JOINT SYMPOSIUM ON THERMAL ANALYSIS AND CALORIMETRY

GEFTA – PTKAT - CWGTA

anlässlich der Jahrestagung der Gesellschaft für Thermische Analyse e.V.

Dresden, 26. – 28.05. 2010

MODELLING AND EXPERIMENTS FOR SOLVING PHASEANALYTICAL, CALORIMETRIC, AND KINETIC PROBLEMS

DRESDEN UNIVERSITY OF TECHNOLOGY

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Dear members and friends of GEFTA,
Dear Guests,
Ladies and Gentlemen!

We welcome you all to Dresden and thank you for your participation in our joint meeting which has been organized for the third time in GEFTA's history, as a trilateral symposium.

From the early beginning of our association, the GEFTA has paid particular attention to European cooperation and thus has organized many bi- and trilateral meetings with the scientific associations of our neighbouring countries:

Constance	1976	STK
Kiel	1978	NoSTAC
Rapperswil	1979	STK
Aachen	1981	TAWN
Copenhagen	1983	NoSTAC
Freiburg/Br.	1986	STK
Munich	1993	STK
Sopron	1995	Hungary
Freiburg / Br.	1996	AFCAT
Dresden	2000	PTKAT
Munich	2001	STK, *eurostar*
Rijswijk	2005	TAWN
Mulhouse	2008	AFCAT, STK

It is our great pleasure to continue this tradition with the current symposium together with the PTKAT and – for the first time – with the “Czech Working Group on Thermal Analysis” CWGTA.

For more than 30 years, the focuses of GEFTA's work have been: support of the national and international scientific exchange, increasing the quality and broadening the field of research. In this sense we are pleased to hold the current joint symposium with the topic: “*Modelling and experiments for solving phaseanalytical, calorimetric, and kinetic problems”.*

Once more, welcome to Dresden and have a good time!

Michael Feist
GEFTA chairman

Peer Schmidt
local Organiser

PROGRAMME

	25.05.2010 17:00 – 18:30	Meeting of working group *Thermophysics*
	26.05.2010	
	08:30 – 10:00	Board meeting (Vorstandssitzung) *GEFTA*
	11:00 – 12:30	Meeting of working group *Polymers*
	13:00 – 13:20	Opening ceremony JSTAC - DD 2010
01	13:20 - 14:00	**Andrzej Małecki (Kraków/PL)** Theoretical Approach to Thermal Decomposition of Chosen Anhydrous Oxalates
02	14:00 - 14:20	**Edgar Langenberg (Lyon/F)** Use of the Calorimetric Techniques in the Evaluation of the CO_2 Capture and Sequestration Technologies
03	14:20 - 14:40	**Barbara Małecka (Kraków/PL)** The Kinetics of Thermal Decomposition of FeC_2O_4 in Inert Atmosphere at Nononisothermal Conditions
	14:40 - 16:00	Coffee break / Poster session
04	16:00 - 16:40	**Jaroslav Sesták (Prague/CZ)** Macro and Micro World of Temperature and Thermal Analysis
05	16:40 - 17:00	**Gerhard Schullerus (Hanau/D)** Fluctuations at DSC Measurements/ *Messschwankungen bei DSC Messungen*
06	17:00 - 17:20	**Hans-Peter Ebert (Würzburg/D)** Aims and Activities of the Working Group “Thermophysics” in the GEFTA
	17:30 - 18:30	General meeting (Mitgliederversammlung) *GEFTA*

	27.05.2010	
07	09:30 – 10:10	**Klaus Hack (Aachen/D)** The Use of an Integrated Thermodynamic Databank System for the Investigation of Enthalpy Related Reactive Systems
08	10:10 - 10:30	**Olga Fabrichnaya (Freiberg/D)** Experimental Studies and Thermodynamic Modelling of ZrO_2-based Systems
09	10:30 - 10:50	**Roland Neher (Dresden/D)** Formation of Liquids in the System Al_2O_3, Y_2O_3, SiC/ *Flüssigphasenbildung im System Al_2O_3, Y_2O_3, SiC*
	10:50 - 11:30	Coffee break
10	11:30 - 12:00	**Detlef Klimm (Berlin/D)** Crystal Growth and Thermal Analysis in Reactive Atmospheres Assisted by Thermodynamic Modeling
11	12:00 - 12:20	**Damian M. Cupid (Freiberg/D)** Thermodynamic Assessment of the Ti–Al–Nb System using Data from Thermal Analysis
12	12:20 - 12:40	**Jörg Acker (Senftenberg/D)** Thermodynamic Consideration of Direct Synthesis of Methylchlor-Silanes/ *Thermodynamische Betrachtung der direkten Synthese von Methylchlorsilanen*
	12:40 - 14:10	Lunch break
13	14:10 - 14:50	**Michael Binnewies (Hannover/D)** Experimental and Theoretical Methods in Gas Phase Thermochemistry
14	14:50 - 15:10	**Bertrand Roduit (Sierre/CH)** Estimation of Time to Maximum Rate under Adiabatic Conditions (TMR_{ad}) Using Kinetic Parameters Derived from DSC - Investigation of Thermal Behavior of 3-Methyl-4-Nitrophenol
15	15:10 - 15:30	**Heiko Huth (Rostock/D)** Calorimetric Investigations of Ultrathin Film of Polyvinylacetate under Controlled Humidity: Material Science, Calorimetry

	15:30 - 16:50	Coffee break / Poster session
16	16:50 - 17:10	**Simone Krüger (Berlin/D)** Chemical Analysis of Spruce Wood during Thermal Exposure
17	17:10 - 17:30	**Sonja Eichholz (Gießen, Berlin/D)** Characterization of Nano-sized Diesel Exhaust Particles by TG-FTIR/MS and Electron Microscopy
18	17:30 - 17:50	**Anka Berger (Berlin/D)** Assessment of the Explosive Properties and Thermal Hazards of Azodicarboxylates
	18:00	Excursion "Dresden 1756"

	28.05.2010	
19	09:30 – 10:10	**Jerzy Blazejowski (Gdansk/PL)** Molecular Interactions in the Context of the Stability and Reactivity of Crystalline Solids
20	10:10 - 10:30	**Nadja Huber (Tübingen/D)** Coupling µ-XRD^2 and DTA: New Insights in Processes with Delicate Temperature Dependence - the Gypsum – Bassanite – Anhydrite System as an Example
21	10:30 - 10:50	**Michael Feist (Berlin/D)** The Interplay of Thermal and Mechanical Activation. An Attempt to Understand Exothermal Water Release from Pseudoboehmite Phases
	11:00	Closing ceremony

	Postersession
P01	**T. Schuffenhauer, J. Feller (Dresden/D)** Phase Relations in the Ternary System $CuO/Ag_2O/P_2O_5$
P02	**R. Wege, J. Feller (Dresden/D)** Phase Relations and Chemical Transport in the System Mo/V/O
P03	**I. Weimann, J. Feller, Z. Zak (Dresden/D; Brno/CZ)** Phase Relations in the Quaternary System Cu/Ni/P/O
P04	**A. Lacz, A. Małecki (Krakow/PL)** Emission of Harmful Compounds During the Thermal Decomposition of Foor Coverings
P05	**L. Hensgen, K. Stöwe (Saarbrücken/D)** Combinatorial Discovery of Catalysts for the Oxidation of Soot from Diesel Exhaust Gases with Thermal Analysis
P06	**P. Pulišová, E. Večerníková, M. Maříková, J. Šubrt, V. Balek (Husinec-Řež/ CZ)** Characterization of Titania Precursors on Heating in Air
P07	**A. Czulucki, M. Schmidt, S. Hoffmann, M. Binnewies, E. Milke, R. Kniep (Dresden/D)** Thermodynamische Modellrechnungen zum Chemischen Transport von Zr–*Pn*–*Q* (*Pn* = P, As; *Q* = Se, Te)
P08	**S. Hoffmann, A. Wosylus, M. Schmidt, M. Ruck (Dresden/D)** Untersuchungen zum Hydrolyseverhalten von $BiCl_3$ in Argon mittels TG-MS
P09	**M. Worzakowska (Lublin/PL)** Curing Reaction of DCPD Terminated Unsaturated Polyesters with Styrene and Methyl Methacrylate
P10	**M. Worzakowska (Lublin/PL)** The Thermal Properties of ST/UP and ST/UEP Copolymers

P11	**L. Strnadlová, P. Šulcová, K. Bořková (Pardubice/CZ)** Thermal Study of $Ce_{0.9}Tb_{0.1}O_2$ Compound
P12	**P. Šulcová, V. Blovská, J. Luxová (Pardubice/CZ)** The Synthesis and Study of $PrFeO_3$ Compound
P13	**P. Šulcová, P. Bystrzycki (Pardubice/CZ)** Thermal Study of the $(Bi_2O_3)_{0.5}(Ln_2O_3)_{0.5}$ Compounds
P14	**L. Bukovská, P Šulcová, M. Vondrášek, (Pardubice/CZ)** Synthesis and Colour Properties of $Lu_2Zr_{1,5}V_{0,5}O_7$ Pigment
P15	**E. Hempel, M. Bauer (Teltow/D)** Calibration of 3-Layer-Calorimeters for Determination of Storage Capacity of PCMs
P16	**L. Adolfová, Ž. Dohnalová, P. Šulcová, M. Trojan (Pardubice/CZ)** Synthesis of Cr-doped $SrSnO_3$
P17	**J. Čech, P. Šulcová, Ž. Dohnalová, M. Trojan (Pardubice/CZ)** Study of Colour Properties of Ni Doped Titanium Dioxide
P18	**D. Merz, O. Dregert (Karlsruhe/D)** Water Vapor TA Experiments for Mathematic Modelling of Combustion Processes
P19	**M. Grochowicz , B. Gawdzik (Lublin/PL)** The Chemical Structure and Thermal Properties of Polymeric Microspheres Obtained from Multifunctional Methacrylate Monomers
P20	**P. Davies, W. Kunze, M. Schennen (Crawley/UK, Eschborn/D)** The Use of High Heating Rates to Characterize Flame Retardant Materials by Thermogravimetric Analysis

