952, line 21). In fact, it is the same process, and if the measurement is correct the results should agree. Also, the authors do not have experimental proof for the assumption of the non-validity of the presence of a non-uniform site distribution in this material. Although correct in principle, this cannot be the reason for the above-mentioned discrepancy between DRIFTS- and ion chromatography-derived gamma values. One should also note that Seisel et al. (PCCP 6, 5498-5508 (2004)) obtain much closer agreement between DRIFT-derived and Knudsen reactor-derived uptake coefficients for the interaction of HNO_3 **with** γ**-**Al_2O_3 **(gamma =** 7.7×10^{-3} **vs.** 1.3×10^{-1}**). I am surprised that this work has not been cited by the authors as it is formally very close to the present paper, both in methodology and structure. As a last remark I**

can offer the statement that the kinetic results (uptake coefficients measured in a Knudsen reactor) of Grassian and coworkers are notoriously unreliable because residual gas rather than molecular beam sampling has been systematically used. The monitoring of all molecules that are "sticky" and build up appreciable background in an all Stainless Steel vacuum chamber are liable to gross errors. Therefore, I suggest to compare the present DRIFTS results with kinetic work obtained using molecular beam sampling or other methods.

Respond: *We thank the referee's advice on using geometric surface and revised on our paper on page 3952 line 5-8: "The BET area may overestimate the surface area of the particles and thus underestimate the uptake coefficient (Goodman and Grassian, 2000). Furthermore, Wagner et al. (2008) have presented convincing arguments in their work for the use of the geometric rather than the BET area. Therefore, the uptake coefficients which were calculated by the geometric surface area are used to further discussed. The uptake coefficient for formic, acetic, and propionic acids are* 2.07×10^{-3}, 5.00×10^{-3}, *and* 3.04×10^{-3} *, respectively."*

According to the suggestion of referee, we revised the whole paragraph on page 3952 line 9-28: "A few studies concerned the uptake of organic acid on surfaces of materials, and most of them were deduced from experimental results using Knudsen Cell reactors (KC). 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* SO_2 *in the presence of* NO_2 *using the two different techniques, and found the difference between them are by a factor of around* 2×10^{4} *(BET ratios). Sabine et al (2004) showed that the reactive uptake coefficient of* HNO_3 *on particles determined by the loss of gaseous* HNO_3 *(KC) and the formation of surface species (DRIFTS) could be compared under similar experimental conditions (temperature, concentration, sample preparation). One important difference in the uptake coefficients from the two methods is that in the KC experiments an initial uptake coefficient has been determined, whereas reactive uptake coefficients are obtained from the DRIFTS experiments. Therefore, this paper* *represents the reactive uptake coefficients which are lower than initial uptake coefficients deduced by KC (Al-Hosney et al., 2005; Carlos-Cuellar et al., 2003). Otherwise, 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 Na-montmorillonite clay at 212 K; Al-Hosney et al. (2005) used* $CaCO_3$ *sample with a BET surface area of 1.4* m^2g^{-1}*, and both of their experimental conditions were at lower pressure."*

We thank the referee for suggesting us to compare the present DRIFTS results with kinetic work obtained using molecular beam sampling or other methods. However, there are a few researches on the heterogeneous reactions between organic acids and particles as we known. Therefore, we can only compare our results with the existed results.

Comment 7: Regarding the influence of adsorbed water upon adsorption of organic acids at elevated RH (pg. 3953/3954): What is the reference spectrum of H2O adsorption on "dry" α**–**Al_2O_3 **(see question above)? Are the bandwidths mentioned on line 25 (pg. 3953) homogeneously or inhomogeneously broadened in the dry vs. wet state? Pg. 3954, line 19: Where does the proton go after hydroxylation of the alumina surface? What is the experimental uncertainty of the individual points in Figure 7? It seems that except for acetic acid the "maximum" of gamma at 20% rh is located with a lot of imagination. There are many results in the literature showing a maximum in gamma anywhere between 20 and 40% rh, but present work is certainly not one of it.**

Respond: *The comment of "the reference spectrum of* H_2O *adsorption on dry* α*–*Al_2O_3*" has been responded above.*

The strongest bandwidths in the dry state are broadened than wet state which mainly due to the adsorbed water on surface. We have deleted these sentences to avoid misunderstanding on page 3953 line 25: We deleted the sentence "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 adsorption sites of slightly different energy.”
Experimental uncertainty of the individual points in Figure 7:

The adsorption of water on α-Al_2O_3 *surfaces has been studied with several techniques (Al-Abadleh and Grassian , 2003; Elam et al., 1998; Liu et al., 1998; Hass et al., 1998). It was shown that hydroxylation occurred on the reaction of water vapor on α-*Al_2O_3 *surface:*

$$Al_2O_3 \quad + \quad 3H_2O \quad \longrightarrow \quad 2Al(OH)_3$$

And the proton will connect with the surface oxygen atom after hydroxylation of the alumina surface.

References:

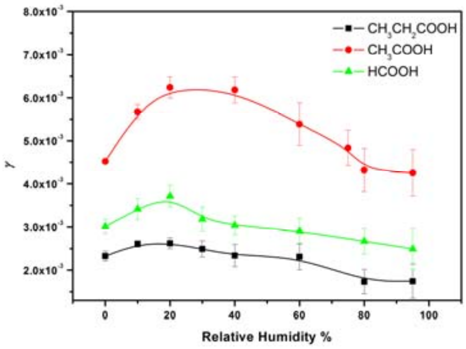
Al-Abadleh, H. A. and Grassian, V. H.: FT-IR study of water adsorption on alumium oxide surfaces, Langmuir, 19, 341-347, 2003.

