Adsorption phenomena *vs*. carrier gas influence - Recent experiences by employing *Pulse*TA®

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The *Pulse*TA® (PTA) method [1] was employed for characterizing the acid and basic surface sites of a series of sol gel - prepared alkaline earth fluorides such as high-surface *HS*-MF_2 (M=Ca, Mg, Ba) and others. The simultaneous occurrence of acid and basic sites causes the promising catalytic acitivity of some of these fluorides. The adsorption behaviour *vs.* CO_2 revealed to be a semiquantitative measure for the catalytic activity [2].

Additional information was obtained by interrupting the usually applied sequence of injected $CO_{2(g)}$ pulses by one or more pulses of $H_2O_{(l)}$ through a heated (115°C) injector. This led to the *in situ* generation of basic sites on the fluoride surface which indeed represented OH groups rather than simply adsorbed water molecules.

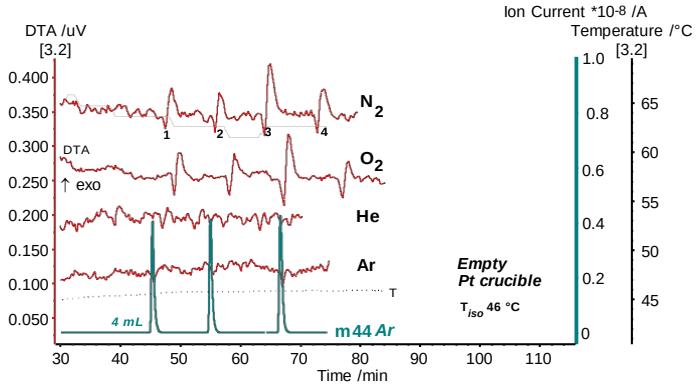

Figure 1 DTA traces for injections of 4 mL CO_2 (Pulses 1,2, and 4) and 7 mL CO_2 (Pulse 3) into a N_2 purge gas stream compared with an identical sequence for O_2. Into He and Ar only three injections were performed. For a better clarity, the IC curve for m/z=44(CO_2^+) only for the Ar case is monitored.

Usually, nitrogen as a carrier gas is preferred for characterizing fluorides: both m/z = 19 (F^+) *and* 20 (HF^+) can be followed, whereas in argon the m/z = 20 (HF^+, Ar^{++}) (!) is less appropriate. Unexpectedly, in the case of sample-free injections of CO_2 pulses into different carrier gases an influence on the DTA traces faking adsorption signals was established (Figure 1).

No meaningful explanation of the origins of the observed phenomenon could be found. Neither a comparison of the gas densities nor of the thermal conductivities of the different carrier gases (N_2, O_2, Ar, He) yielded a convincing interpretation. If the exothermicity with the endothermal pre-effect would represent a mixing phenomenon, which is uncertain, then probably the ideal character of Ar and He could explain the absence of any exothermicity.

[1] M. Maciejewski, C.A. Müller, R. Tschan, W.-D. Emmerich, A. Baiker, *Thermochim. Acta* **295**, 1997,167-82.
[2] M. Feist, K. Teinz, S. Robles Manuel, E. Kemnitz, *Thermochim. Acta* **524,** 2011, 170-8.