P21	**S. Krüger, A. Berger, N. Gude, U. Krause, (Berlin/D)** Thermoanalytical Investigations During a Car Fire
P22	**S. Krüger, T. Raspe, U. Krause, (Berlin/D)** Investigations of Smoke Emission and Smoke Gas Composition in the Smoke Density Chamber
P23	**M. Wszelaka-Rylik, M. Sokołowska, J. Poznański, W. Bal (Warsaw/PL, Wroclaw/PL)** Three Distinct Binding Sites for Co(II) Ions Human Serum Albumin – Thermodynamic Calculation
P24	**P. Gierycz, M. Wszelaka-Rylik (Warsaw/PL)** Thermal Analysis of Nanostructured Calcite Crystals Covered with Phospholipid Layers
P25	**R. Geißler (Neuherberg/D)** Assays of Complex Samples Using Mass Spectrometry with Soft Single Photon Ionisation Coupled to Thermal Analysis
P26	**M. Schöneich, T. Lorenz, M. Bawohl, T. Nilges, P. Schmidt (Dresden, Münster, München/D)** Phase Formation in the System Hg/P/I Induced by Evaporation Pressure
P27	**E. Füglein (Selb/D)** Some Remarks on ASTM E 2105-00: Standard Practice for General Techniques of Thermogravimetric Analysis (TGA) Coupled with Infrared Analysis (TGA/IR)
P28	**S. Eichholz, E. Füglein (Selb/D)** Zinc Stearate a Standard Material for the TG-FTIR Method? Related to ASTM E 2105-00: Standard Practice for General Techniques of Thermogravimetric Analysis (TGA) Coupled with Infrared Analysis (TGA/IR)

Abstracts

Theoretical Approach to Thermal Decomposition Process of Chosen Anhydrous Oxalates

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Anhydrous oxalates ZnC_2O_4 [1], CdC_2O_4 [2] and CaC_2O_4 [3] decompose according to the following chemical equations:

$$\mathrm{ZnC_2O_4 \rightarrow ZnO + CO + CO_2} \qquad \mathrm{CdC_2O_4 \rightarrow CdO + 2CO_2}$$

$$\mathrm{CaC_2O_4 \rightarrow CaCO_3 + CO}$$

Which factors decide about the decomposition ways? The detailed answer for this question remains unknown. In the present work the results of theoretical analysis of the properties of crystal structure and bonding of oxalates in relation to thermal decomposition process in mentioned above oxalates are presented.

The methods used in this analysis – the Bader's quantum theory of atoms in molecules and bond order model (as defined by Cioslowski and Mixon), applied to topological properties of the electron density, obtained from DFT calculations performed by Wien2k package (full potential linearized augmented plane wave method), as well as Brown's bond valence model (bonds valences and strengths, and bond and crystal strains, calculated from crystal structure and bonds lengths data) are described. Presented results allow to state, that these methods, when used simultaneously, make possible the description and analysis of the crystal structure and bonding properties and give us the additional insight into their behavior during thermal decomposition process.

The proposed theoretical approach can be considered as promising and reliable tool for theoretical analysis, allowing explanation and prediction of the properties of the structure and bonding and hence the most probable way of thermal decomposition process to take place in such a structure.

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References

[1] A.Kolezynski, A. Malecki, *Journal of Thermal Analysis and Calorimetry, (2009), 97, 77*

[2] A.Kolezynski, A. Malecki, *Journal of Thermal Analysis and Calorimetry, (2009), 96, 167*

[3] A.Kolezynski, A. Malecki, *Journal of Thermal Analysis and Calorimetry,* DOI 10.1007/s10973-009-0535-0, MEDICTA 2009 Special Issue, published online 07 November 2009

Use of the Calorimetric Techniques in the Evaluation of the CO_2 Capture and Sequestration Technologies

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CO_2 capture technologies have long been used by industry to remove CO_2 from gas streams where it is not wanted or to separate CO_2 as a product gas. There are currently three primary methods for CO_2 capture: post-combustion, pre-combustion and oxy-fuel.

Post-combustion involves scrubbing the CO_2 out of flue gases from combustion process, through the use of chemical sorbents. This is today one of the most popular absorption technique for the **CO_2 capture** in post combustion processes. In such an industrial process, the amine solution is introduced at the top of an absorption tower while the exhausted fume containing carbon dioxide is introduced at the bottom. As an intimate contact is reached in the absorption tower, the amine solution chemically absorbs the carbon dioxide from the gaseous stream. Such a process especially requires two types of thermodynamic parameters: gas solubility and enthalpy of adsorption. The enthalpy of absorption, according to the amount of absorbed gas and the corresponding heat capacities of solutions, define the temperatures of the fluids when they exit the adsorption columns.

Flow mixing calorimetry is the ideal technique for measuring such enthalpies of adsorption. In order to work under pressure, a dedicated high pressure mixing vessel is adapted to be used on the Setaram C80 calorimeter. The mixing vessel is made of a stainless steel tube in a helicoidal shape into a cylindrical container. The length of the tube in closed thermal contact with the cylinder is about 240 cm. The fluids (CO_2 and amine solution) are introduced at the bottom part of the vessel in two vertical and concentrical tubes. The mixing (dissolution, reaction) starts when the thinner part of the tube is reached. The heat that is associated with the reaction, is exchanged between the rolled tube and the calorimetric block through the wall of the vessel in a isothermal mode. The flow mixing vessel operates from room temperature to 200°C and for a range of fluid pressure from 0.1 to 20 MPa. The fluid flowrates vary from 50 to 1500 $\mu l.min^{-1}$, that allow to cover a wide range of mixture composition.

CO_2 sequestration involves the injection of CO_2 into a geologic formation to enhance carbon recovery. The three options for geological CO_2 storage are saline formations, oil and gas reservoirs, and deep unminable coal seams. Among the storage possibilities, the injection of CO_2 in large amounts of natural methane hydrate that exists in ocean sediments is one investigated option. In that case the formation of CO_2 hydrates is expected with a dissociation of the methane hydrates. High pressure calorimetry has proved to be a very interesting technique in the investigation of formation and dissociation of gas hydrates under high pressure conditions and is applied to the investigation of CO_2 hydrates.

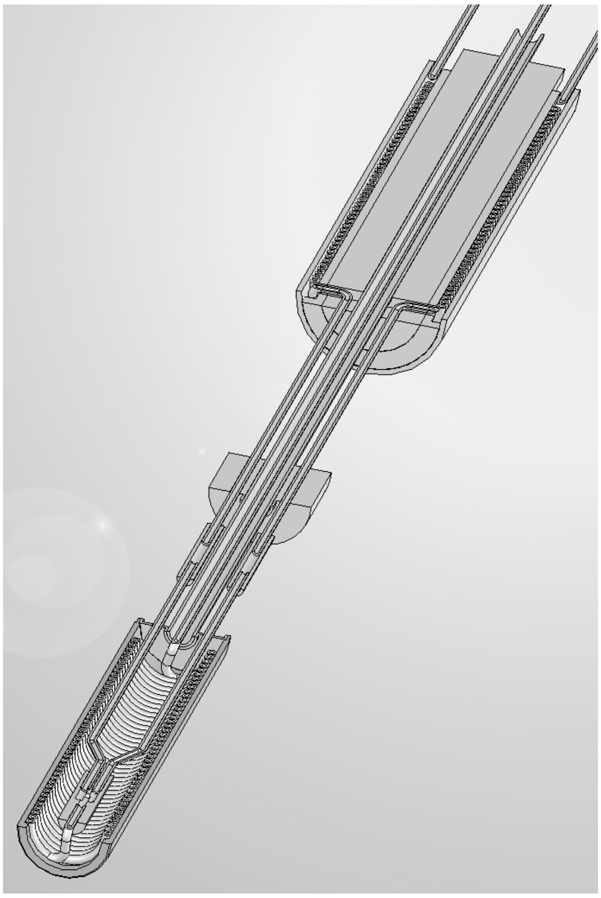

Figure: The high pressure flow mixing vessel
for the study of CO_2 capture in amine solutions

The Kinetics of Thermal Decomposition of FeC_2O_4 in Inert Atmosphere at Nononisothermal Conditions

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The thermal decomposition of d-electron metal oxalates is often used as the way for production of metals or metal oxides in powder form for catalytic, metallurgic or electronic applications. From this point of view the information about the kinetics of decomposition is important and helps to obtain product of the desired properties.

