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# Characterization of surfacial basic sites of sol gel-prepared alkaline earth fluorides by means of *PulseTA*<sup>®</sup>

### M. Feist, K. Teinz, S. Robles Manuel, E. Kemnitz\*

Institute of Chemistry, Humboldt University, Brook-Taylor-Strasse 2, D – 12489 Berlin, Germany

### ARTICLE INFO

### ABSTRACT

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*Keywords:* Alkaline earth fluorides CO<sub>2</sub> adsorption Pulse Thermal Analysis The  $CO_2$  adsorption properties of a series of different sol gel-prepared metal fluorides of the alkaline earth row and aluminium, among them two mixed (doped) metal fluorides was investigated by applying Pulse Thermal Analysis. The alkaline earth fluorides, which exhibit nanoscopic properties, have not only acid, but basic sites as well. For the first time, these basic sites have been characterized by the exothermicity of the first  $CO_2$  injection pulse. If the basicity is weak or absent, the alternating injection of water can generate OH groups at the surface of the fluorides. They mostly act as basic sites and allow a stronger differentiation of the basic properties, but the formed OH groups can exhibit an acid character as well. The impact of OH groups can affect a different influence on the sorption properties of the solids: the adsorption ability vs.  $CO_2$  can be promoted, suppressed or remain unaffected.

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### 1. Introduction

Sol gel-prepared metal fluorides such as the recently described nano-sized, mesoporous high-surface aluminium fluoride (HS-AlF<sub>3</sub>) [1] exhibit extraordinary catalytic properties which were attributed to its extreme Lewis acidity [2]. Analogously prepared alkaline earth fluorides show interesting properties as well. Here, not only the catalytic activity, but the potential to act as precursors for forming thin layers is noteworthy. These coatings, e.g. deposited on glassy surfaces, form stable transparent films of the metal fluoride and can markedly change the optical properties of the coated material [3].

In case of the alkaline earth fluorides, not only acidic, but basic sites as well have been discussed to be responsible for several catalytic applications. For the first time, the simultaneous occurrence of acid and basic sites on a fluoride surface was evidenced in a detailed spectroscopic study of sol gel-prepared MgF<sub>2</sub> [4]. A structural model for the coordinative interaction of probe molecules such as pyrrole or chloroform with the MgF<sub>2</sub> surface has been proposed thus explaining strong Lewis acidity parallel to weak basicity: Lewis basic electron pairs of the chlorine atoms in CHCl<sub>3</sub> donate into Lewis acid Mg sites whereas neighbouring fluorine atoms of CHCl<sub>3</sub>. This kind of interaction with surfacial acid–base pairs does not occur with pyrrole due to another molecule geometry. It can be adsorbed, however, alternatively on acid or basic sites and, in the case of MgF<sub>2</sub>, gave the first clear evidence for basic sites on the surface.

The remarkable catalytic activity of such a sol gel-prepared MgF<sub>2</sub> was tested in various important reactions [4]. BaF<sub>2</sub>, similarly prepared exhibits a catalytic potential as well that might be related to basic properties. It is able, for instance, to promote "basic" reactions such as the hydrogen abstraction resulting in the formation of carbanions, e.g. as observed in the system BaF<sub>2</sub>/BaCl<sub>0.7</sub>F<sub>1.3</sub>/3-chloro-1,1,1,3-tetrafluorobutane where a 100% selectivity towards dehydrochlorination (instead of dehydrofluorination) of the halocarbon was established [5].

In this concern, it was interesting for us to extend the experimental possibilities to characterize and, if possible, to quantify the basic properties of the substances investigated. Usually, this can be achieved by means of IR spectroscopy with various probe molecules. CO, CO<sub>2</sub>, and pyridine are widely used to compare the Lewis acidity of oxides [6] and fluorides [7], but CO and CO<sub>2</sub> are also suitable to characterize basic sites. CO<sub>2</sub> has been used for weakly basic metal oxides and for basic hydroxides, whereas CO was applied for highly basic sites on metal oxides activated at higher temperatures [8].

The aim of the present work is to study how *Pulse Thermal Analysis*<sup>®</sup> [9–11] reputed to be a promising tool both in solid state chemistry and adsorption studies, can contribute to this issue. Primarily, the interaction of  $CO_2$  with the fluoride surface was studied. In case of weak or absent interaction, a procedure was tested that was supposed to generate basic sites *in situ* by interrupting the  $CO_2$  injections by water pulses.

