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The challenge of methods of thermal analysis in solid state and materials chemistry

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Abstract: Thermogravimetry (TG) and differential thermal analysis (DTA) are traditional, but still useful, experimental techniques for obtaining information in the realms of materials and solid state chemistry. This paper presents two case studies (many more could be cited) to illustrate the strengths (and limitations) of these techniques: (1) Iron doping of clinoptilolite (the most common zeolite): the typical parameters of both components appear clearly in the TG and DTA curves. The decrease of the T_{max} value of the structurally-typical DTA effect of FeOOH by approximately 100 °C is attributed to the weakening of chemical bonds in FeOOH due to the incorporation of the doping component into the structure of this zeolite. (2) Macrodefect-free (MDF) materials: the results of both TG and DTA unambiguously locate the typical temperature range of the decomposition of the P{4}–O–Al/Fe{6} cross-links within the interval of 200–300 °C. The presence of cross-links is shown by the DTA data while the TG data can be used to measure the degree of cross-linking, which is valuable information when studying both raw mixes and the final materials for a variety of MDF materials.

Keywords: differential thermal analysis; iron doped clinoptilolite; macrodefectfree materials; SSC-2016; thermogravimetry.

Introduction

The methods and methodologies of thermal analysis investigate the temperature dependence of properties of the sample. A variety of techniques exist for the various physical quantities or properties (including phase composition of sample) whose changes with temperature can be measured [1]. This dependence provides information on the behavior of solid compounds and materials on controlled heating/cooling. The most frequent are examples that comprise thermal events due either to decompositions or to phase changes, or both. Vital data on degree of conversion, stoichiometry of decomposition reactions, thermochemical parameters of phase changes, and phase diagrams of various systems are available in the literature. The limits and conditions of thermal stability for a material or system are also very important information for materials and solid state chemistry. Examples in the literature are many; our discussion below will cite only a few representative examples, mainly taken from the open-access version of the Journal of Thermal Analysis and Calorimetry, to show the variety of research questions to which TG and DTA are relevant.

Vitrification is the most effective method of immobilization of hazardous waste. In it, toxic elements are encased in a glass matrix. Iron phosphate glasses are presently being considered as a matrix for storage of those radioactive wastes which cannot be vitrified using a conventional borosilicate glass. The glass' characteristic temperatures, glass crystallization ability, and crystallizing phases were determined in [2]. It was shown that ΔC_p is a suitable structure-sensitive glass crystallization ability parameter. Results of the research on the possibility of determining the properties and detailed characteristics of waste combustion by-products

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by means of the combined techniques of thermal analysis appear in [3]. The investigated materials underwent coupled thermal analysis (with a mass spectrometer connected to the TG and DSC apparatus), which allowed for detailed interpretation of the processes taking place during the examination of thermal resistance. Additionally, the harmful substances content was examined.

Ceramizable (ceramifiable) silicone composites are among the most important elastic technical materials produced industrially. These composites are commonly used to increase the flame retardancy of electrical cables and to ensure the integrity of electricity networks in the event of fire, by virtue of their ability to form a continuous ceramic structure. In one study [4], ceramizable silicone composites filled with different carbon fiber contents were tested. To describe the process of the ceramic structures' creation, TG/DSC analysis was carried out. These tests demonstrated that increasing the amount of carbon fibers improves the mechanical properties of the ceramic structure regardless of heat treatment conditions. Another example regarding thermal properties and fire hazard is a report [5] on thermo-kinetic analysis and the destruction activation energy of diene rubber elastomers and their vulcanizates, investigated under both air and inert gas.

The thermal decomposition of hydrothermal micro- and nano-sized CrO_2 powders with an iron dopant was also studied by thermal analysis [6], with the obtained data showing that nanopowders are highly stable up to 200 °C and can be used for magneto-electronic devices. Thermoanalytical methods in particular showed that the decomposition of chromium dioxide happens with formation of $CrO_{1.5}$ at 450 °C–540 °C, but that the process happens at a 100 °C lower temperature for nano-sized than for micro-sized CrO_2 samples. The decomposition of nanopowders occurs in two stages, with DTG and DSC peaks at about 470 °C and 500 °C, respectively (shell vs. core particles). For the iron-containing powders, an additional endoeffect and mass loss was found at 550 °C, which is determined by the presence of an $Fe_xCr_{1-x}O_2$ solid solution mainly located in the particle shell. The shift toward lower temperatures for the nano-sized samples' decomposition peak, and the observed peak splitting, indicate the impact of the effect of particle dimensions on powder thermal stability.