FeC_2O_4 is obtained in result of dehydration of ferrous oxalate dihydrate. On the basis of TG/DTA/MS measurements of thermal decomposition of FeC_2O_4 it was found that this process consists of two parallel reactions:

1. $FeC_2O_4 \rightarrow Fe + 2CO_2$
2. $3FeC_2O_4 \rightarrow Fe_3O_4 + 2CO_2 + 4CO$

As the process is complex and the loss of mass in TG experiment is the sum of both reactions there was no possibility to determine the kinetics of individual reactions at isothermal conditions. However it was possible to find kinetic description of both reactions at nonisothermal conditions on the basis of the detection of gaseous products evolution by mass spectrometer.

The degree of conversion of reaction 2. is equal to the degree of evolution of CO, α_{CO}. The degree of conversion of reaction 1. was calculated based on the evolution of CO nad CO_2 according to the following relationship:

$$\alpha_1(T) = \frac{(3\xi + 1)\alpha_{CO_2}(T) - \alpha_{CO}(T)}{3\xi}$$

where α_{CO2} is degree of CO_2 evolution and ξ represents the ratio between the reactions 1. and 2.

It was found that the kinetics of reactions 1. and 2. can be described with high accuracy by the Avrami-Erofeev kinetic equation, which means that the rate of both reactions is determined by the rate of nucleation and the rate of nuclei growth.

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Macro and Micro World of Temperature and Thermal Analysis

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The essence of thermal analysis [1] is the observation of *heat exchange*, which is literally an energetic "communication" between various macroscopic, mesoscopic and microscopic scales. Their thermal representation is given by the state of *temperature* often targeted what does it actually mean? This is a classically simple question often amazingly lacking an appropriate answer even though there is no doubt that the temperature is a central concept of thermal physics. Let us see first the terms entering the energy balance equations [2] in the *dimensional relation for energy* = [X]×[Y], which are associated with an extensive-intensive pair of conjugate variable,. X-Y,. Their existence "aspect" was already recognized by *J. Black* [3,4] as the "intensity of heat" and "matter of heat". Formal compatibility of these two quantities with the system of quantities already introduced in other branches of physics is thus only a matter of proper choice of suitable operative definitions and units, such as volume-pressure or electric charge-electric potential and also caloric-temperature, the caloric recalled entropy in the successive discipline of thermodynamics, which alternative form can be contemplated providing, e.g., the *efficiency of real heat engines* proportional to $\{1 - \sqrt{(T_2/T_1)}\}$ as a direct consequence of the linearity of Fourier's law of heat transfer [2,4].

The role of temperature shows its face from the super-macro-world of the Universe and its gradual growth from its initial singularity to the present state, which can be imagined as a thought TA experiment („Gedankenversuch"). In this aspect it is worth noting the so called Planck-Einstein transformation for universal temperature conveyed as $T = T_o \sqrt{\{1- (v/c)^2)\}}$ latter reformulated in the inverse form (temperature as observed in moving system is higher). However, if the thermometer reading is transferred to a moving system, e.g., by means of digital coding, the temperature, in the contrast to both above formulae, must be seemingly considered as ralativisticly invariant as all other intensive properties of fields (pressure, etc.). Therefore, we need to look for an alternative relativistic transformation aimed towards the habitually adjusted meaning of certain physical constant [5], such as the traditional thermal constant viewed as a substitute, $k \cong k_o \sqrt{\{1- (v/c)^2\}}$. Yet macroscopic is the world of thermal analysis of the Earth's climate, both from its historical development (climate records and its development|) and the present state of weather controlled by external (albedo) and internal (green-hose-effect) reflections of incoming Sun rays (imaginable thermoanalytical set-up of the Sun-furnace and the Earth-sample) [6].

Not accounting on typical circumstances of nowadays thermal analysis within the mesoscopic range of standard instrumentation [1] we should mention the need of temperature modulation and the high-resolution of temperature derivatives fighting thus against noise in the heat flow signal [7] (often fussy in temperature swinging modifications). Increasing instrumental sophistication and sensitivity provided a better chance to search more thoroughly toward the worth of baselines, which contains additional but hidden information on material structure and properties (inhomogeneities, local non-stoichiometry, interfaces between order-disorder zones, etc.). Popular computer in-build smoothing the noised experimental traces (chiefly baselines) can, however, become counterproductive. In the future, we may expect certain refining trends possible returning to the original single-sample set-ups with recording mere heating/cooling curves but at the level of fully computerized thermal evidence involving self-evaluation of 'calibration' behavior of the sample thermal inertia and its subtraction from the entire thermal record in order to propagate thermal effects possibly figuring artificially the DTA-like records. In addition, it may even incorporate the application of an arbitrary temperature variation enabling the use of self-heating course by simple placing the sample into the preheated thermostat and consequent computer evaluation of standardized effects or hitherto making possible to introduce fast temperature changes by shifting the sample within the temperature gradient of a furnace [1], etc..

Measurement at extreme thermal conditions [1] brings about extra incongruity such as sample quenching and associated phenomena of the sample constrained states due to non-equilibrating together with a side effect and/or competition between the properties of the sample bulk and its entire surface exposed to the contact with the cell holder. A special target of such a crucial exploration can be focused toward the mutual determinability of paired temperature and heat [4]. The crucial assumption concerning the temperature inside the sample is that there is a smooth continuation of the environment temperature distribution over the whole sample [1] but for the resolving at an ultrafast heat exchange the value of temperature become uncertain and *vice versa* (analogy of the Heisenberg law of uncertainty).

Entering micro-world the truthful temperature measurements at very small dimensionality (nano-range at the radius r) becomes size affected due to increasing role of the surface energy [8], which could be depicted by a universal equation: $T_r/T_\infty \cong (1 - C/r)^p$ where ∞ portrays standard state and C and p are empirical constants ($\approx 0.15 < C < 0.45$ and $p = 1$ and/or ½) [9]. Entering the micro-world requires, however, the introduction of special techniques based on small sized samples [10], micro-detecting techniques [11] and in limit quantum aspects of measurements [12] significant for self-organized reactions [1].

[1] J. Šesták. books: *Heat, Thermal Analysis and Society*, Nucleus, Hradec Králové 2004; and *Science of Heat and Thermophysical Study: a generalized approach to thermal analysis*, Elsevier, Amsterdam 2005

[2] J. Šesták, J.J. Mareš, P. Hubík, I. Proks: *Contribution by Lazare and Sadi Carnot to the Caloric Theory of Heat: its Role in Thermodynamics.* J. Thermal Anal. Calor. 97, 679 (2009)

[3] J. Black: *Lectures on the Elements of Chemistry*. W. Creech, Edinburgh (1803), German transl.: *Vorlesungen über Chemie*. Crell, Hamburg (1804)

[4] 4. J. J. Mareš, P. Hubík, J. Šesták, V. Špička, J. Krištofik, J. Stávek:: *Phenomenological Approach to the Caloric Theory of Heat* Thermochim. Acta 474 (2008) 16

[5] J.J. Mareš, P. Hubík, J. Šesták, V. Špička, J. Stávek: *Temperature relativistic transform. and Mosengeil-Ott's antinomy*, Physica E, 42, (2010) 487

[6] J. Šesták, P. Hubík, J.J. Mareš: *Thermal analysis scheme aimed at better understanding of the Earth's climate due to the alternating irradiation,* J. Thermal Anal. Calor, in print 2010

[7] B. Wunderlich: *Temperature-modulated calorimetry in the 21st century,* Thermochim. Acta 355 (2000) 43

[8] Z. Zhang , J.C. Li, Q. Jiang: *Modelling for size-dependent and dimension -dependent melting of nanocrystals,* J. Phys. D: Appl. Phys. 33, 2653 (2000)

[9] G. Guisbier, L. Buchaillot: *Universal size/shape-dependent law for characteristic temperatures,* Phys. Lett. A374, 305 (2009)

[10] A.A. Minakov, S.A. Adamovsky, C. Schick: *Non-adiabatic thin-film (chip) nanocalorimetry,* Thermochimica Acta 432 (2005) 177

[11] D. M. Price, M. Reading, A. Hammiche, H. M. Pollock: *Micro-thermal analysis: scanning thermal microscopy and localised TA,* Int. J. Pharmaceutics 192, (1999) 85

[12] J.J. Mareš, J. Šesták: *An attempt at quantum thermal physics*" J. Thermal Anal. Calor. 82 (2005) 681

Messschwankungen bei DSC Messungen
Konsistenztest nach Schullerus

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Die Probenkonfiguration, (thermischer Kontakt, Position, Masse, Dicke und Form) ist in der DSC ein Faktor, den man zwar kennt, doch den man meistens nicht berücksichtigt. Das ist verständlich, da man in vielen Fällen hier experimentell keine Reproduzierbarkeit sicherstellen kann.

Beobachtet man nun bei einer Folge von Messungen von Proben ein und desselben Materials Schwankungen der gemessenen Größe, so stellt sich die Frage, ob diese tatsächliche Unterschiede in den verschiedenen Proben spiegeln, oder nur eine Folge von Schwankungen im Messverfahren sind.