<sup>\*</sup> Corresponding author. Tel.: +49 30 2093 7555; fax: +49 30 2093 7277. *E-mail addresses:* feistm@chemie.hu-berlin.de (M. Feist),

katharina.teinz.1@chemie.hu-berlin.de (K. Teinz), saul.robles@chemie.hu-berlin.de (S.R. Manuel), erhard.kemnitz@chemie.hu-berlin.de (E. Kemnitz).

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#### Table 1

Caloric results of the first exothermal interaction step of the CO<sub>2</sub> adsorption for a series of sol gel-prepared metal fluorides obtained in PTA experiments with injections of CO<sub>2</sub> and/or H<sub>2</sub>O.

Phase	Synthesis <sup>a</sup> and PTA treatment <sup>b</sup>	Sample mass <sup>c</sup> (mg)	M(g/mol)	$S_{\text{BET}}^{d}$ (m <sup>2</sup> /g)	$A_{\rm DTA}^{\rm e}$ ( $\mu Vs/m^2$ )	$-\Delta H$ (J/mol)
$MgF_2$	SG	15.31	62.31	10	5.1	14
CaF <sub>2</sub>	SG	9.28	78.08	250	26.3	1663
SrF <sub>2</sub>	SG	12.71	125.62	115	1.0	52
BaF <sub>2</sub>	SG	30.92	175.33	20	3.9	123
BaF <sub>2</sub>	SG wet	36.51	175.33	60	11.3	209
BaF <sub>2</sub>	$SG + H_2O$	30.92	175.33	20	8.4	224
BaCl <sub>0.7</sub> F <sub>1.3</sub>	+H <sub>2</sub> O	31.10	186.85	60	2.2	222
BaF <sub>2</sub>	cryst.	28.51	175.33	-	-	-
BaOHF	SG	26.50	173.34	30	72.1	3631
$MgBaCrF_{2+x}$	$SG + H_2O$	25.29	75.16	240	7.3	158
$MgAlF_{3+x}$	SG	16.62	-	200	1.4	-
HS-AlF <sub>3</sub>	SG	12.12	83.98	200	-	-

<sup>a</sup> SG: sol-gel route; wet: exposed to humid air.

<sup>b</sup> +H<sub>2</sub>O means: CO<sub>2</sub> injections (2 mL) interrupted by injection of 2 µL liquid water (see explanations in the text).

<sup>c</sup> Sample mass for the PTA run (corrected by the mass loss during the thermal pretreatment).

<sup>d</sup> Surface determination after the thermal pretreatment (cf. Exptl. part).

<sup>e</sup> Exothermal partial area for the first injection pulse normalized to the surface.

### 2. Experimental

### 2.1. Synthesis

Eleven different sol gel-prepared metal fluorides of the alkaline earth row and aluminium, among them two mixed (doped) metal fluorides, and one commercially available fluoride (crystalline BaF<sub>2</sub>, Aldrich) were investigated (Table 1).

The binary alkaline earth metal fluorides  $MF_2$  (M = Mg, Ca, Sr, Ba) were synthesized by the *fluorolytic* sol gel synthesis [1–3] via the metal alkoxides; they will be denominated in the text as MF<sub>2</sub>-SG. The alkoxides were dissolved or suspended in tetrahydrofuran (Mg) or methanol (Ca, Sr, Ba) followed by addition of a stoichiometric amount of hydrogen fluoride (Solvay), dissolved in methanol. After fifteen hours, dry xerogels were obtained by evaporating the solvents from the wet gel under vacuum ( $\sim 5 \times 10^{-3}$  mbar) at 100 °C for at least 2 h. Magnesium ethoxide (Aldrich, 98%) and calcium methoxide (Aldrich, 97%) were used as received, whereas strontium and barium methoxides were prepared by reacting the respective metal with methanol excess (Sr metal, Aldrich, granular 99%; Ba metal rods, Aldrich, 99+%). Methanol (Aldrich, 99%), isopropanol (Aldrich, 99%), and tetrahydrofuran (Aldrich, 99%) were dried according to standard procedures before use. All operations were carried out under inert conditions.

 $BaCl_{0.7}F_{1.3}$  was obtained by treating  $BaF_2$ -SG with 3-chloro-1,1,1,3-tetrafluorobutane at 200 °C [5].

Ba(OH)F was synthesized by modifying the fluorolytic sol gel synthesis which started with the formation of the methanolate, Ba(OMe)<sub>2</sub>, by dissolving 0.0164 mol Ba in 0.25 L MeOH. After storing the methanolate solution 4 h for ageing, an *understoichiometric* amount of an anhydrous methanolic solution of HF was added (0.0128 mol HF). After further 2 h 0.02 mol of distilled water were added and the resulting sol stored for further ageing overnight. This ageing process is necessary to obtain transparent sols later yielding nanosized particles [2,3]. The subsequent vacuum drying step transformed the sol into a gel; it was stored under argon until use; its final composition was Ba(OH)<sub>0.97</sub>F<sub>1.03</sub>.