Aluminum-pillared montmorillonites are useful materials for their application as catalysts, adsorbents and ceramic composites. The authors of [7] used X-ray diffraction and thermogravimetric analysis to determine the structural and thermal transformations of the precursors on heating to 1200 °C. Thermal analysis of these precursors below 600 °C showed the influence of OH–Al polymers upon the formation of pillared montmorillonite from two solutions.

Thermal analysis as a laboratory technique has an associated working vocabulary, with IUPAC recommendations [1] as to a consistent set of definitions to permit clear and precise communication and promote proper understanding of the results (the recommendation defines 13 techniques and 54 terms within the glossary, as well as symbols and units). There are several conditions which constitute best practice for modern thermoanalytical research. Of those pertaining to the execution of thermal analysis and evaluation of collected data, the most important are: (i) an up-to-date thermoanalytical device, (ii) appropriate software for analysis of the thermoanalytical curves (either general-purpose, or specialized or purpose-built, as needed), (iii) combination of the results with those of a "twinned" experimental method or relevant calculations. Properly-executed thermoanalytical research, in conjunction with appropriate analysis and interpretation of the results, contributes directly to the progress of materials and solid state chemistry. The reader interested in a recent, coherent and authoritative overview of important topics in thermal analysis in the fields of solid state chemistry and materials chemistry, focused on micro-, nano-, and non-crystalline materials may find the monograph edited by Šesták and Šimon [8] useful.

The present paper deals with the capabilities of the most frequent methods of thermal analysis – thermogravimetry (TG) and differential thermal analysis (DTA) in the fields of solid state and materials chemistry. Two examples – iron-doped clinoptilolite and macrodefect-free (MDF) materials – are reported here and discussed to illustrate the strengths and limitations of these techniques.

Experimental

Thermoanalytical measurements were conducted on an Sdt 2960 device from T. A. Instruments. Data on TG, its derivative (DTG), and also DTA curves, were simultaneously acquired under the following measurement conditions: heating from laboratory temperature to 1000 °C, at a heating rate of 10 °C min^{-1}, under normal air atmosphere. These experimental conditions were chosen on the basis of available reference data on the thermal stability components of the two systems. The data collected for both systems were evaluated using the Thermal Analyst 3100 software. The mass loss steps in TG and the T_{max} values of DTA effects are reported for both examples. In studies on MDF materials, TG mass losses have been straightforwardly used as a basis for proposals of further methodology for estimating and comparing the relative degree of cross-linking. DTA effects and T_{max} values of particular events on heating will be discussed and compared with the reference data and earlier reports on components and systems relevant for both examples.

Clinoptilolite is one of the most common zeolites in the Earth's crust. Due to its huge abundance in the country and the cost effectiveness of mining it, Slovakian clinoptilolite-rich tuffs are a common object of study, especially as they have a large surface area, rigidity and surface functionality, both in their virgin state and in combination with iron oxide hydroxides as promising interface carriers. The thermal properties of clinoptilolite samples depend on the exchangeable cations, as well as the source of the zeolitic rocks. For these reasons, knowing the thermal stability and thermal transformation properties of zeolitic tuffs is advantageous for some applications in catalysis, ceramics and lightweight aggregates, among other fields. It has been shown [9] that clinoptilolite samples exert major and rapid mass losses between 30 °C and 200 °C – a single-step dehydration process with a specific endotherm on the DTA curve. Mass losses at higher temperatures were reported to be slower and less significant. The iron (III) doping affects such properties of zeolites as biomimetic parameters, impregnation ability, and sorption of environmental pollutants from (mainly aqueous) solutions. The iron doping of clinoptilolite was achieved by simple sorption of iron oxidehydroxide in amounts of up to 6 mass-% of Fe(III) in the doped sample. This procedure led to a modification of the Al/Fe ratio. It is generally agreed [9] that before using a zeolitic tuff (either virgin or doped) for any application, its thermal and structural properties should be carefully investigated. Methods of thermal analysis (namely TG and DTA) have been applied with the aim of contributing to the understanding of the nature and changes in thermal and structural properties of Fe-bearing species in the doped clinoptilolite.

