Silane-modified aluminium chlorofluoride - Various ways of qualitative evaluation of *Pulse*TA measurements

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Aluminium chlorofluoride (ACF), studied under various aspects since ca. 20 years [1], exhibits an extraordinary Lewis acidity and, as a consequence, promising catalytic properties [2]. A recent topic is its surfacial modification by interaction with triethyl silane, Et_3SiH [3]. The formed product ACF-*Sil* was successfully used in solution as a hydrodefluorination catalyst which was assigned to surface-bound entities of the type $ACF\cdots H\text{-}SiEt_3$. These entities exhibit a considerable silylium character and were proposed to initiate the C-F activation step for small hydrofluorocarbon (HFC) molecules via the formation of thermodynamically stable Si-F bonds thus mediating the hydrodefluorination reaction.

Taking into account recent experiences with Pulse Thermal Analysis (*Pulse*TA®, PTA [4]) as a powerful tool for investigating the adsorption behaviour of metal fluorides [5], it was challenging to follow not only the modification process of solid ACF itself via the injection of the silane, Et_3SiH, onto ACF, but afterwards the reaction of the modified ACF-*Sil* with HFC's as well.

The first approach for evaluating PTA curves is the usual one, *i.e.* trying to determine a surface loading together with an inspection of shape and area of the DTA signals. As expected here, the interaction of ACF with the silane could be followed quantitatively and confirms the basic idea of a surface modification of ACF. Exclusively chemisorption with a surface coverage of 0.13 mol% Et_3SiH was established. The comparably low value is in line with preparative results.

Interestingly enough, the ion current (IC) curves, *e.g.* m/z=19(F^+), demonstrate that during the ACF modification no HF formation, indicating side reactions, occurs.

Another important aspect for evaluating PTA curves is, of course, to answer the question whether a given species is formed or not. This qualitative approach can consist of:

(a) Following the appearance of distinct mass numbers for proving the formation of a species. This was successful in the case of CH_2F_2 interacting with ACF-*Sil* where m/z=16(CH_4^+) undoubtedly proved the formation of methane. The same is true for the mass number m/z=91($C_6H_5\text{-}CH_2^+$) representing toluene with its 100% peak (M-1) which proved a successful dehydrofluorination reaction of ACF-*Sil* with pulsed α,α,α-Trifluorotoluene.

(b) Comparing the integral surface area ratio for the signals of appropriate mass numbers in order to conclude on the formation of a species. The aim is to separate an additional contribution to the intensity of a given mass number thus indicating its formation. This is complicated, especially if the total concentrations are low.

This second way allowed for proving the methane formation in the reaction of CH_3F with ACF-*Sil*. The injected educt is represented by m/z=34(CH_3F^+), but the educt contains a small amount of the presumed product CH_4 already. Consequently, only an inspection of the area ratio evolution for A_{m34}/A_{m16}, *i.e.* the educt/product ratio, yielded satisfying results.

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