Doped alkaline earth fluorides such as  $Mg_{0.8}Ba_{0.05}Cr_{0.15}F_{2.16}$  were obtained from three separately prepared solutions: magnesium methanolate, barium methanolate, both prepared by dissolving the metal in dry MeOH, and the chromium precursor solution obtained by *in situ* reduction of an acid solution of  $CrO_3$  with methanol. To obtain 6g of the solid  $Mg_{0.8}Ba_{0.05}Cr_{0.15}F_{2.16}$ , a methanolic solution of  $0.063 \text{ mol } Mg(OMe)_2$  and  $0.004 \text{ mol } Ba(OMe)_2$  in a final volume of 200 mL (i.e. the required stoichiometric ratio  $Mg_{1.8}Ba$ ) was prepared and then subjected to a two-step

fluorination. At first, the half of the stoichiometrically required amount of methanolic HF solution (total: 0.07 mol HF, i.e. 0.063 mol HF/Mg+0.004 mol HF/Ba) was added. Then, the chromium precursor solution containing the necessary amount to host 15 mol% Cr (0.012 mol) in the final solid was added. Simultaneously, the remaining quantity of methanolic HF solution (0.423 mol HF) to achieve the total fluorination of all precursors (i.e. Mg, Ba and Cr) was added under stirring. The formed sol was treated as described above.

MgAlF<sub>3+x</sub>-SG, a sol gel-prepared MgF<sub>2</sub> hosting 15 mol% of HS-AlF<sub>3</sub>, was obtained analogously. Even for this high AlF<sub>3</sub> content, its amorphicity indicates the formation of a real solid solution and, therefore, corresponds to the structure model proposed precedingly [12].

*HS*-AlF<sub>3</sub>, was obtained as reported elsewhere [1] via an isopropanol-based sol gel process using commercially available aluminium isopropoxide (Aldrich, >98%).

Both the BET surface determination procedure (see below) and the formation (or post-fluorination) process effect a decrease of the solid surface due to the applied thermal treatment. In order to enlighten this influence, in the case of Ba(OH)F, a thermal treatment of 1 h N<sub>2</sub> flow at 120 °C, then held at 160 °C for 20 min was applied. This simulated to some extent the formation process required for activating the solid, but excluded a chlorine impact into the solid.

### 2.2. Surface determination

A Micromeritics ASAP 2010 apparatus was used to record the  $N_2$  adsorption isotherms at 77 K. Prior to each measurement, the samples were degassed at  $4\times 10^{-3}$  Torr and  $120\,^\circ\text{C}$  overnight. The surface area was calculated according to the BET method.

### 2.3. Thermal analysis

The Pulse Thermal Analysis<sup>®</sup> (PTA) experiments have been performed using a thermoanalyzer Netzsch STA 409 C Skimmer<sup>®</sup>. It is equipped with a Balzers QMG 421 mass spectrometer, enabling on line-coupled TA–MS measurements, and a commercial PTA box. The latter was used to perform the injection of permanent gases such as CO<sub>2</sub> (preferentially 2 mL). The self-made liquid injection unit comprises a heated (120 °C), septum-tightened GC injector implemented in the heated stainless steel tube of the gas supply system. It is placed between the PTA box and the thermobalance. A microliter GC syringe was used to perform the liquid injection (preferentially 2  $\mu$ L). The average volume error both for the CO<sub>2</sub> and H<sub>2</sub>O injection amounts to 6%. The dead time between injection and MS detection amounted to 60–70 s for the given flow conditions. The thermoanalytical curves (T, DTA, TG, DTG) were recorded together with the ionic current (IC) curves in the multiple ion detection (MID) mode [13,14]. A DTA–TG sample carrier system with platinum crucibles (baker, 0.8 mL) and Pt/PtRh10 thermocouples was used. Samples of 10–35 mg each were measured versus empty reference crucible. A constant purge gas flow of 70 mL/min argon 5.0 (Air Liquide), a constant heating rate of 10 K/min or a isothermal regime with  $T_{\rm iso} \sim 50$  °C were applied. The raw data have been evaluated utilizing the manufacturer's software *Proteus*<sup>®</sup> (v. 4.3) and *Quadstar*<sup>®</sup> 422 (v. 6.02) without further data treatment, e.g. such as smoothing.