Macrodefect-free (MDF) materials belong to the category of promising cement-based chemically-bonded ceramics and composites. The raw composition of MDF materials consists of a cement paste containing up to 7% by mass of a water soluble plasticizing agent (polyvinyl alcohol/acetate or sodium polyphosphates are the most frequent choices) and up to 20% water [10, 11]. The key part of the procedure to form MDF materials should be understood to be the moderate mechanochemical treatment of the raw mixture, in the form of simultaneous mixing and application of medium pressure (5 MPa) at room temperature. The cement components of experimental MDF samples have comprised either Portland cement or the newly-tested hydraulically active composition (H-cement). The effect of pre-treatment of the dry raw mix – a mechanochemical activation applied prior to the key procedure of the MDF formation process – has also been of interest. Details on the procedure and compositions can be found in [12, 13]. Prior to that, it was also shown that thermal events (TG, DTG, DTA) in the region of 200 °C–330 °C were sensitive to the presence (and thermal decomposition) of cross-links [11, 12, 14]. The choice of methods of thermal analysis (namely TG and DTA) and the precise methodology of their application were, in this example, directed towards investigating the presence and scope of cross-linking in a variety of both raw mixes and final MDF materials.

Results and discussion

Example 1 – thermal analysis of iron doped clinoptilolite

The losses of physically and structurally bound water molecules (and the typical TG/DTA effects displayed in Figs. 1–4 at temperatures below 350 °C are obvious features of the thermal decomposition of both clinoptilolite [9] and FeOOH [15, 16]. Figs. 2–4 show that the DTA curves differ in the region 400 °C–600 °C for virgin FeOOH, Fe-doped clinoptilolite and powdered Fe-doped clinoptilolite. The powdering of the doped sample results in a DTA exoeffect with a T_{max} value of 460 °C (cf. Figs. 2, 3, and 5), while the reference FeOOH shows

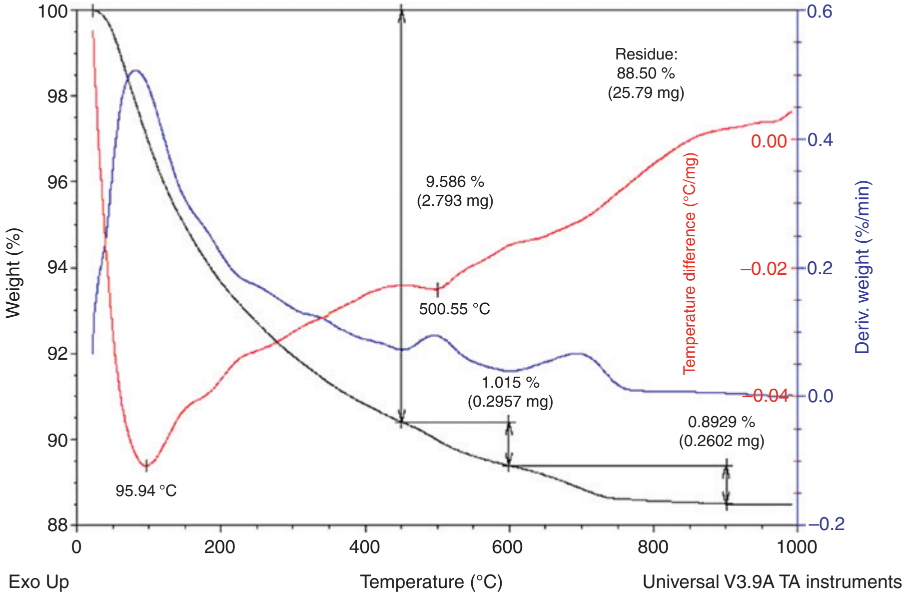

Fig. 1: Thermoanalytical curves of clinoptilolite – TG curve (black), DTG curve (blue) and DTA curve (red).