Anhand von experimentellen Daten wird zunächst für ein Material vorgestellt, wie groß solche Schwankungen ausfallen können und mit welchem Fehler man dabei rechnen muss. Daraufhin wird gezeigt, wie man diesen Fehler reduzieren kann, wenn man eine weitere Messgröße hinzuzieht. Tatsächlich misst man in einer klassischen DSC eigentlich eine einzige Messgröße, nämlich den Temperaturunterschied zwischen Probe und Referenz. Größe und Änderung dieses Temperaturunterschiedes liefert über Kalibration und verschiedene Konventionen dann Werte für unterschiedliche physikalische Größen, von denen die einfachsten die spezifische Wärme, der Schmelzpunkt und der thermische Effekt einer Phasenumwandlung sind. Unterliegt die gesamte Messung gewissen Schwankungen, so müssen sich diese also in allen gemessenen Größen widerspiegeln oder anders gesagt, die vorher genannten Messgrößen sind miteinander korreliert. Das beschränkt sich natürlich nur auf die im Messverfahren ermittelten Schwankungen, denn tatsächlich sind diese physikalischen Größen unabhängige Stoffkonstanten.

Auf diese Tatsache stützt sich der vorgestellte Konsistenztest nach Schullerus, der anhand dieser Korrelationen die Stichhaltigkeit eines Messergebnisses in bestimmten Fällen charakterisiert. Als Beispiel werden dafür noch Messergebnisse von Kalibrationsproben von In vorgestellt, in denen allein die Probenposition durch exzentrische Anordnung der Probe und das Drehen dieser Probe variiert wurde. Dabei werden Schmelzpunkt und Schmelzenthalpie gegen den absoluten Wert des DSC – Messsignals bei 150°C grafisch aufgetragen. Eine gute Korrelation ist dann auch ein Maß für die Güte der Messung bzw. des Messsystems. Andererseits kann man daraus auch bestimmte Messunsicherheiten abschätzen.

Anwenden lässt er sich natürlich auf alle Arten von Reihenuntersuchungen, bei denen es möglich ist, vor dem untersuchten Prozess einen stabilen Punkt der Basislinie auszumachen (wo allein die spezifische Wärme zur Wirkung kommt), anhand dessen diese Korrelation untersucht werden kann.

The Use of an Integrated Thermodynamic Databank System for the Investigation of Enthalpy Related Reactive Systems

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The concept of using Gibbsean thermodynamics as an approach to tackle problems of industrial or academic background is not new at all. Its early applications go back to the beginning of the 20th century, however mostly on the basis of investigating stoichiometric reactions. Only the later development of model equations for the Gibbs energy of non-ideal condensed solutions, the collection of comprehensive databases and the development of computer code for the calculation of complex equilibria, which have all taken place in the second half of the 20th century, have led to what we now call Computational Thermodynamics. The standard tools are called Integrated Thermodynamic Databank Systems since they incorporate on the one hand modules for the administration of thermodynamic data for large and complex systems and on the other application modules which permit the use of the data for stoichiometric reaction calculations as well as for complex multi-component multi-phase equilibria. The ultimate use of such programs is the generation of phase diagrams based on the Gibbs energies of the various phases and the rules of zero-phase fraction lines.

An outline of the development of the databases and the application software will be given and case studies related to reactive systems with strong heat effects will be demonstrated, among these the prediction of adiabatic flame temperatures, the thermite process for the welding of rails, and the isothermal and adiabatic reduction of molybdenum oxide with aluminium. Furthermore, a short overview of the proper calculation of Cp in multi-phase systems with strongly temperature dependent phase boundaries is given. Finally, phase diagrams with enthalpy as one axis will be demonstrated.

Experimental Studies and Thermodynamic Modelling of ZrO_2-based Systems

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The RE_2O_3 additives (RE are Rare Earth metals) improve properties of YSZ in application for thermal barrier coating (TBC). Two main groups of candidates for new TBC materials are reported, one based on co-doping of YSZ with one or more Rear Earth oxides and the other on pyrochlore type zirconates $RE_2Zr_2O_7$. The aim of present investigation is to develop thermodynamic database for the ZrO_2-RE_2O_3-Y_2O_3 (RE=La, Nd, Sm) systems. Thermodynamic modelling is an important tool to evaluate stability of TBC materials on thermal cycling. The heat capacity is an important thermodynamic property which is used for temperature extrapolation of enthalpy and entropy. On the other hand, thermal conductivity, which is one of the major properties of TBC, can by calculated from thermal diffusivity and heat capacity data.

Thermodynamic databases for the ZrO_2-RE_2O_3-Y_2O_3 systems (RE=La, Nd) were derived using binary extrapolations into ternary systems. The calculated phase diagrams were used to select compositions for experimental investigations. Samples obtained by co-precipitation technique were heat treated at 1250, 1400 and 1600°C. Phase assemblages formed during heat treatment were identified by XRD. Selected samples in the ZrO_2-RE_2O_3-Y_2O_3 and ZrO_2-Nd_2O_3-Y_2O_3 systems heat treated at 1250°C were investigated by DTA and afterwards by XRD.

DTA investigation confirmed that at temperatures ~1400°C $La_2Zr_2O_7$ (pyrochlore structure) reacted with Y_2O_3 forming disordered fluorite structure. The obtained experimental results were used for more advanced modelling of pyrochlore and fluorite phases. Substitution of La^{+3} and Zr^{+4} by Y^{+3} was taking into account in modelling of pyrochlore phase by sublattice model. Binary La-Y and ternary La-Y-Zr mixing parameters were introduced into fluorite phase to reproduce extension of fluorite homogeneity range with the temperature in the ZrO_2-La_2O_3-Y_2O_3 system. The phase equilibria in the ZrO_2-Nd_2O_3-Y_2O_3 systems were experimentally investigated at 1250-1600°C and obtained results were used to assess mixing parameters in fluorite, A and C phases. DTA investigations confirm chemical reactions in the system.

The differential scanning calorimetry was used to determine heat capacity of the $La_2Zr_2O_7$, $Nd_2Zr_2O_7$ and $Sm_2Zr_2O_7$ phases with pyrochlore structure. The obtained results agree with literature data within uncertainty limits. The heat capacity data for the $LaYO_3$ orthorhombic perovskite was obtained in present work for the first time. The obtained results are slightly below calculations based on the Neumann-Kopp rule. The obtained data will be used to improve thermodynamic modelling of the La_2O_3-Y_2O_3 system.

Flüssigphasenbildung im System Al_2O_3, Y_2O_3, SiC

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Die Flüssigphasenbildung im System Al_2O_3, Y_2O_3, SiC wurde mittels Simultaner Thermischer Analyse (Thermogravimetrie/Differenz Thermo Analyse) untersucht. Zu diesem Zweck wurden Proben mit unterschiedlichen Yttriumoxid und Aluminiumoxid Mol- Verhältnissen und 10 und 20 Gewichtsprozent SiC verdichtet und bei unterschiedlichen Temperaturen thermisch nachbehandelt. Die thermoanalytischen Ergebnisse zeigen, dass der SiC- Gehalt geringen Einfluss auf die Schmelztemperatur der oxidischen Phase hat. Die ausgebildeten Phasen und das ausgebildete Gefüge wurden per REM, EDX und XRD untersucht. Die Ergebnisse wurden mit thermodynamischen Berechnungen verglichen.

Crystal Growth and Thermal Analysis in Reactive Atmospheres Assisted by Thermodynamic Modeling

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Bulk crystal growth processes on an industrial scale are based mainly on crystallization from melts, e.g. by the Czochralski (pulling from a crucible) or by the Bridgman (crystallization inside a crucible) methods. The transport of crystallization heat from the growing crystal is performed via thermal gradients. Consequently, crystal, melt, and constructive parts such as crucible must be stable within a given atmosphere over an extended temperature range. For oxygen-free substances, chemical stability can often be reached working in an oxygen-free "inert" atmosphere (Ar, N_2). The same holds for thermal analysis where "inert" atmospheres are useful e.g. for the analysis of metals and alloys.

The valence state m of an oxide $MeO_{m/2}$, however, is stable only within a temperature dependent oxygen partial pressure range $\left(p_{O_2}^{\min}(T), p_{O_2}^{\max}(T)\right)$, as otherwise reduction to m-1 or oxidation to m+1 will occur [1]. The $G(T)$ curves for such redox equilibria ("Ellingham diagrams") are defining phase fields where one specific valence state m for every component Me of the system is stable, and such phase fields can easily be calculated by software packages such as FactSage [2]. It will be shown that for some systems no "inert" atmosphere can be found that maintains the desired valence stable for all components. Modeling and experiments showed that e.g. iron(II) oxide and zinc oxide [3] can be stabilized by carbon dioxide as "reactive" part of the atmosphere. Especially for ZnO this is relevant from the practical point of view as this material is an interesting semiconductor and as TCO (*transparent conducting oxide*).

References

[1] D. Klimm et al., *J. Cryst. Growth*, **2009**, *311*, 534–536.
[2] FactSage 6.1, GTT Technologies Herzogenrath, Germany, www.factsage.com
[3] D. Schulz et al., *J. Cryst. Growth*, **2006**, *296*, 27–30.

Thermodynamic Assessment of the Ti–Al–Nb System using Data from Thermal Analysis

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The calculations of phase diagrams (CALPHAD) method was used to develop a thermodynamic description for the Ti–Al–Nb system, which is a critical system for the development of new materials for gas turbine engine blades. These new materials are based on two phase alloys consisting of disconnected σ–Nb_2Al precipitates in a γ–TiAl matrix and are promising as they are expected to display high temperature strength, creep resistance, and fracture toughness properties as well as low temperature ductility.