### 3. Results and discussion

### 3.1. The PulseTA<sup>®</sup> method

The essential features and advantages of the *PulseTA*<sup>®</sup> (PTA) technique [9,10] for the investigation of the adsorption properties of solid metal fluorides together with the preconditions for a meaningful experimental approach were described precedingly [15]. Earlier results obtained by employing PTA in the solid state chemistry of fluorides were reported in [16,17]. Certain limitations related to the constructive design of the coupled TA device have to be taken into account if one utilizes a skimmer-coupled instead of a capillary-coupled TA-MS system [18,19], but they are less important in the case of isothermal measurements such as preferentially undertaken in this study.

### 3.2. The behaviour of binary fluorides $MF_2$ -SG characterized by $CO_2$ adsorption

The DTA and TG curve shapes as well as the integral peak areas of the relevant IC signals for injections into the empty apparatus must be known before starting a PTA investigation (Fig. 1). The water injection is a part of this blank experiment, but the intention behind will be explained in more details below. Both the  $CO_2$ and the water injections show neither a buoyancy effect (e.g. as a little TG jump) nor a DTA effect that would indicate an interaction with sample holder parts or any adsorption at the inner surface (constant integral IC peak area for all injections). This is important as the expected DTA effects for the adsorption by the fluorides to be investigated are supposed to be rather small. The very weak and rapidly disappearing TG effect caused by the water injection must be understood as a buoyancy effect. As the water vapour density is lower than the Ar density, the temporary mass gain is positive.

### 3.2.1. Two qualitatively different kinds of interaction

Fig. 2 shows the comparison of the adsorption behaviour of MgF<sub>2</sub>-SG and CaF<sub>2</sub>-SG. For MgF<sub>2</sub>-SG, three very small exothermal DTA effects followed by broader endothermal post-effects indicate weak adsorption which is immediately followed by desorption in the carrier gas flow. This is typical for very weak physisorption and fully corresponds to the curve shape features already discussed in [15] for the case of methanol adsorption by fluorides. In the case of CaF<sub>2</sub>-SG, however, the first CO<sub>2</sub> pulse effects chemisorption being clearly expressed in the TG step ( $\Delta m = 50 \mu$ g). It is accompanied by a strong exothermal DTA effect without an endothermal post-effect. Obviously, the injected amount of CO<sub>2</sub> is sufficient to cover the available surface as the following injections show the features of weak physisorption only.

The two phases exhibit a qualitatively different adsorption behaviour.  $CaF_2$ -SG weakly chemisorbs (0.84 mol% CO<sub>2</sub> coverage,

0.17 mmol/g), whereas MgF<sub>2</sub>-SG shows only physisorption. This would be in line with the usual regard that Ca is more basic than Mg, but would not confirm an extraordinary position of MgF<sub>2</sub>-SG in this substance group (e.g. the simultaneous occurrence of acid and basic sites, cf. introduction, [4]).

As no detailed explanation is obvious, we tried to generate basic sites *in situ* and expected a stronger differentiation of the  $CO_2$  adsorption behaviour.<sup>1</sup>

## 3.2.2. Three different types of influencing the adsorption properties by OH groups—in situ generation of basic sites by water injection

Fig. 3 illustrates the first of three different kinds of influencing the CO<sub>2</sub> adsorption behaviour of the fluoride phases as a result of in situ-induced basic sites. In the case of the partly fluorideexchanged  $BaCl_{0.7}F_{1.3}$ , the two first CO<sub>2</sub> injections 1 and 2 show the DTA and TG features of physisorption especially clearly: exothermal adsorption followed by the endothermal post-effect without a remaining mass gain. The subsequent water pulse 3 causes a large exothermal DTA effect together with a distinct TG step of +50 µg in the typical form of chemisorption. This clearly proves that the water injection enforced the formation of OH groups, possibly together with adsorbed water, at the fluoride surface. The following next two CO<sub>2</sub> injections 4 and 5 indicate a markedly weaker interaction as can be deduced from the change in the exothermal partial peak area: it decreases by 42%. The following repeated injection of 2 µL water (pulse 6) reinforces this effect markedly: the DTA partial peak area for the CO<sub>2</sub> pulse 7 is decreased by 85% and has completely disappeared at pulse 8 (surface area values in Table 2). This means that surfacially created OH groups suppress the CO<sub>2</sub> adsorption. A further conclusion might be that in this case the generated OH groups belong to the Brønsted acid type and do not act as basic sites. As CO<sub>2</sub> usually reacts with basic sites, a reduction of its interaction with the surface must be due to an acid character of the created sites

