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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous chemistry of monocarboxylic acids on alpha;-Al₂O₃ at ambient condition" *by* S. R. Tong et al.

Anonymous Referee #2

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Tong et al present experiments conducted to identify species formed when alpha-alumina is exposed to three different monocarboxylic acids and measure their reactive uptake coefficients as a function of changing relative humidity. Infrared data were taken by Diffuse Reflectance FTIR spectroscopy (DRIFTS). Ion chromatography was used to determine the uptake coefficients as function of relative humidity and results were compared to literature values.

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 acid is the only new species reported, but even that, they mistakenly assign CH to Propionic acid while Propionic acid CH3CH2COOH doesn't have CH group (p 3946, line 27).

I also have some comments and a few questions concerning the manuscript:

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.

2. Initially in their reactions, the authors raised the temperature of their reaction chamber to 573K for 3 hr "to remove...loosely bounded 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)?

3. Peak assignments mentioned in the text are either not labeled in the figures (pg 3945, line 19, where is 3450 cm-1 in Figure 1?; pg 3946 line 28, where is 1259 cm-1 in Figure 3?) or are different (pg 3946, line 25, in text 1568 cm-1, in Figure 1566 cm-1). 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 (Al2O3) instead of alpha-alumina (e.g. pg 3945, line 7 and line 13). Which one is it?

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. If they look closely to their DRIFTS spectra, the initial exposure on the gases to 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

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they do that 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?

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.

6. How do they acquire integrated absorbance of any of the peaks 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 iy to the positive growth of the organic species on the surface. Again no explanation is given in the experimental section

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”.

Like I mentioned earlier, the manuscript doesn’t add anything new to the scope of the scientific knowledge. The authors used DRIFTS and Ion chromatography to basically repeat what others have done. If their values don’t agree with other literature values as they report (pg 3952, line 21 and 23) why are they comparing values in Table 1? In any case, I would recommend major revision to the manuscript to account for some of these and other reviewers comments.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3937, 2010.