The key advantage of the CALPHAD approach is the ability to predict phase equilibria in unknown regions of the phase diagram using phase diagrams calculated from an optimized thermodynamic dataset developed for the multi-component system. Thermodynamic optimization using the CALPHAD approach relies heavily not only on tie-line data of the phases in equilibrium, but also on phase transformation and phase reaction temperatures which can be determined using the methods of thermal analysis. Therefore, in this work, differential thermal analysis (DTA) was performed on selected alloys of interest to determine phase transformation and reaction temperatures. This was combined with high temperature XRD as well as heat treating and quenching experiments to identify the phases before and after DTA peaks. The measured phase reaction temperatures were used as direct input data for the optimization of the thermodynamic parameters of the phases.

Various kinds of phase diagrams and phase fraction diagrams were calculated to assess the agreement between the calculated phase diagrams and the experimental data. Particular emphasis was placed on the agreement between the calculations and the phase transformation temperature data determined using the thermal analysis measurements. The calculations show that the generated dataset is now in good agreement with the measured temperatures of the $\beta \rightarrow \beta + \gamma$–TiAl, $\beta + \gamma$–TiAl $\rightarrow \beta + \gamma$–TiAl + σ-Nb_2Al, and $\beta + \gamma$–TiAl + σ-$Nb_2Al \rightarrow \gamma$–TiAl + σ-Nb_2Al reactions for the alloys of interest.

Eine thermodynamische Betrachtung der Direkten Synthese von Methylchlorsilanen

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Die kupferkatalysierte Herstellung von Methylchlorsilanen, die sogenannte Direkten Synthese, ist eine sehr komplexe Reaktion, über die seit Jahren sehr kontroverse Diskussionen über den Mechanismus oder den Einfluss von Metallen und Promotoren geführt werden. Die Komplexität der Reaktion liegt in einer sehr breiten Produktverteilung, die von zahlreichen Faktoren beeinflusst wird. Hierzu zählen die Zusammensetzung des Metallkatalysators und seine Herstellung, Art und Menge von Promotoren bzw. Promotorengemischen, der Reaktionsdruck, die Reaktionstemperatur, der verwendete Reaktortyp und damit die hydrodynamischen Gegebenheiten (z.B. Verweilzeiten, Stofftransport), wie auch Anreicherungs- und Transportprozesse in der Katalysatormasse oder die elektronische Dotierung des eingesetzten Siliciums.

Aus thermodynamischer Sicht ist es bemerkenswert, dass das Hauptprodukt der Direkten Synthese Dimethyldichlorsilan zu den Verbindungen mit der höchsten freien Bildungsenthalpie im Stoffsystem Si-C-H-Cl zählt, die Reaktion aber eine bemerkenswerte Selektivität für dieses Produkt zeigt. Andere Silane, wie Siliciumtetrachlorid oder Trichlorsilan, welche sehr negative freie Bildungsenthalpien besitzen, werden nur in Spuren gebildet. Deshalb wurden die thermodynamischen Gegebenheiten der Direkten Synthese einer genaueren Analyse unterzogen, um die grundlegenden chemischen Gleichgewichtsprozesse unabhängig von anderen Einflussfaktoren, wie z.B. von Transportprozessen, hydrodynamischen Einflüssen oder Inhomogenitäten betrachten zu können.

Die thermodynamische Modellierung der Direkten Synthese basiert auf einem Datensatz, der alle Silane, Chlorsilane, Methylsilane und Methylchlorsilane mit einem Siliciumatom, weiterhin Kohlenwasserstoffe, Chlorkohlenwasserstoffe sowie verschiedene Verbindungen von Katalysatormetallen besteht. Durch ein systematisches Unterdrücken der Entstehung bestimmter Verbindungen gelingt es, Stabilitätsreihenfolgen der Reaktionsprodukten aufzustelle. Weiterhin konnten drei prinzipielle Reaktionswege identifiziert werden, die erst bei vollständiger Unterdrückung zur Bildung des Hauptproduktes Dimethyldichlorsilan führen. Hierbei handelt es sich um 1) die Entstehung von Kohlenstoff, Kohlenwasserstoffen, Chlorkohlenwasserstoffen, Wasserstoff und Chlorwasserstoff aus der Spaltung der C-H-Bindung, 2) die Bildung von wasserstoffhaltigen Methylchlorsilanen in Gegenwart von Chlorwasserstoff oder Wasserstoff sowie 3) die Konkurrenz der thermodynamisch bevorzugten Chlorsilane mit Methylchlorsilanen. Weiterhin zeigte sich, dass die Anwesenheit bestimmter Metalle keine Auswirkung auf die Silanbildung hat.

Experimental and Theoretical Methods in Gas Phase Thermochemistry

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An overview of the most important classical methods for determination of thermodynamic data of gaseous species is given:

Manometric Techniques
Transpiration method
Knudsen effusion method
Vapour density measurements

In more detail massspectrometric measurements are discussed, especially the analysis of molecular beams formed by Knudsen effusion techniques. Simple evaporation reactions lead to gas phase compositions above solids or liquids. From these compositions thermodynamic data of gaseous species, even in low concentrations, can be derived. This is shown at the example of the evaporation of solid $PbCl_2$. In order to get information about thermochemistry of chemical reactions at high temperatures under participation of gaseous species, special Knudsen cell assemblies have been constructed. By means of these the gaseous products of a lot of solid/gas-reactions have been analyzed. As an example the reaction of solid $CoCl_2$ with gaseous $AlCl_3$ is discussed.

The gas phase composition can be determined qualitatively and quantitatively within the limits of error. The determination of gas phase composition as a function of temperature leads to enthalpy and entropy of the reaction under discussion. Introducing the entropy of reaction (by estimation or quantum chemical calculation) a determination of the equilibrium constant at a given temperature leads to the reaction enthalpy.

An overview about new results on gaseous sulphide-, selenide- and telluride halides of As, Sb, Bi, Nb, Ta, Mo and W is given. As an example the determination of the heats of formation of gaseous WS_2X_2 (X = Cl, Br, I) is described. In addition the thermodynamic data of these compounds have been determined by quantum chemical methods using the TURBOMOLE program package. The experimental and theoretical results are in excellent agreement. Quantum chemistry appears to be a suitable method for determination of thermodynamic data of gas phase species.

Estimation Of Time To Maximum Rate Under Adiabatic Conditions (TMR_{ad}) Using Kinetic Parameters Derived From DSC - Investigation Of Thermal Behavior Of 3-Methyl-4-Nitrophenol

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Kinetic parameters of the decomposition of hazardous chemicals can be applied for the estimation of their thermal behavior under any temperature profile [1-3]. Presented paper describes the application of the advanced kinetic approach for the determination of the thermal behavior also under adiabatic conditions occurring e.g. in batch reactors in case of cooling failure.

The kinetics of the decomposition of different samples (different manufacturers and batches) of 3-methyl-4-nitrophenol were investigated by conventional DSC in non-isothermal (few heating rates varying from 0.25 to 8.0 K/min) and isothermal (range of 200-260°C) modes. The kinetic parameters obtained with AKTS-Thermokinetics and AKTS-Thermal Safety Software [4] were applied for calculating reaction rate and progress under different heating rates and temperatures and verified by comparing simulated and experimental signals. After application of the heat balance to compare the amount of heat generated during reaction and its removal from the system, the knowledge of reaction rate at any temperature profiles allowed the determination of the temperature increase due to the self-heating in adiabatic and pseudo-adiabatic conditions.

Applied advanced kinetic approach allowed simulation the course of the Heat-Wait-Search (HWS) mode of operation of adiabatic calorimeters. The thermal safety diagram depicting dependence of Time to Maximum Rate (TMR) on the initial temperature was calculated and compared with the results of HWS experiments carried out in the system with Φ-factor amounting to 3.2. The influence of the Φ-factor and reaction progress reached at the end of the HWS monitoring on the TMR is discussed.

Presented calculations clearly indicate that even very minor reaction progress reduces the TMR_{ad} of 24 hrs characteristic for a sample with initial reaction progress amounting to zero.

Described estimation method can be verified by just one HWS-ARC, or by one correctly chosen ISO-ARC run of reasonable duration by knowing in advance the dependence of the TMR on the initial temperature for any □-factor. Proposed procedure results in significant shortening of the measuring time compared to a safety hazard approach based on series of ARC experiments carried out at the beginning of a process safety evaluation.

References

[1] B. Roduit, W. Dermaut, A. Lunghi, P. Folly, B. Berger and A. Sarbach, J. Therm. Anal. Cal., **2008**-1, 93, 163.

[2] B. Roduit, P. Folly, B. Berger, J. Mathieu, A. Sarbach, H. Andres, M. Ramin and B. Vogelsanger, J. Therm. Anal. Cal., **2008**-1, 93, 153.

[3] B. Roduit, L. Xia, P. Folly, B. Berger, J. Mathieu, A. Sarbach, H. Andres, M. Ramin, B. Vogelsanger, D. Spitzer, H. Moulard and D. Dilhan, J. Therm. Anal. Cal., **2008**-1, 93, 143–152.