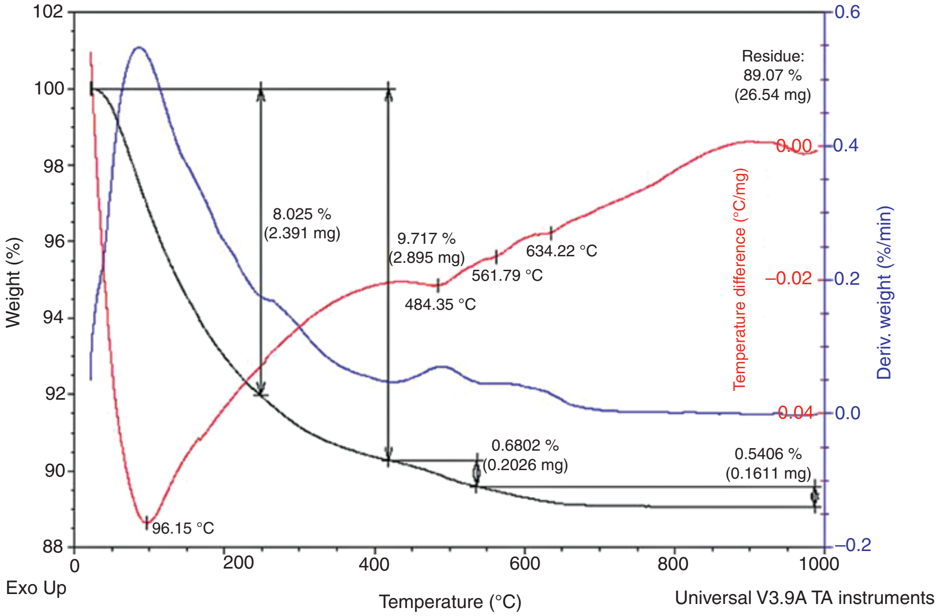

Fig. 2: Thermoanalytical curves of iron doped clinoptilolite – TG curve (black), DTG curve (blue) and DTA curve (red).

a DTA exoeffect with $T_{max} = 560$ °C (cf. Figs. 4 and 5). This effect is slightly dependant on the modification of FeOOH and even more so on the agglomeration of its particles [15, 16]. Both clinoptilolite and FeOOH have also been detected in samples of Fe-doped zeolite by IR and Raman spectroscopy.

Additional measurements and detailed analysis of DTA curves of Fe-doped clinoptilolite and FeOOH in the temperature range 400 °C–600 °C were carried out with the aim of distinguishing whether the DTA effect under discussion is a feature of the doped zeolite under study or should be attributed to the doping material, FeOOH, itself. The results (cf. Fig. 5) can be summarized as follows: no DTA effect was observed in "as synthesized" Fe-doped clinoptilolite. An exoeffect with a T_{max} value of 460 °C was identified in the powdered Fe-doped clinoptilolite. An exoeffect with $T_{max} = 560$ °C was confirmed in the virgin FeOOH. In-depth studies

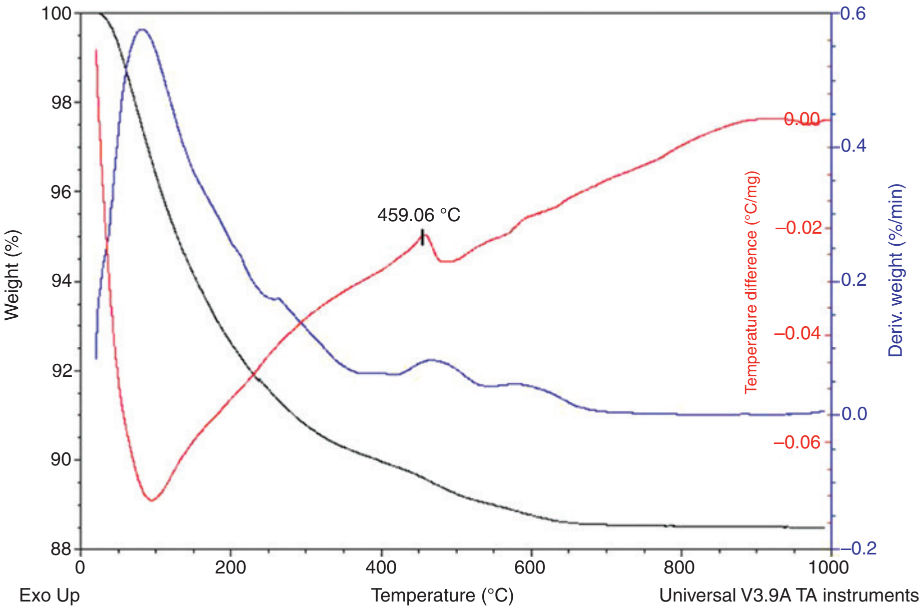

Fig. 3: Thermoanalytical curves of powdered iron doped clinoptilolite – TG curve (black), DTG curve (blue) and DTA curve (red).