A positive effect on the CO<sub>2</sub> adsorption that can be reached by OH deposition is illustrated by the results for BaF<sub>2</sub>-SG in Fig. 4. The area of the exothermal partial peak for pulse 4 increases by 18% compared with the area for pulse 1 thus indicating a greater exothermicity of the CO<sub>2</sub> adsorption (Table 2). Two interpretations seem possible: (a) If the CO<sub>2</sub> adsorption is stronger, the OH groups formed on BaF<sub>2</sub>-SG must have basic character which would correspond to the original intention of our experiments, but the behaviour is different to that observed for BaCl<sub>0.7</sub>F<sub>1.3</sub>. (b) The basic behaviour can also be related to the presence of carbonate ions on the surface of BaF<sub>2</sub>-SG.<sup>2</sup>

Finally, no influence at all was established in the case of crystalline  $BaF_2$  (Fig. 5) which was exactly as expected. The water pulse 3 does not change the  $CO_2$  adsorption tendency at all. Interestingly enough, the water injection affects an exothermal signal indicating hereby a slight physisorption of water by the solid as easily understandable, but surely no deposition of OH groups. In case of the empty apparatus, on the other hand (cf. Fig. 1), no signal at all could be recorded. This observation supports our assumption that in cases where the water pulse effects a real mass gain (cf. Figs. 3 and 4) this mass gain in fact represents the formation of OH groups, whereas temporarily adsorbed water is easily removed in

<sup>&</sup>lt;sup>1</sup> Here a range of 0.8  $\mu$ V instead of 0.4  $\mu$ V.

 $<sup>^2\,</sup>$  Even if BaF<sub>2</sub>-SG was handled and investigated under inert conditions, it cannot be fully excluded that during the crucible positioning on the sample holder (60–70 s) a certain water uptake occurs which would yield the carbonate formation via the reaction with H<sub>2</sub>O and CO<sub>2</sub>. Wet BaF<sub>2</sub>-SG, for instance, exhibit weak IR absorptions of carbonate.



**Fig. 1.** Blank experiment for preparing the *PulseTA* measurements with CO<sub>2</sub> injections. The sequence of CO<sub>2</sub> pulses interrupted by one pulse of liquid water is represented by the IC signals for the mass numbers m44 (CO<sub>2</sub><sup>+</sup>), dotted line, and 18 (H<sub>2</sub>O<sup>+</sup>). Neither a DTA effect nor a detectable mass gain can be recorded (further explanations in the text).



**Fig. 2.** TA-MS curves for *PulseTA* experiments on pre-heated (240 °C in Ar) MgF<sub>2</sub>-SG (15.31 mg) and CaF<sub>2</sub>-SG (9.28 mg) in Ar. For a better legibility only the IC curve (dotted line) for the CO<sub>2</sub> injections onto CaF<sub>2</sub>-SG are shown (TG and DTA curves labelled with the suffixes Ca or Mg, respectively). Note the two times less-sensitive DTA scaling.



Fig. 3. PTA curves of pre-treated (250°C; Ar) BaCl<sub>0.7</sub>F<sub>1.3</sub> (31.10 mg) in Ar, isothermally at 49°C with alternating CO<sub>2</sub> and water injections to generate basic sites in situ.

### Table 2

Experimental data obtained from the PTA curves of different sol gel-prepared fluorides (cf. Table 1 mass change,  $\Delta m$  (µg); exothermal partial peak area,  $A_{DTA}$  (µV s); integral IC peak area for the indicated mass number, e.g.  $A_{m44}$  (E-7As). If the experimental curves are shown in the text, the figure number is given respectively.