Elam, J. W., Nelson, C. E., Cameron, M. A., Tolbert, M. A., George, S. M.: Adsorption of H2O on a single-crystal α-Al_2O_3 *(0001) surface, J. Phys. Chem. B, 102, 7008-7015, 1998.*

Hass, K. C., Schneider, W. F., Curioni, A., Andreoni, W.: The chemistry of water on alumina surfaces: reaction dynamics from first principles, Science, 282, 265-268, 1998.

Liu, P., Kendelewicz, T., Brown, G. E., Jr., Nelson, E. J., Chambers, S. A.: Reaction of water vapor with α-Al_2O_3 *(0001) and α-*Fe_2O_3 *(0001) surfaces: synchrotron X-ray photoemission studies and thermodynamic calculations. Surf. Sci., 417, 53-65, 1998.*

We revised the Figure 7 to show the experimental uncertainty of the individual points.



The result in Figure 7 is deduced from our experiment. The maximum of gamma at 20% rh is not very obvious which may be due to the weak impact of relative humidity. The difference between our result with reference have been explained on page 3955: "The result in this paper is a little different from that of heterogeneous reactions between $CaCO_3$ *and carboxylic acid (Al-Hosney et al., 2005) at wet condition.* $CaCO_3$ *are reactive soluble particles (Goodman et al., 2001). And the heterogeneous reaction of acids on* $CaCO_3$ *is not limited to the surface, the bulk oxygen atoms participate in the reaction as well as the surface oxygen atoms, this participation is enhanced in the presence of water vapor. Nevertheless,* α-Al_2O_3 *are reactive insoluble particles. The uptake coefficients of carboxylic acids on* α-Al_2O_3 *decreased above 20% RH which suggest the bulk oxygen doesn't participate in the reaction and the reactions happen only on the surface. The similar phenomenon was observed in the study of* HNO_3 *adsorption on oxide particles at wet condition (Goodman et al., 2000; Goodman et al., 2001)."*

Comment 8: Regarding the overall mechanism the authors venture into a field whose conclusions are not supported by their own data. So why talk about the existence of an intermediate that does not come up in the present work? Equations (7) and (8) offer little insight in the present context. Equation (4) is unbalanced.

Respond: *We thank the referee's comment on our mechanism and we are sorry for misunderstanding explanation of mechanism. We revised the mechanism on part 3.5: "According to the analysis and the results of the experiments, there is a one step mechanism for the carboxylic acids –* α–Al_2O_3 *reaction.*

$$RCOOH_{(g)} + Al{-}OH \longrightarrow RCOO{-}Al + H_2O \qquad (3)$$

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.

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

$$RCOOH_{(g)} + H_2O_{(a)} \longrightarrow H_3O^+_{(aq)} + RCOO^-_{(aq)} \qquad (4)$$ *"*

Comment 9: In Tables S2, S3 and S4 the two sets of calculated frequencies for each type of adsorbate is not labeled (one line presumably corresponds to the raw result, the second to the scaled one).

Respond: *We thank the referee's suggestion and added labels in Tables S2, S3 and S4 on supplement: "*[a] *Scaled calculated frequencies."*

Comment 10: There are many typographical errors throughout the manuscript: the authors should carefully go over the text and perhaps enlist the help of a native English speaker.

Respond: *Following the reviewer's suggestion, we checked the article carefully and revised some sentences such as:*

Page 3938 line 10: "Furthermore, the effect of various relative humid (RH) on this heterogeneous reactions was studied."

Page 3939 line 9: "There is also strong experimental evidence that indicates an important role of mineral dust in modifying atmospheric trace gas distributions."

Page 3940 line 7: "Moreover, the carboxylic acids are more polar and more surface active as they contain both a double-bonded oxygen and a single-bonded oxygen."

Page 3940 line 16: "Approximately 40% of the analyzed particles contained fragments associated with organic acids, such as formic and acetic acid."

Page 3940 line 26-29: "Despite the results of field observations, few studies have been devoted on the heterogeneous chemistry of organic acids with various types of minerals. Most of them have been done at low pressure. In the previous studies,"

Page 3942 line 20: "HCOOH (> 97%, Alfa Aesar), CH_3COOH *(> 99.7%, Alfa Aesar), and* CH_3CH_2COOH *(> 99%, Alfa Aesar) were diluted and mixed with* N_2 *(> 99.999%, Beijing Tailong Electronics Co., Ltd) before used, respectively."*

Page 3943 line 10: "The sample could be heated and the temperature of the sample cup could be measured by a thermocouple located directly underneath."

Page 3944 line 5: "adsortption" was revised to "adsorption".

Page 3945 line 12: "shows" was revised to "show".

Page 3945 line 21: "present" was revised to "presented".

Page 3946 line 28 to page 3947 line 1: "The peaks at 1259, 1303, 1382, 1420, and

1475 cm^{-1} *are assigned to the vibrational features of C–H of* CH_3 *and* CH_2 *groups (Yang et al., 2006), respectively."*

Page 3952 line 23: "Besides" was deleted in revised paper.

Page 3953 line 9: "indepecdent" was revised to "independent".

Page 3957 line 15: "with" was revised to "by".

Page 3958 line 1: "salvation" was revised to "solvation".

Also, we have revised some sentences in the article to improve the English.