Interactive comment on "Heterogeneous chemistry of monocarboxylic acids on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at ambient condition" by S. R. Tong et al.

We are grateful to the Referee #2 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 manuscript doesn't represent a substantial contribution to scientific progress, as the identity of species formed when monocarboxylic acids adsorb on alpha-alumina are currently known and have been reported by a number of researchers (see references in the paper). I would say the infrared data of propionic acids is the only new species reported, but even that, they mistakenly assign CH to propionic acid while propionic acid CH<sub>3</sub>CH<sub>2</sub>COOH doesn't have CH group (P 3946, line 27).

Respond: *We greatly thank the reviewer* #2.

Firstly, although some species have been reported, our results are based on different conditions (pressure and relative humidity). The previous works have been investigated at low pressure and by Knucen Cell reactor. In this paper, DRIFTS was used to detect the surface species in the heterogeneous reactions between organic acids and particles at ambient pressure. We hope to systematically gain insight into the molecular level details of the adsorption process how mineral dust sink these acids. There are some errors in our manuscript, we think the quality of this paper will be improved and these errors will be revised through the revised process with the help of referees.

Secondly, we are sorry for the confusion of assigning CH to propionic acid. In our opinion, the propionic acid have an extra  $CH_2$  group compared with acetic acid, and have two extra  $CH_3$  and  $CH_2$  groups compared with formic acid. The assigned bands all belong to C-H vibration in these groups. However, we didn't express our opinion exactly. We have revised these problems on our revised paper on Page 3946 line 26-28: "Due to  $CH_2$  and  $CH_3$  group of  $CH_3CH_2COOH$ , more bands are appeared at

## the region in $1200-1500 \text{ cm}^{-1}$ ."

Comment 1: The paper has many grammatical and typographical errors (pg 3958, line 1...organic acid "salvation"?!), not using "respectively" to separate given values (pg 3947, line 1), the overuse/misuse of "besides" (pg 3938, line 10, pg 3940, line 7) just to name a few. I would suggest the authors give the manuscript to an English speaking native to help them with proofreading.

Respond: We thank the referee's suggestion and revised some sentences in revised paper, 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<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  $N_2$  (> 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<sup>-1</sup> are assigned to the vibrational features 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 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."

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.

Comment 2: Initially in their reactions, the authors raised the temperature of their reaction chamber to 573 K for 3 hr "to remove…loosely bonded water" pg 3945 line 2. I would assume at this temperature, the surface hydroxyl groups will also be removed? If so, how are they explaining the negative loss of OH groups (pg 3945, line 19) from the DRIFTS spectra? Where are these OH groups from the surface coming from (assuming the surface is "clean" of OH after the heat treatment)?

Respond: The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface is covered by both isolated and vicinal AlOH groups at room temperature. Vicinal AlOH groups H bond to one another, broadening the O-H stretching band toward lower wavenumbers. The O-H stretch bond is also broadened by physisorbed H<sub>2</sub>O which bonds to surface AlOH via H bonds. Heating the sample drives off physisorbed H<sub>2</sub>O and desorbs some of the vicinal OH groups, the number of isolated AlOH groups is more than that of vicinal AlOH groups. The band isolated AlOH groups in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> appears at 3730 cm<sup>-1</sup> as seen in our result. Isolated AlOH groups is the reactive center on the surface (Morterra and Magnacca, Koretsky et al.). Many similar researches used this method in the treatment of particles (e. g. Börensen et al., Liu et al., Szayi et al.). We added references to support this treatment on our revised paper on page 3944 to 3945:" 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 synthetic air before the experiment was started. This treatment gives stable conditions and also removes adsorbed species such as adsorbed water, from the surface (Koretsky et al., 1997; Morterra and Magnacca, 1996; Börensen et al., 2000)."

References:

Azanyi, J., Kwak, Ja H., Chimentao, R. J., and Peden, C. H. F.: Effect of H2O on the adsorption of  $NO_2$  on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: an in situ FTIR/MS study, J. Phys. Chem. C, 111, 2661-2669, 2007.