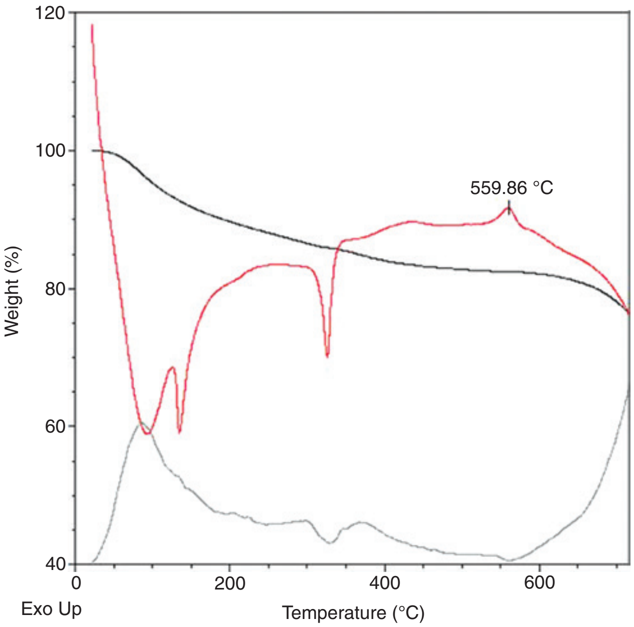

Fig. 4: Thermoanalytical curves of FeOOH – TG curve (black), DTG curve (blue) and DTA curve (red).

for lepidocrocite-like FeOOH [15, 16] attribute the DTA effect between 400 °C and 550 °C to the transformation of γ-Fe_2O_3 or β-Fe_2O_3 into hexagonal α- Fe_2O_3, and report that the aggregation processes influence the value of T_{max}. The structurally-typical DTA effect of virgin FeOOH, with shifted T_{max} value (varying T_{max}), as reported here, suggest that it is the same process in the iron dopant which is causing this effect in the iron-doped clinoptilolite, i.e. the effect occurs due to aggregation of iron-containing phase(s) in the doped zeolite. The difference in T_{max} values (there is a decrease of approximately 100 °C in Fe-doped zeolite compared to virgin FeOOH) we attribute to the weakening of the original chemical bonds in FeOOH, due to interactions incorporating the doping component into, or adsorbing it onto, the structure of the zeolite.

