Atmos. Chem. Phys. Discuss., 10, C563–C566, 2010
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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 #1

Received and published: 12 March 2010

The authors report on the identity of surface species resulting from exposure of formic, acetic and propanoic acid to alpha-Al2O3, 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 quantitative desorption/elution of the adsorbates using ion chromatography 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 propanoate, 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). Apart from the English I would like the authors to respond to the following questions in some detail to the benefit of the reader:

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

- What is “loosely-bounded water” (adsorbed on alpha-Al2O3)? What sets it apart from “strongly-bounded water (pg. 3945, line 2)? What is the basis of that distinction?

- Regarding the measurement of the uptake coefficient using integrated band areas (absorbance) the authors never justify their choice of the symmetric stretch nue/sym(OCO) + delta(CH) or delta(CH3) as opposed to taking the strong isolated carboxylate band corresponding to nue/as(OCO). I would have expected that this isolated band (nue/as) was a much better marker for the surface concentration of adsorbed organic acids than nue/sym + delta(CH). Where (or what) is the snag (pg. 3950, lines 13 and 14)?

- 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 (line27).

- 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 H2O are never mentioned in the discussion of the role of water vapor and adsorbed H2O. 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 H2O vapor on dry alpha-Al2O3 is never presented although, as the authors rightly point out, H2O is a reaction product resulting from the interaction of organic acids on the alpha-Al2O3 substrate (pg. 3948, lines 6 to 17. I understand that the authors are unable to determine the uptake coefficient of H2O using ion chromatography, however, DRIFTS spectra should yield valuable information when referenced against dry samples.

- 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 HNO3 with gamma-Al2O3 (gamma = 7.7x10-3 vs. 1.3x10-1). 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.

- 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” alpha-Al2O3 (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 the present work is certainly not one of it.

- 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.

- 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).

- 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.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C563/2010/acpd-10-C563-2010-supplement.pdf

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