Börensen, C., Kirchner, U., Scheer, V., Vogt, R., and Zellner, R.: Mechanism and kinetics of the reaction of NO<sub>2</sub> or HNO<sub>3</sub> with alumina as a mineral dust model compound, J. Phys. Chem. A, 104, 5036-5045, 2000.

Koretsky, C. M., Sverjensky, D. A., Salisbury, J. W., and D'Aria, D. M.: Detection of surface hydroxyl species on quartz,  $\gamma$ -alumina, and feldspars using diffuse reflectance infrared spectroscopy, 61, 2193-2210, 1997.

Liu, Y., Ma, Q., and He, H.: Comparative study of the effect of water on the heterogeneous reactions of carbonyl sulfide on the surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and MgO, Atmos. Chem. Phys., 9, 6273-6286, 2009.

Morerra, C. and Magnacca, G.: A case study: Surface chemistry and surface structure of catalytic aluminas, as studied by vibrational spectroscopy of adsorbed species, Catal. Today, 27, 497-532, 1996.

Comment 3: Peak assignments mentioned in the text are either not labeled in the figures (pg 3945, line 19, where is 3450 cm<sup>-1</sup> in Figure 1?; pg 3946 line 28, where is 1259 cm<sup>-1</sup> in Figure 3?) or are different (pg 3946, line 25, in text 1568 cm<sup>-1</sup>, in Figure 1566 cm<sup>-1</sup>). Also, which spectra are the authors discussing on pg 3948, line 6-12? For most of the article, the substrate is mentioned as only Alumina (Al<sub>2</sub>O<sub>3</sub>) instead of alpha-alumina (e.g. pg 3945, line 7 and line 13). Which one is it?

Respond: We thank the referee's suggestion and we have labeled these bands in our revised paper:



We are sorry for these errors and 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<sup>-1</sup> are assigned to  $v_{as}$  (OCO) and  $v_s$  (OCO) of OCO group, respectively. Due to CH<sub>2</sub> and CH<sub>3</sub> group of CH<sub>3</sub>CH<sub>2</sub>COOH, more bands are appeared at the region between 1200–1500 cm<sup>-1</sup>. The peaks at 1259, 1303, 1382, 1420, and 1475 cm<sup>-1</sup> are all assigned to 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 2980cm<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 around 1475 cm<sup>-1</sup> is assigned to two antisymmetric CH<sub>3</sub> deformational overlap with one CH<sub>2</sub> 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<sup>-1</sup> for propionate."

According to the referee's suggestion, we have check the whole paper carfully and revised  $Al_2O_3$  to  $\alpha$ - $Al_2O_3$  on page3943 line 20, page 3944 line 5, page 3945 line 7, page 3946 line 25, page 3951 line 10, page 3953 line 10, page 3953 line 22, page 3954 line 8, page 3954 line 13, 3955 line 4, page 3955 line 20 and line 25, page 3956 line 18, Table 1S in supplement.

Comment 4: The authors make a comment concerning their mechanism (pg 3956, line 4) on the uncertainty of the presence of the physisorbed HCOOH species on the surface, there exists a peak close to the reported  $v(C=O) \sim 1700$  cm-1, that shifts to lower wavenumbers to the vs(OCO) peak for the formate. They also use the absence of the CH peak at 1100 cm-1 to deduce absence of adsorbed formic acid. How did they do when the fundamental vibrations of alpha alumina absorb strongly at that wavelength and below (pg 3945, line 7)? Furthermore, where is

## proof of the existence of the intermediate that they mention in their mechanism?

Respond: As the referee's comment, there exists a peak close to ~1700 cm<sup>-1</sup>, but the peak is at 1640 cm<sup>-1</sup> which belongs to the vibration of water (pg 3948 line 6-18 in original manuscript). Furthermore, we have gained a spectra of molecular HCOOH adsorbed on  $Al_2O_3$  and the v(C=O) is at 1730 cm<sup>-1</sup>. The discrepancy of 1730 and 1640 cm<sup>-1</sup> is 90 cm<sup>-1</sup> which indicate the inexistence of v(C=O).