Phase		Fig.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
MgF <sub>2</sub> -SG	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$	2,7	- 0.78 5.4	- 0.53 5.5	- 0.50 5.4											
CaF <sub>2</sub> -SG	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$	2	50 73.2 2.8	10 4.8 2.8	0 3.7 2.7	10 3.0 2.7										
SrF <sub>2</sub> -SG	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$		- 1.4 5.4	- 1.9 5.3	- 1.9 5.3											
BaF <sub>2</sub> -SG	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$		10 2.4 2.3	- 2.1 2.5	- 2.2 2.4											
BaF <sub>2</sub> -SG wet	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$		10 24.7 3.0	20 8.5 3.1	10 7.2 3.1	-10 6.3 3.0	- 5.9 2.9	- 5.5 2.9	-10 6.6 2.8							
$BaF_2$ -SG + $H_2O$	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$ $A_{ m m18}$	4	10 4.4 2.8 -	10 4.3 2.7 -	60 101 - 1.7	- 5.2 2.8 -	- 5.4 2.7 -	- 5.6 2.7 -								
BaCl <sub>0.7</sub> F <sub>1,3</sub>	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$ $A_{ m m18}$	3	- 4.1 3.2 -	- 4.2 3.3 -	50 109 - 1.7	- 2.4 3.2 -	- 1.4 3.2 -	50 94 - 1.8	- 0.6 3.2 -	- 0 3.3 -						
BaF <sub>2</sub> cryst.	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$ $A_{ m m18}$	5	- 0 1.8 -	- 0 1.9 -	- 10.8 - 1.6	- 0 1.9 -	- 0 1.9 -									
Ba(OH)F-SG	$\Delta m$ A <sub>DTA</sub> A <sub>m44</sub>	6	40 72.1 6.0	50 70.2 6.4	30 67.2 6.3	40 66.4 6.4	30 63.8 6.4	40 63.9 6.6	30 55.8 6.3	20 51.7 6.3	20 44.8 6.1	0 32.8 6.3	0 18.8 6.3	0 15.1 6.7	0 11.5 6.5	0 11.2 6.2
MgBaCrF <sub>2+x</sub> -SG+H <sub>2</sub> O	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$ $A_{ m m18}$		- 7.3 6.2 -	10 5.4 6.6 -	- 6.2 6.4 -	50 111 - 4.3	- 4.7 6.6 -	- 4.2 6.3 -	- 4.2 6.2 -							
$MgAlF_{3+x}$ -SG	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$	7	- 4.6 5.2	- 4.5 5.2	- 4.6 5.2											
HS-AlF <sub>3</sub>	$\Delta m$ $A_{ m DTA}$ $A_{ m m44}$	7	- - 5.5	- - 5.5	- - 5.4											



Fig. 4. PTA curves of pre-treated (240 °C; Ar) BaF<sub>2</sub>-SG (30.66 mg) in Ar, isothermally at 49 °C with CO<sub>2</sub> injections interrupted by a water pulse.



Fig. 5. PTA curves of pre-treated (240°C; Ar) BaF<sub>2</sub>-cryst (28.51 mg) in Ar, isothermally at 49°C with CO<sub>2</sub> injections interrupted by a water pulse. Note the qualitatively different features for the water pulse compared with Fig. 1.

the dry carrier gas flow thus representing a simple "drying" of the solid (cf. Figs. 1 and 5).

It should be mentioned here that one of the substituted systems,  $Mg_{0.8}Ba_{0.05}Cr_{0.15}F_{2.16}$ , that revealed to be slightly more acidic, behaves in the same way, i.e. no influence of the impacted OH groups was observed (see Section 3.4 below).

### 3.2.3. The influence of mechanochemical activation

Mechanochemical treatment is known to be an interesting tool both for inducing particular properties to solids and, generally, for opening unusual reaction pathways as reported previously for fluorides [20] and alumogels [21]. Bearing in mind this potential of mechanochemical activation, we tried to change the surface properties of inactive phases such as the crystalline BaF<sub>2</sub> described above. Unexpectedly, the obtained measuring results are practically identical with those depicted in Fig. 5. The activation reached during two hours of so-called high-energy milling in a planetary mill is not sufficient to enforce a greater adsorption capacity for CO<sub>2</sub>.

### 3.3. The behaviour of Ba(OH)F

The results reported above prove the original assumption that (a) it is possible to generate basic sites probably in the form of OH groups at the surface of nanoscopic metal fluorides, and (b) that a differentiation of the basic properties seems possible as well. The absolute amount of induced basic sites, however, is certainly very small for this procedure. It was interesting, therefore, to investigate a phase with a molar amount of available OH groups which, on the other hand, would be similar to the substance class investigated and chemically far enough from systems such as CaO being known for a rather aggressive uptake of water<sup>3</sup> (and of CO<sub>2</sub> [22] accelerated by water [23]). Such a kind of phase was found in the case of Ba(OH)F-SG. Fig. 6 shows that the experimental curves of the PTA measurement which was performed in an analogous way as described for the preceding systems exhibit a quite different shape. Practically all of the nine first CO<sub>2</sub> injections effect a certain persisting mass gain (i.e. chemisorption), but a slight desorption flank in the TG step is always observable and becomes predominant with the 10th pulse. The CO<sub>2</sub> uptake is finished now, and one calculates a surface coverage of 4.3 mol% CO<sub>2</sub> (0.26 mmol/g). This is a remarkably high value and is of the same order of magnitude as observed for the MeOH adsorption of HS-AlF<sub>3</sub> (7.7 mol%) [15].