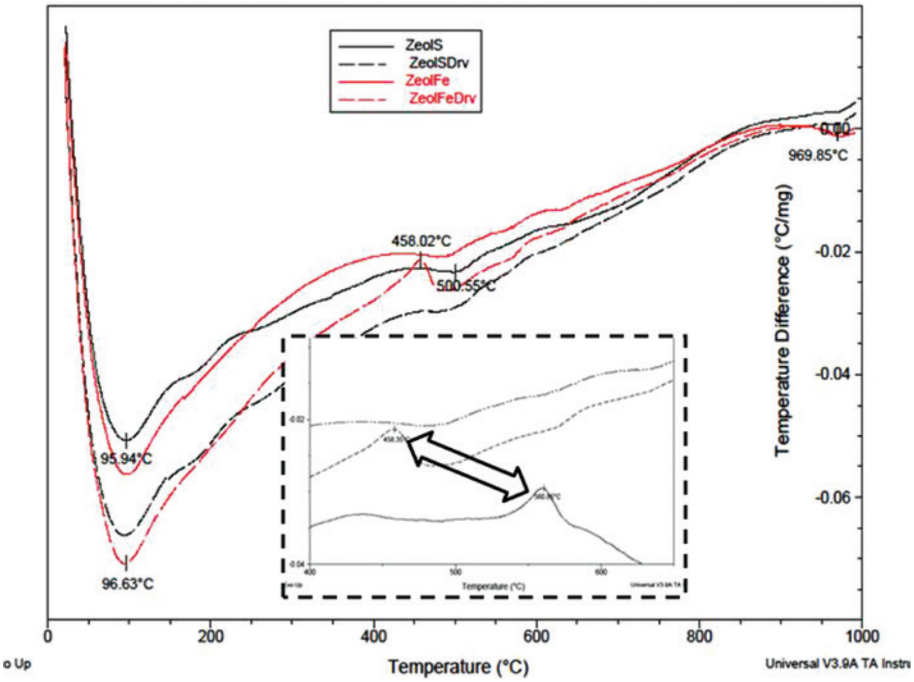

Fig. 5: DTA curves of clinoptilolite (black) and iron doped clinoptilolite (red), full lines –sample as synthesized, dashed lines – powdered sample. The figure shows also (in dashed area) comparison of the T_{max} values of the structurally-typical exoeffects of the powdered sample (460 °C) and the sample of FeOOH (560 °C).

The reported data contribute to our understanding of the structure of clinoptilolite tuffs with embedded nano-dispersed FeOOH hydrogels intended for heavy metals removal [17]. This information, besides showing the expected features of the thermal decomposition of both clinoptilolite and FeOOH, also confirms successful incorporation of the doping compound into the structure of zeolite. The absence of the DTA effect of FeOOH in “as synthesized” doped samples shows a state of affairs in which the FeOOH dopant’s own thermal properties are suppressed. However, after powdering, when the sample is partly destroyed, a DTA effect characteristic of FeOOH is observed, namely a shifted value of T_{max}. This observation suggests agglomeration of the FeOOH in the structure of Fe-doped zeolite, sufficient for the bulk properties of FeOOH to appear, and thus the resulting composite shows the functional properties of both components.

Example 2 – thermal analysis of macrodefect-free (MDF) materials

Cross-links binding the cement phase to the polymeric phase in a portion of an MDF sample have been reported [10–12] and are viewed as the key feature of MDF synthesis. During the MDF formation procedure, atomic/nano-level assemblies of composition P{4}–O–Al/Fe{6} are formed. We have studied the scope of this cross-linking as a key item of the successful MDF synthesis by three independent experimental methods – thermal analysis, IR spectroscopy and MAS-NMR spectroscopy. A selection of thermoanalytical data and results is reported below to illustrate the capabilities of thermal analysis in this field.

An overview of the key features of the TG, DTG and DTA curves of several series of MDF-related samples is shown in Fig. 6. A successful (or partially successful) MDF synthesis is indicated by specific effects in the temperature region of 200 °C–300 °C. The DTG curve (the derivative of TG) indicates that mass change occurs with the highest intensity around a temperature of 300 °C. This mass change is directly connected to the exoeffect in the DTA curve at $T_{max} = 300$ °C. It should be noted that the reported temperature interval is above the range of thermal stability of the major hydraulic phases [18, 19]. As a result, we have suggested [11, 14] that the cross-links (and MDF materials) have higher thermal stability than the classical hydraulic phases (and concretes). Moreover, the combination of a mass change on the TG curve and an exoeffect on