[4] AKTS-Thermokinetics & AKTS-Thermal Safety software, AKTS AG, TECHNOArk 1, 3960 Siders, Switzerland, Advanced Kinetics and Technology Solutions, http://www.akts.com.

Calorimetric Investigations of Ultrathin Film of Poly-Vinylacetate under Controlled Humidity: Material Science, Calorimetry

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The film thickness dependency of glass transition in polymer films is still controversially discussed. For different experimental probes different dependencies are observed and a generally accepted link to molecular mobility is not yet established. AC-chip calorimetry is used as a very sensitive tool for calorimetric investigations of such thin films as demonstrated for thin polymeric films in a wide frequency range [1]. In several cases a direct comparison with results from other dynamic methods like dielectric spectroscopy is possible giving further insights.

There is also an increasing interest in thin films from a technological point of view. As these applications often include the presence of water the controlled humidity is used as a new parameter in addition to temperature for calorimetry. As a first example thin films of polyvinylacetate are measured where a large influence of humidity on the glass transition is known from literature.

References

[1] Huth, H., Minakov, A. A., Schick, C., J. Polym. Sci. B Polym. Phys. 2006 44: 2996.

Chemical Analysis of Spruce Wood during Thermal Exposure

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Wood is a typical component of homes equipment. If a fire is sparked in homes, the emanating smoke spreads rapidly and large quantities of toxic smoke gases are produced. Often it is a case of arson. The assessment of smoke emission and composition is essential for safety in flats and other facilities. A typical fire scenario, the smouldering, was experimentally realised in the Smoke Density Chamber (SDC). Aim of this work is to investigate the compositions of 3 kinds of products: gases, residues and particles during smouldering of spruce wood. The smoke emission and composition are depending on the thermal exposure. In a closed test chamber (SDC) the samples were exposed to horizontal thermal irradiation of 25 kW/m² (EN ISO 5659-2). During the smouldering procedures, under controlled ventilation conditions, the sample mass were continuously measured, thus, giving the weight loss vs. time. In addition, the transmission and the optical density of the smoke gases were determined during the smouldering of spruce wood. Thereby, the composition and the quantity of smoke gases (such as carbon monoxide, hydrogen cyanide, hydrochloric acid, etc.) were determined by using Fourier transformed infrared spectroscopy (FTIR). A mobile FTIR-spectrometer was directly coupled with the chamber and the gases were collected through a removable probe sensor, which offers the advantage to measure components of gases continuously. The composition of the gases changed during the smouldering, depending on the temperatures, and the exposure time. Furthermore it is certain that the type and amount of fire accelerants have also influence on the gas components as well as the impact of an additional gas ignition source. In addition to the gas components the resulting particles with their according particle size distribution were investigated during the smouldering in the Smoke Density Chamber as using Scanning Mobility Particle Sizer (SMPS) and Laser Counter (LC). Thereby, particle sizes can be detected from 6 nm up to 560 nm (SMPS) and from 300 nm up to 20 µm (LC). The third part of this work is the chemical analysis of the fire residues. The burned spruce wood samples were extracted in different solvents (toluol, methanol etc.) using the Accelerated Solvent Extraction (ASE). The extracts were evaporated and analyzed by gas chromatography coupled with mass spectrometry (GC-MS) in order to detect substances, like polycyclic aromatic hydrocarbons, PAH. Furthermore, the fire residues were investigated by Headspace-GC analysis in order to detect low concentrations of volatile components.

Holistically analytic observation of smouldering involved substances, such as solids and liquid fire residues, particles, and combustion gases were presented and discussed depending on the thermal exposure.

Characterization of nano-sized Diesel Exhaust Particles by TG-FTIR/MS and Electron Microscopy

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Nanoparticles are formed in modern combustion processes such as in diesel engines. In a view of increase of traffic, it is urgent to clarify the health risks involved with nanoparticles (also called “ultrafine particles” in the occupational safety field). An in-depth discussion about the potential hazards to human health of airborne biostable dust particles such as diesel exhaust requires the use of state-of-the-art characterization methods.

A combination of electron microscopy and thermal analysis is best suited for characterization of the diesel exhaust particles. Electron microscopy yields information on the morphology of the particles: dust agglomerates composed of primary particles 10-50 nm in size can be seen.

Thermal analysis can be of further assistance here. TG-FTIR/MS tests in an air atmosphere show differences in transformation behavior (decomposition and oxidation) at the same heating rate (20 K·min^{-1}). The FTIR coupling determines the composition of the gaseous oxidation products emitted (figure 1): CO_2 is developed in several steps by oxidation of the diesel exhaust particulates, and SO_2 is also produced.

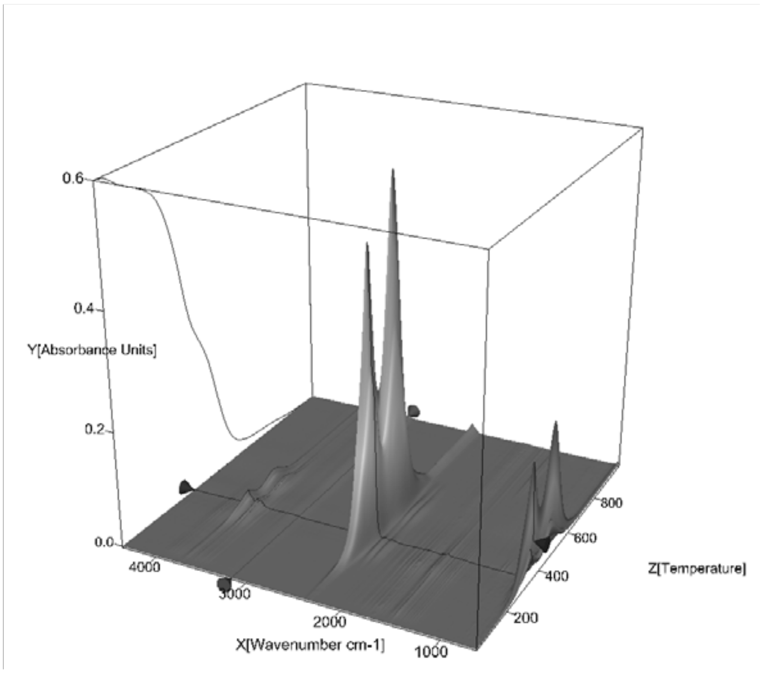

Figure 1: Results of a TG measurement with subsequent FTIR analysis

Diesel exhaust particulates of interest in occupational and environmental medicine consist of agglomerates of toxicologically-relevant ultrafine particles, which can optically barely be differentiated from one another. Due to their differing thermal stabilities, however, diesel exhaust particles of different modern diesel engines can be differentiated quickly and reliably by means of thermoanalytical characterization.

References

M. Heck; B. Brückel, R. Arhelger, D. Walter: Charakterisierung von Kfz-Dieselrußstäuben unterschiedlicher Provenienz, *Arbeitsmed. Sozialmed. Umweltmed.* **2009**, *44*, 187.

Assessment of the Explosive Properties and Thermal Hazards of Azodicarboxylates

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A large number of Azodicarboxylates are produced and used in research institutes and in the chemical industry for chemical synthesis. Therefore, the aim of our work was to assess the explosive properties and the thermal hazards of Azodicarboxylates. Diethylazodicarboxylate (DEAD) for instance is a very important reagent used in many chemical reactions [1, 2]. On the other hand DEAD represents an explosive hazard. It is very shock-sensitive and thermally unstable - it is sensitive if heated under defined confinement [3]. Therefore DEAD is only available in solution (e.g. 35% in toluene). But Toluene seems to be not suitable to suppress the explosive properties of DEAD. Because of the hazard risks the use of DEAD decreases and exchanges partly against the more stable Diisopropylazocarboxylate (DIAD) [4]. The intention of our work was to obtain a prediction about the structure-response relationship regarding the explosive properties and the thermal hazards of versatile used Azodicarboxylates. To describe the thermal stability of the Azodicarboxylates we used the Differential scanning calorimetry (DSC) and the simultaneous thermal analysis (STA) coupled with an infra red spectrometer (FT-IR).

As BAM is the competent authority in Germany for testing, classification and assignment of substances showing explosive properties, tests on selected Azodicarboxylates have been performed on the basis of the criteria given in the UN Recommendations on the Transport of Dangerous Goods [5].

References

[1] Mitsunobu, O., *Synthesis* **1981**, 1-28.

[2] Vijay, N., Smith, C. M., Akkuttu, T. B., Eringathodi, S., *Angew. Chem. Int. Ed.*, **2007**, *46*, 2070-2073.

[3] Urban, P.G. (Ed), *Bretherick’s Handbook of Reactive Chemical Hazards (6 th ed.),Butterworth–Heinemann Ltd., Oxford*, **1999**.

[4] Lu, Jian-Mei, Zhu, Zhi-Bin, Shi, Min, *Chem. Eur. J.* **2009**, *15*, 963-971.

[5] UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 4 th revised ed., United Nations, New York and Geneva, **2003**.

