Studies on the reactivity of solid oxides and fluorides by means of *Pulse*TA®

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The great potential of the *Pulse*TA® (PTA) method [1,2] was demonstrated in a series of studies on the reactivity of differently prepared (e.g. via sol-gel syntheses) oxides, fluorides, chlorofluorides including surfacially silane-modified aluminium chlorofluoride (ACF-*Sil*) [3]. Interesting chemical information was gained regarding the distinction between reaction pathways, the adsorption properties, and even the simulation of the formation conditions of an industrially employed fluorination catalyst.

Various gases and liquids such as $CO_{2(g)}$, $HF_{(g)}$, $CH_3F_{(g)}$, $CH_2F_{2(g)}$, $CH_3OH_{(l)}$, $H_2O_{(l)}$, Ph-$CF_{3(l)}$, and others were successfully applied both as probe molecules or reaction partners.

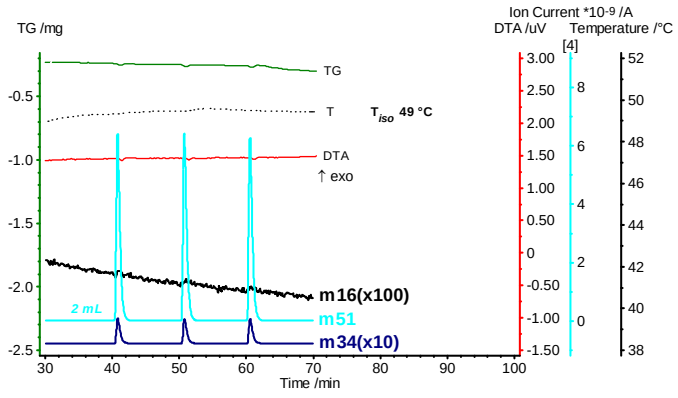

Figure 1. TA-MS curves of a sample-free isothermal (50 °C) *PulseTA* experiment in Ar serving as a blank measurement. 2 μL gaseous CH_2F_2 were injected. The IC curves for the mass numbers m/z = 16 (CH_4^+), 34 (CH_3F^+), and 51 (CHF_2^+) are monitored. The IC curves are shifted for a better legibility.

Either the commercially available PTA box or, for injections of liquids, a heated (115°C) injector placed into the gas supply system between PTA box and TA cell were utilized.

Figure 1 shows a suitable blank experiment for investigating the dehydrofluorination reactions of hydrofluorocarbons (HFC's) under participation of ACF-*Sil*. It clearly reveals that the injected educt gas difluoromethane, CH_2F_2, represented by the mass number m/z = 51(CHF_2^+), contains no methane (m16), but, unfortunately, already a certain amount of monofluoromethane, CH_3F (m34), both being possible products of the reaction investigated. Accordingly, the question whether a supposed partial dehydro-fluorination occurs or not, can be answered not by the absence or presence of selected fragments, but only via changes of the surface area ratio of the relevant IC signals, in this case of the ratio $A_{m16} : A_{m34}$. This and further illustrative evaluation examples will be elucidated.

[1] M. Maciejewski, C.A. Müller, R. Tschan, W.-D. Emmerich, A. Baiker, *Thermochim. Acta* **295**, 1997,167-82.
[2] M. Feist, *ChemTexts* (2015) 1:8 DOI: 10.1007/s40828-015-0008-y
[3] M. Feist, M. Ahrens, A. Siwek, Th. Braun, E. Kemnitz, *J. Therm. Anal. Calor.* (2015) in press.