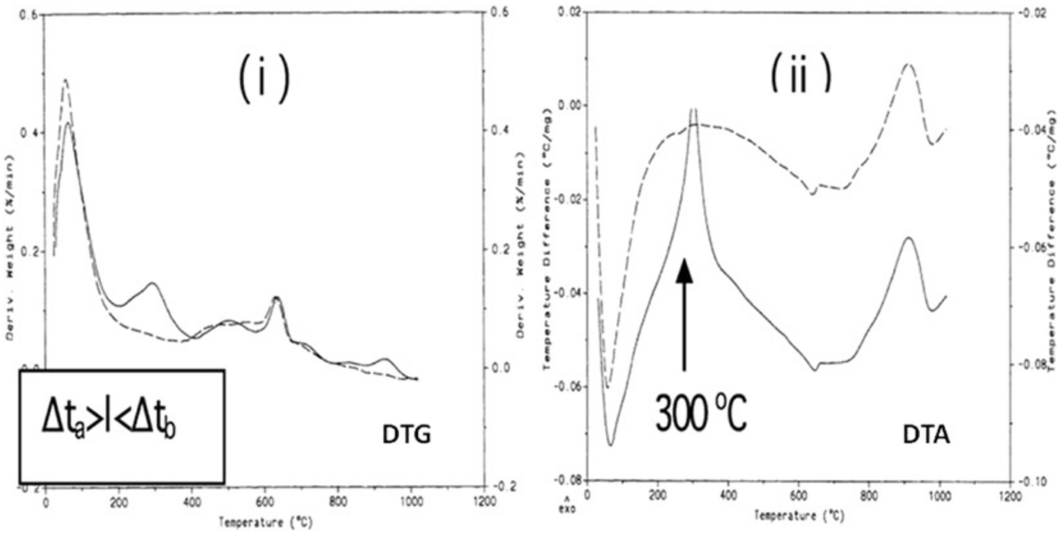

Fig. 6: DTG curves (i) and DTA curves (ii) of MDF related samples, full lines – curves after successful synthesis, dashed lines – curves after unsuccessful synthesis; originally published in [11].

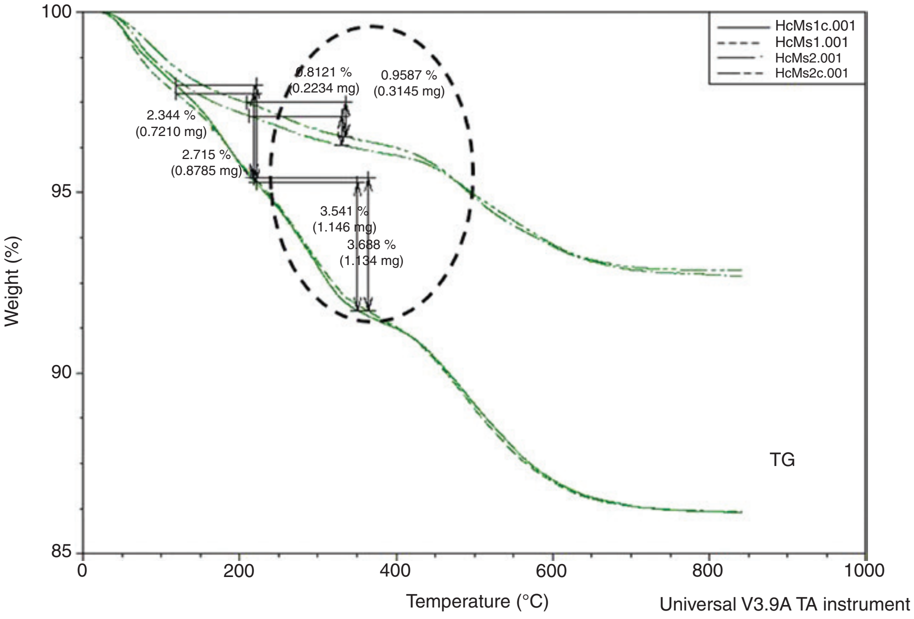

Fig. 7: TG curves of MDF related samples, mass changes in the region 200 °C–300 °C (encircled area) cf. Table 1 for AM 2 and for MDF samples of AM 2.

the DTA curve is generally considered as a sign of decomposition of a phase of more complex composition. The atomic-level model of the position and role of the cross-linked portion in the composition of MDF material [10–12] is based on (in addition to these data and characteristics) information obtained from MAS NMR and IR spectroscopy.

TG mass losses in the interval between 200 °C and 300 °C (cf. Fig. 7 and Table 1) were used to estimate the different amounts of cross-linked portions present in individual MDF-related compositions (in the final samples or intermediates). This approach is illustrated in Fig. 7 for the MDF samples made from the promising new cement-based compositions. These results are given more fully in Table 1. Data on TG mass losses in the temperature interval of 200 °C–300 °C enable comparison of the relative amounts of phase decomposed in this step, which reflects on the extent of cross-linking in the different samples. Thus, the data in Table 1 indicate that:

Table 1: Data sets extracted from DTG, DTA and TG curves in the temperature region 200 °C–300 °C.