Molecular Interactions in the Context of the Stability and Reactivity of Crystalline Solids

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Solid phases exist as a result of interactions between the entities from which they are constructed. In the case of crystalline substances, these interactions can be identified and described in various ways. Although generally electrostatic in nature, such interactions can be examined in terms of covalent, ionic or coordination bond formation, or specific (H-bonding and electron-donor-acceptor) or non-specific (dispersive) interactions [1-3]. Crystals of organic substances exist as a result of specific and non-specific interactions between molecules (molecular crystals) or ionic interactions between charged entities. The crystal lattice energy of such substances, reflecting the energy released when a crystal is formed from gaseous entities (molecules, ions), can be predicted by summing the electrostatic, dispersive and repulsive contributions predicted from knowledge of atomic partial charges, atomic parameters and structural data. Values of the latter two quantities can be obtained by fitting equations describing crystal lattice energies to experimentally determined sublimation enthalpies [3]. Prediction of crystal lattice energies enables further thermodynamic characteristics of crystalline substances to be determined [2,3]. On the other hand, analysis of the mutual arrangement of molecules in crystals reveals numerous hydrogen-bond, π-π or interatomic interactions, the energy relations of which can be analyzed with the aid of quantum chemistry calculations for model systems. No general approach exists, however, for converting this knowledge to a description of the global interactions that retain molecules (entities) in crystals. These problems will be developed and discussed in the presentation.

In detail, the presentation will cover the analysis of molecular interactions in crystals and of molecular interactions in model systems, as well as the possibilities of determining sublimation enthalpies by thermoanalytical techniques (DSC, TG), computationally predicting crystal lattice energies and evaluating the stability and reactivity of selected organic crystalline substances [2,3]. These topics will be illustrated by the results of our and others original investigations.

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[1] J. J. Novoa, F. Mota, E. D'Oria, *Hydrogen Bonding - New Insights*, edited by S. Grabowski, Springer, The Netherlands, 2006, pp. 193-244.
[2] M. Sawicka, P. Storoniak, J. Blazejowski, J. Rak, *J. Phys Chem A.*, 110 (2006) 5066.
[3] K. Krzyminski, P. Malecha, P. Storoniak, B. Zadykowicz, J. Blazejowski, *J Therm Anal Cal.*, DOI 10.1007/s10973-009-0154-9.

Coupling µ-XRD^2 and DTA: New Insights in Processes with Delicate Temperature Dependence - the Gypsum – Bassanite – Anhydrite System as an Example

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The *in-situ* real-time combination of time and temperature resolved X-ray powder diffraction with differential thermal analysis (DTA) or differential scanning calorimetry (DSC) is a promising technique for a more detailed understanding of many temperature-dependent processes like phase transformations or dehydration processes with or without structural changes.

In this study, we show that the additional information about the dehydration process of gypsum to anhydrite in the temperature range from room temperature up to 450°C gained from coupled DTA/µ-XRD^2 measurements is necessary to truly reveal the complex nature of phase transitions, crystal structure relaxation and dehydration in the calcium sulfate system. For this, we used the combination of a self constructed DTA-system with a commercially available BRUKER D8 DISCOVER GADDS XRD^2-microdiffractometer. Due to the short measurement times of 10sec. for each diffraction pattern the 3 phase transformations from gypsum to the hemihydrate bassanite, a water-free bassanite structure (in literature referred to as γ-anhydrite, anhydrite-III) and finally the formation of the anhydrite (anhydrite II) structure could be observed in detail parallel by both methods in the same sample. Additionally, the reversible dehydration/rehydration process of the incorporation of H_2O-molecules into the channels of the bassanite/γ-anhydrite-structure at around 100°C could be studied for the first time parallel by coupling XRD and DTA measurements.

Demonstrating the striking advantages of the combined X-ray / thermal analysis approach, we see a high potential of this method not only for inorganic solids like the gypsum dehydration outlined in our study, but also for organic materials and especially pharmaceutical compounds.

The Interplay of Thermal and Mechanical Activation. An Attempt to Understand Exothermal Water Release from Pseudoboehmite Phases

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Thermal analysis *on line* coupled to mass spectrometry (TA-MS) or *off line* combined with ESR, Mössbauer spectroscopy, XRD, and chemical analyses were employed for the investigation of mechanically activated alumogels. Sol gel - prepared alumogels are precursors for the formation of α-Al_2O_3 (*e.g.* in the form of protective coating) upon thermal treatment. An important applicational aspect is the aim to decrease the crystallization temperature of corundum which shall be achieved by iron doping, by starting from sol gel - prepared xerogels, by mechanical activation of crystalline precursors (such as AlOOH) or by the combination of all [1].

Exothermal DTA effects for the water release exibiting a quite unusual curve shape have been observed both for mechanically activated alumogels obtained via the sol gel route (possibly containing residual nitrate) and strongly amorphisized AlOOH samples. The exo effects appear at comparably low temperatures (150-350°) and in presence of hydrogen. The combination of TA-MS with ESR allowed the identification and, to some extent, the quantification of trapped NO_2 molecules as well as to follow the mechanically and thermally induced changes in the transforming Al-O-H matrix via the contained (or doped) Fe^{3+} impurities.

The appearence of the exothermal DTA effects is related not only to a strong mechanical activation and the access of hydrogen during the thermal treatment but also to the interaction of hydrogen with metallic platinum, *e.g.* as crucible material or as metal powder. This interaction is discussed to be the origin of the chain start of the radicalic reaction between H_2 and NO_2 yielding H_2O and NO [3].

References

[1] M. Nofz, R. Stößer, G. Scholz, I. Dörfel, D. Schultze, *J. Europ. Ceram. Soc.,* **2005**, *25*, 1095-107.

[3] R. Stößer, M. Feist, *J. Phys. Chem. C*, **2008**, *112*, 16438-44.

Poster Abstracts

Phase Relations in the Ternary System $CuO/Ag_2O/P_2O_5$

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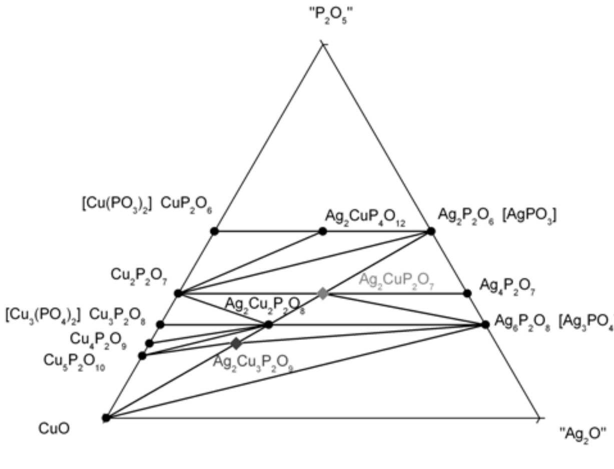
The phase relations in the ternary System $CuO/Ag_2O/P_2O_5$ were investigated by solid state reaction and analyzed using X-ray powder diffraction, thermal analysis, UV-vis spectroscopy and IR spectroscopy [1]. The samples were prepared by stoichiometrically amounts of $AgNO_3$, CuO and $(NH_4)_2HPO_4$, which are grinded up in agate mortar and subsequently heated in muffle furnace at a temperature range of 400 – 750 °C for several days.

In agreement with Laügt [2] and Quarton [3] the quaternary phases $Ag_2Cu(P_2O_6)_2$ and $Ag_2Cu_2P_2O_8$ could be synthesized. Furthermore there could be determine two more quaternary phases with independent diffractograms, which can described with the formula $Ag_2CuP_2O_7$ and $Ag_2Cu_3P_2O_9$. The results of the whole phase analysis are shown in the phase diagram.

The thermal analysis of $Ag_2CuP_2O_7$ shows one sharp endothermic peak at 508 °C and a spread endothermic effect, that incipient at 800 °C. There is also a wide endothermic effect starting at 300 °C. This new phase is unstable starting at 400 °C and decomposes in $Ag_4P_2O_7$ and $Cu_2P_2O_7$.

For $Ag_2Cu_3P_2O_9$ there could be captured 6 endothermic effects. One little spread peak at 720 °C and a bigger sharp one at 763 °C. Continue two little spread peaks at 886 and 926 °C as soon as a maximum peak, which incipent at 939 °C. Single crystals were received of a melt in a platinum crucible at 800 °C. In cooperation with Dr. Borrmann (MPI CfPS Dresden) we could enlighten the cell and lattice parameters of this new phase. $Ag_2Cu_3P_2O_9$ belongs to a monoclinic unit cell with a possible space group P21/c and with lattice parameters of a = 8,44 Å, b = 11,50 Å, c = 16,44 Å and β = 90,17°.



Phase Relations in the Quaternary System $CuO/Ag_2O/P_2O_5$
at a temperature range of 400 till 750°C

References

[1] T. Schuffenhauer; Diploma Thesis, HTW Dresden, **2009.**

[2] M. Laügt; Comp. Rend. Sea. de l'Academie des Sciences, Serie C: Sciences Chim., **1968**, 267(22), 1489-91.

[3] M. Quarton, T. Oumba; Mat. Res. Bull., **1983**, 18, 967-974.