### 3.4. The behaviour of mixed systems $M^{a}M^{b}F_{2}$ -SG. Substitution by Cr, Mg, or HS-AlF<sub>3</sub>

Substitutions in the halide sublattice were exemplarily studied in the case of the formation product BaCl<sub>0.7</sub>F<sub>1.3</sub>, but the results were disappointing as the formed OH groups seemed to exhibit acid character (see Section 3.2.2). It was interesting, therefore, to investigate the consequences of substitutions at the metal positions. Firstly, the effect of Mg doping was tested as a basicity-promoting influence whereby the idea was supposed basing on recently reported results [4]. We compared the behaviour of the extremely Lewis acidic compound HS-AlF<sub>3</sub> with that of MgAlF<sub>3+x</sub>-SG representing a</sub> solid solution of HS-AlF<sub>3</sub> in MgF<sub>2</sub>. The experimental curves depicted in Fig. 7 can be interpreted in terms of a basicity impact due to the presence of Mg sites.

At a first glance, the "integral" Mg effect is not very strong here, but if one considers the extreme Lewis acidity of the 15% guest phase HS-AlF<sub>3</sub>, than the resulting basicity, being unambiguously due to the Mg sites, is noteworthy. It can be completely suppressed, however, if a certain amount of chromium is additionally contained in the phase. The case of

As the pulses for each of the three different measurements are set at different times, for a better legibility only the CO<sub>2</sub> injections for MgAlF<sub>3+x</sub>-SG are shown. The injection times for the trace</sub> DTA-MgAl are 30, 39, 48 min, respectively.

Mg<sub>0.8</sub>Ba<sub>0.05</sub>Cr<sub>0.15</sub>F<sub>2.16</sub> is an example. The PTA measurements analogously performed as described above (including intermediate water injections such as presented in Figs. 3-5) did not show any change in the adsorption capacity. Obviously, the basicity created by the Mg sites is overcompensated by the acidity-promoting effect of Cr<sup>3+</sup> which is in line with earlier findings [12].

Summarizing the results obtained for the differently mixed systems, it is concluded that the Mg doping indeed generates basic sites which clearly reinforce the CO<sub>2</sub> adsorption ability. Even a phase, which contains an extremely Lewis acid component such as HS-AlF<sub>3</sub> (not showing any CO<sub>2</sub> adsorption at all) in the form of a solid solution, finally exhibits a weak CO<sub>2</sub> adsorption. This proves

<sup>&</sup>lt;sup>3</sup> The applicability of the PTA method for studying the interaction of a solid with injected water was tested with freshly prepared CaO (calcination of Ca(OH)2 in a preceding heating run) both with CO and CO<sub>2</sub>.



Fig. 6. PTA curves of pre-treated (170°C; Ar) Ba(OH)F-SG (26.50 mg) in Ar, isothermally at 51°C. The total mass gain reached with pulse 10 or 11 amounts to 0.3 mg; as a consequence, the DTA peak areas decrease down to the physisorption level.

the extraordinary basic Mg influence enabling a successful competition with an extremely strong Lewis acid, but chromium doping can overcompensate this effect.

### 3.5. Attempts for quantification

With the results presented above, one can conclude that the most diversified information about the adsorptive interaction of the injected gas with the solid is contained in the DTA and TG signals for the first step of interaction, i.e. the first injection pulse. Generally, it was quite surprising to establish to which extent especially the shape and the intensity of the DTA signals allowed to deduce very fine details of the adsorption process. This observation, on the other hand, is in line with the known advantages of a classical DTA sample holder with its high thermal resistance (other than a heat flow measuring unit) that produces higher sensitivity, but lower resolu-

tion of thermal effects [24]. Furthermore, the isothermal measuring mode was an additional promoting factor to get comparably precise insights.

As a consequence, we focused the quantification attempts on the first pulses and compared the exothermal partial areas of the DTA peaks. Fig. 5 exemplarily demonstrates the integration procedure. A compilation of all peak area values is given in Table 2. The enthalpy values were obtained according to the well-established procedure for the caloric calibration of TA devices, i.e. by comparing the integral peak area of the DTA peaks (in  $\mu$ Vs) of a calibration substance (here the melting point of benzoic acic ( $\Delta_F H = -147.3 \text{ J/g}$ or -17.34 kJ/mol [25]) close to the measuring temperature of the isothermal runs ( $\sim$ 50 °C) with that of the substance investigated. These  $\Delta H$  values not representing an equilibrium state cannot be regarded as real adsorption enthalpies, but have orientational character as a measure for comparison. Their order of magnitude,



Fig. 7. PTA curves of pre-treated (240°C; Ar) HS-AlF<sub>3</sub> (12.12 mg) (Al), MgF<sub>2</sub>-SG (15.31 mg) (Mg), and MgAlF<sub>3+x</sub>-SG (16.62 mg) (MgAl) in Ar, isothermally at 49°C.

however, correctly reflect the differences between physisorption and real chemisorption (exothermicity ca. 100 times stronger, cf. Table 1).