Series no.	DTG, DTA	TG mass loss, Δm/%	Composition of the analyzed sample
I	−, −	–	Raw mixtures 1 (RM 1)
II	−, −	–	*Raw mixtures 2 (RM 2)*
III	+, +	0.54 ± 0.05	Activated mixtures 1 (AM 1)
IV	+, +	*0.89 ± 0.05*	*Activated mixtures 2 (AM 2)*
V	+, +	1.21 ± 0.05	MDF samples of RM 1
VI	+, +	*1.96 ± 0.06*	*MDF samples of RM 2*
VII	+, +	1.58 ± 0.05	MDF samples of AM 1
VIII	+, +	*3.62 ± 0.06*	*MDF samples of AM 2*

Signs − or + in the column DTG, DTA denote the occurrence of the indicative thermoanalytical events of cross-links; TG mass losses/% give insight into the scope of cross-links formation in AM 1 and AM 2 (arising due to the mechanochemical activation), in MDF samples of RM 1 and RM 2 (arising during the standard MDF procedure) and in MDF samples of AM 1 and AM 2 (due to mechanochemical activation included within the MDF procedure). Italics is used to distinguish the data of raw mixtures and MDF materials based on two types of cement – Portland cement (AM 1) vs. *H-cement (AM 2)*.

1. Cross-links form already during the mechanochemical activation of the dry raw mixtures (cf. the values in column TG of series III and IV – activated mixtures vs. those of series I and II in Table 1).
2. When the mechanochemical activation is incorporated into the synthesis procedure of MDF samples, the content of cross-linked areas increases to between one-third higher and double the level of such content in the MDF samples without mechanochemical activation (cf. values in column TG of series VII and VIII – MDF samples of activated mixtures vs. those of series V and VI in Table 1).
3. The effect of mechanochemical activation occurs independently of the type of cement phase present in the raw mixture. However, these data show that the effect is less pronounced in the raw mixtures and final samples with Portland cement than in those with H-cement (cf. the data on AM 1 vs. AM 2 and also on MDF samples of AM 1 vs. MDF samples of AM 2 in Table 1).

Simultaneous thermal analysis of the thermal decomposition of cross-links in MDF materials enabled insight into both the occurrence (from the DTA data) and scope (from the TG data) of cross-links formation. Thus, the reported data contributed to our knowledge on the role of atomic-level cross-links in MDF materials [11, 12]. Thermoanalytical data in addition to and in accord with the insight gained by MAS NMR and IR spectroscopy of MDF materials confirm (i) higher decomposition temperatures (thermal stability) of cross-links than for "standard cement hydrates", (ii) that cross-links form already in the raw mixes, if these are mechanochemically activated, (iii) a higher content (from one-third higher to doubled) of cross-links in MDF materials synthesized from mechanochemically activated raw mixtures than in samples formed after standard mixing of raw materials. The described methodology is a tool enabling further study of new and promising MDF compositions [13], with special focus on both the occurrence and scope of atomic-level cross-links in the individual steps of the procedure and the final samples.

The examples which we have reported and discussed illustrate the strength and limitations of thermal analysis in studies of both iron-doped clinoptilolite, a potential sorption material of environmental pollutants (especially heavy metals), and MDF materials, a class of chemically bonded ceramics (featuring P{4}–O–Al/Fe{6} cross-links). Appropriately used, this insight and this or similar methodologies can form a powerful tool for investigating a range of solid state and materials chemistry topics.

Conclusions

1. Thermogravimetry (TG) and differential thermal analysis (DTA) are traditional but still useful techniques for obtaining information in materials/solid state chemistry. Knowledge extracted from the TG and DTA

data needs to be supported by the results of "twinned" method (e.g. calculation of degrees of conversion or stoichiometries of decomposition reactions). Critical awareness of the limitations of the methods is needed.

2. Detailed analysis of the DTA curves of iron doped zeolites (showing the structurally-typical DTA effect of virgin FeOOH, and the shift of its T_{max} value in the doped zeolite) has confirmed both the encapsulation of doping iron oxidehydroxide into the structure of zeolite and a degree of retention of the FeOOH dopant's original bulk properties. The decrease of the T_{max} value by approximately 100 °C is attributed to the weakening of chemical bonds in FeOOH due to incorporation of the dopant into the structure of zeolite.
3. Simultaneous thermal analysis (DTA, TG) of MDF samples over a temperature range of 200 °C–300 °C – typical of the decomposition of cross-links – is a powerful tool for the detection of the presence and scope of cross-links formation. The DTA data indicate the occurrence, and the TG data the scope, of cross-links formation. The methodology can be applied both for specific steps of the MDF procedure (mechanochemical activation) and for analysis of the composition of the final samples of MDF material.

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