According to the suggestion of referee, 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  $-\alpha -Al_2O_3$  reaction.

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

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

Comment 5: In Table 1, they are comparing uptake coefficient of the organic acids to values reported in literature. The uptake coefficient taken from reference "a" is formic acid on calcium carbonate; I don't see how this value is used to compare to the uptake coefficient on alpha-alumina (not mentioned in the reference). Furthermore, the value they use to compare formic acid uptake on alpha Alumina (reference b) is not the formic acid (HCOOH) value, but is actually a formaldehyde (HCOH) uptake coefficient, as reported by Carlos-Cuellar et al 2003. I think this is a serious mistake on their part that needs to be explained.

Respond: We admit that the substrate of our research and reference "a" is different. However, there are a few researches gave the uptake coefficients on the heterogeneous reactions between organic acids and particles as we known. We can only compare our results with these known reports.

The referee mentioned reference b is wrong. We are sorry for this error, in fact, the

reference b and c are exchanged in our prooftype, the reference b was corresponded to the research of "Hatch et al. (2007)", and the reference c was corresponded to the research of "Carlos-Cuellar et al. (2003)", respectively. Calos-Cuellar et al. (2003) reported uptake kinetics of three volatile organic compounds (acetic acid, formaldehyde, and methanol, respectively) on particles. We use the uptake coefficient of acetic acid on  $\alpha$ –Al<sub>2</sub>O<sub>3</sub> particles of their report to compare with our result. We have revised this error on page 3967 Table 1: "<sup>b</sup> from Hatch et al. (2007)." and "<sup>c</sup> from Carlos-Cuellar et al. (2003)."

Comment 6: How do they acquire integrated absorbance of any of the peak if the baselines keep changing as a function of concentration of organic acid? This is not mentioned in the experimental section. How are they measuring the integrated absorbance of the negative OH peak and comparing it to the positive growth of the organic species on the surface. Again no explanation is given in the experimental section.

We thank the referee's suggestion on improving our experimental section. Respond: The integrated absorbance of the peaks were obtained by using Series program in OMINC software. A set of spectral data collected during a series experiment, and we can acquire series absorbance integrate in experimental time by setting the integrated and baseline regions which are the same range in our experiment. We use the same method for measuring the integrated absorbance of the absolute value of negative OH peak. Because of the integrated absorbance are smaller for negative OH peak than organic species (Figures 1-3), we amplified all the value of OH peak integrated absorbance three times in these figures for been better compared with that of surface species. According the referee's suggestion, we added some explanation on page 3943 line 5-8 and page 3950 line 22-23: "The flow cell in DRIFTS optics has been described in detail elsewhere (Li et al., 2006). The spectra were recorded at a resolution of 4 cm<sup>-1</sup>, and 100 scans were usually averaged for each spectrum corresponding to a time resolution of 40 s. All the spectral data were automatically collected by Series program in OMINC software in the experimental time. Simultaneously, integrated absorbance of researched peaks for every spectrum are

obtained by this program." And "In addition, the absolute values of the integrated absorption band due to surface OH–groups ( $3600-3800 \text{ cm}^{-1}$ ) are shown in the inset of Figs. 1–3. For better comparing the OH peak and surface species, the integrated absorption bands of OH-group were amplified for three times."

Comment 7: No standard deviations in experimental data are reported in Figures 5 and 7. In figure 7 (pg 3974), the label is "hummidity" instead of "humidity".

Respond: We thank the referee's suggestion, the standard deviations in Figures 5 (a), (b), and (c) are 3.26%, 3.27%, and 3.37%, respectively. We added the RSD of these figures in revised paper.

We revised the Figure 7 to show the RSD of the individual points.





Respond: Because of the different experimental conditions, the reported values are different from ours. However, there are a few researches gave the uptake coefficients on the heterogeneous reactions between organic acids and particles as we known. We can only compare our results with these known reports. And all of the known uptake coefficients of organic acids adsorbed on particles were given in the Table 1. We think this will be convenient for the readers to compare our results with others. Furthermore, we discussed the reasons why these differences were existed.