### 3.6. Discussion

The compounds investigated were supposed to exhibit rather similar chemical and adsorption properties as they all represent sol gel-prepared phases with a more or less large surface. Nevertheless, the experimental findings have to be interpreted in a more diversified way.

Three methodological considerations and a more chemical aspect can be deduced from a comparison of the experimental values listed in Table 1:

- (i) It was rather surprising to establish to which extent the DTA traces show fine details of the sorption process. This is especially true for the change from the exothermal adsorption range to the immediately following endothermal desorption range in the case of physisorption thus allowing a precise distinction of various adsorption features.
- (ii) The interruption of the CO<sub>2</sub> injections by one or more water pulses allowed us to generate basic sites on the fluoride surface which indeed represented OH groups rather than simply adsorbed water molecules. The latter show another desorption behaviour than do deposited OH groups. In certain cases, however, the generated OH groups showed acid rather than basic behaviour.
- (iii) A limiting factor for comparing spectroscopical information on the adsorption behaviour such as given in [4] with the results of PTA measurements is the different time scale of the physicochemical processes. The spectroscopic investigations of the CO<sub>2</sub> adsorption are performed at near-to-equilibrium conditions, sometimes under reduced pressure, whereas the PTA measurements proceed under flow conditions at normal pressure. That is why the first step of interaction revealed to be so characteristic and yielded the principal information. If, on the other hand, the interaction is strong enough – as it is the case for chemisorption – the PTA information is unequivocal and convincing.
- (iv) Chemical conclusions cannot be drawn for the substance group *in toto*, but only by separating three subgroups: firstly, the four binary, unsubstituted fluorides of Mg, Ca, Sr, and Ba; secondly, the three BaF<sub>2</sub>-based phases obtained by various treatments of BaF<sub>2</sub>-SG; and, thirdly, the three metal-substituted fluorides. The four binary fluorides, at first, do not exhibit a systematic evolution of the exothermicity as for Ca a surprisingly high value was found. The row of the remaining elements from Mg to Ba, on the other hand, correctly reflects the increasing electropositive character which effects a stronger basicity and, consequently, a greater exothermicity of the CO<sub>2</sub> adsorption just as observed (Table 1).

The three different treatments of  $BaF_2-SG$  as listed in Table 1 showed that the water injection is able to simulate the situation reached by exposing dry  $BaF_2-SG$  to humid air: the exothermicity of the first  $CO_2$  adsorption stage for  $BaF_2-SG+H_2O$  approximates that for  $BaF_2-SG$  wet (Table 1).

The influence of doping by a second metal is somewhat different than expected. HS-AlF<sub>3</sub>, as expected, did not show any basicity, but if MgF<sub>2</sub> is hosting 15 mol% AlF<sub>3</sub>, a certain basicity is observed. This proves, on the other hand, the strong basicity-generating force of implemented Mg as one succeeds to generate basic sites in presence of one of the strongest known Lewis acids. The behaviour of the ternary phase Mg<sub>0.8</sub>Ba<sub>0.05</sub>Cr<sub>0.15</sub>F<sub>2.16</sub> demonstrated that the

basicity-creating effect of Mg sites can be overcompensated by Cr doping.

The behaviour of Ba(OH)F-SG was completely different compared with all other phases investigated. 4.3 mol% CO<sub>2</sub> uptake with a qualitatively different curve shape possibly indicate another chemical situation compared to those of all other MF<sub>2</sub>-SG. The bonding situation of the OH groups must be different from those induced by the water injection pulses and might be of the monodentate M–OH (type 1) according to the classification proposed in [26].

### 4. Conclusions

The results presented here demonstrate that sol gel-prepared alkaline earth fluorides have not only acid, but basic sites as well which can contribute to the interpretation of the promising catalytic activity of some of them. In particular, they confirm the main conclusions reported on MgF<sub>2</sub>-SG and its weak basicity simultaneous with a strong Lewis acidity [4].

For the first time, these basic sites have been characterized by the exothermicity of the first interaction step with pulsed  $CO_2$ . If the exothermal interaction was weak or absent, the injection of gaseous water led to the deposition of OH groups predominantly acting as basic sites on the surface of the fluorides, but in few cases as acid sites as well. This enabled us to establish that the impact of OH groups onto different fluorides can exhibit a different influence on the sorption properties of the solids: the adsorption ability vs.  $CO_2$  can be promoted, suppressed or remain unaffected. Hindering of the  $CO_2$  adsorption can be a hint to acid rather than to basic character of the deposited OH groups. This aspect will be investigated in more detail in a following study. Again the great potential of Pulse Thermal Analysis for the investigation of solids is demonstrated by the results presented here.

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