Phase Relations and Chemical Transport in the System Mo/V/O

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In the ternary system Mo/V/O were due to solid state reaction of three solid solutions prepared and analyzed using X-ray diffraction [1]. In accordance with Hörlin [2] be in the quasi-binary system of dioxides formed two solid solutions. The solubility of MoO_2 in VO_2 is more then 70% ($V_{1-x}Mo_xO_2$, $0 \leq x \leq 0.7$). The solubility of VO_2 is significantly lower at up to 25% ($V_{1-x}Mo_xO_2$, $0.75 \leq x \leq 1$). The miscibility gap is with less then 10 % too small to be accurately determined by X-ray diffraction. Another solid solution series is derived from V_2O_3 in agreement with Tenailleau et al. [3] and can be described by the formula $(V_{1-x}Mo_x)_2O_3$ ($0 \leq x \leq 0.2$). The results of phase analysis are shown in the phase diagram.

The sintered samples were placed to 50 mg $HgCl_2$ in evacuated sealed quartz ampoules in a temperature gradient from 900 to 800 ° C. The obtained crystals have a size of up to 5 mm and vary in their habit. The molybdenum-rich solid solutions show a bronze colour and an isometric shape similar to MoO_2. The vanadium-rich solid solutions show a silver-grey colour and form rod-shaped crystals. The migration rates amount to 2 to 3 mg/h. The composition of the crystals was analyzed by EPMA. It is usually found crystals with different composition. It is usually molybdenum-rich mixed crystals deposited next to depleted vanadium mixed crystals. The solid solution $(V_{1-x}Mo_x)_2O_3$ shows nearly the same behaviour.

The simulation of the transport experiments carried out with the program TRAGMIN [4]. The values for the heat capacity of solid solutions were estimated according to the Neumann-Kopp rule. The mixing enthalpy have been approached about $\Delta_{mix}H = \Omega \cdot x \cdot (1-x)$ with $\Omega = -140$ KJ/mol [5]. The mixing entropy was derived through $S_{mix} = x \cdot R \cdot \ln x + (1-x) \cdot R \cdot \ln(1-x)$ [5].

From the transport efficiency calculation can formally be derived for the transport reaction of $V_{0,5}Mo_{0,5}O_{2,s}$ with $HgCl_2$ the following equation:

$$V_{0,5}Mo_{0,5}O_{2,s} + 5/4\ HgCl_{2,g}\ D\ ½\ MoO_2Cl_{2,g} + ½\ VOCl_{3,g} + ¼\ O_{2,g} + 5/4\ Hg_g$$

The calculated migration rate is 2.4 mg/h. The molybdenum enrichment could be not simulated.

References

[1] R. Wege; Diploma Thesis, HTW Dresden, **2007.**
[2] T. Hörlin, T. Niklewski, M. Nygren; Mat. Res. Bull. **1973**, 8, 179.
[3] C. Tenailleau, E. Suard, J. Rodrigues-Cravajal, A. Gibaud, P. Lacorre; J. Solid. State Chem. **2003**, 174, 431.
[4] G. Krabbes, W. Bieger, K.-H. Sommer, T. Söhnel; TRAGMIN 4.01; IFW Dresden und TU Dresden (1993-95).
[5] G. Krabbes, W. Bieger, K.-H. Sommer, E. Wolf; J. Cryst. Growth **1991**, 110, 433.

Phase Relations in the Quaternary System Cu/Ni/P/O

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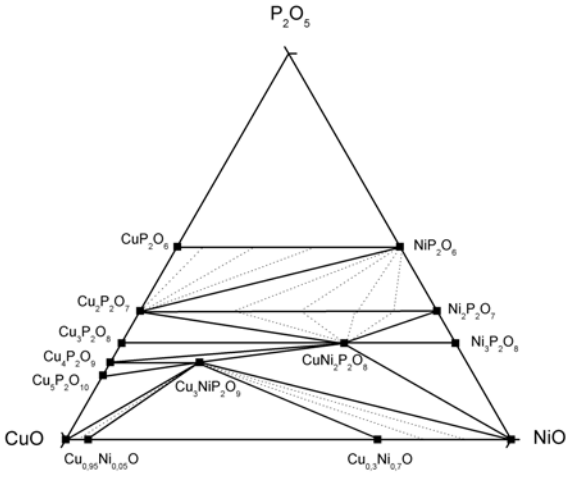
In the quaternary system Cu/Ni/P/O were due to solid state reaction of a stoichiometric mixture of CuO, $NiCO_3$ and $(NH_4)_2HPO_4$ several samples prepared and analyzed using X-ray diffraction, UV-Vis spectroscopy and TG-DTA [1].

XRD examination indicated complete miscibility (solid solution) of metaphosphates of copper and nickel that can be described by the formula $Cu_{1-x}Ni_xP_2O_6$ ($0 \le x \le 1$) and in accordance with Handizi et al. [2] mixed pyrophosphates, according to $Cu_{2-x}Ni_xP_2O_7$ ($0 \le x \le 2$). The obtained UV-Vis spectra approved the infinite substitution of Ni^{2+} for Cu^{2+} during its quasi-binary systems.

The X-ray phase analysis of the orthophosphates in the composition $Cu_{3-x}Ni_xP_2O_8$ ($0 \le x \le 3$) indicated the presence of three several phases against sample compounding: more precisely there was observed a two-phases-area consisting of $Cu_3P_2O_8$ and the heterometallic phosphate $CuNi_2P_2O_8$, alternatively $Ni_3P_2O_8$ and $CuNi_2P_2O_8$. The quaternary phase $CuNi_2P_2O_8$ was obtained, as expected from the results of J. Escobal et al. [3].

For metall-rich products in the composition $Cu_{4-x}Ni_xP_2O_9$ ($0 \le x \le 4$) a new quaternary single phase $Cu_3NiP_2O_9$ was obtained. According to single crystal X-ray analysis $Cu_3NiP_2O_9$ exhibits a monoclinic structure that belongs to space group P1 21/n1 (14). The calculated lattice parameters are a = 8,2288(2) Å, b = 9,8773(2) Å and c = 8,2777(3) Å, with α, γ = 90(0)°, β = 107,82(2)° and V = 640,50(3) Å , Z = 2. The UV-Vis spectrum shows strongest light reflectance at 572 nm. The TG-DTA of the $Cu_3NiP_2O_9$ showed between 940 - 1100 °C four endothermic peaks, caused by the incongruently melting. The results of phase analysis are shown in the phase diagram.



Phase diagram of the Quaternary System Cu/Ni/P/O (900 °C)

References

[1] I. Weimann; Diploma Thesis, HTW Dresden, **2007.**
[2] A. Handizi, A. Buokhari; Mat. Res. Bull. **1993**, 28, 1241.
[3] J. Escobal, A. Goni, L. Lezama, J. Pizzaro, M. Arriortua, T. Rojo; J. Solid State Chem. **2006**, 179, 3052.

Emission of harmful compounds during the thermal decomposition of floor coverings

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Today almost all furniture, building materials, equipment used in offices, schools, apartments consist of synthetic materials based of organic compounds. Expose to increasing of temperature they can be the source of harmful and toxic chemical compounds putting our health and life to endanger. The thermal analysis combined with mass spectrometry was used to identify gaseous products of thermal decomposition of some floor coverings for home and commercial use. As a subject of investigation laminate flooring (panels), carpets and floor coverings with PCV were used. All of these materials consist of layers and every layer was isolated as an experimental material. Panels are based on HDF – Hight Density Fibreboard, with top surface coated with a decorative melamine film. Carpets are mainly consists of synthetic materials like polyamides or polypropylene. The vinyl floor coverings are based on PCV pure and with inorganic filler (like carbonates).

The thermal decompositions with gaseous products analysis (by quadrupole mass spectrometer) were carried out in oxidizing (synthetic air) and inert (helium) atmosphere. The gaseous products of thermal decomposition of laminate flooring in helium and air are: formaldehyde, CO, CO_2, ammonia,H_2O, C_xH_y, HCN and in air also NO_x are observed. Analysis of mass spectrum leads to identifying the C_xH_y, HCl, methane, chlorine, benzene, toluene, CO_2 and H_2O as the main gaseous products of thermal decomposition of flooring based on PCV. For decomposition of carpets carbohydrogens, NH_3, HCN, carbon dioxide, cyclopentanone and caprolactam were identifying.

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Combinatorial Discovery of Catalysts for the Oxidation of Soot from Diesel Exhaust Gases with Thermal Analysis

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At the end of 2005 the German “Bundesministerium für Bildung und Forschung” (BMBF) launched the collaborative project “NanoKat” aiming at the development of using nano-scaled materials on the surfaces of combustion engines as well as in the exhaust tract to avoid diesel engine particulate emissions via catalytically coated DPFs. In its initial stages the project focused on the combustion of particulate matter in the filter system. Currently the catalytically active materials are in the optimization process in terms of stability and poisoning by exhaust gas components like sulphur compounds.

Our part of this project concentrates on the combinatorial synthesis of libraries of doped substrate materials such as CeO_2, TiO_2, ZrO_2, Al_2O_3 and SiO_2. The corresponding DoE was developed according to prior knowledge, e.g. literature data concerning catalytically active elements for soot oxidation. The combinatorial libraries were synthesized via acid-catalyzed sol-gel methods using nitrate or alkoxide solutions of the substrate elements and alcoholic solutions of the doping elements. The high-throughput characterisation of the libraries was accomplished by screening the combustion of soot in varying amounts of synthetic air using the emissivity-corrected IR thermography (ecIRT).

The most active materials detected by IR-measurement were further analyzed in a Diesel exhaust model gas through simultaneous thermoanalytical measurements (TG, DSC)[2,3] as well as in a conventional flow reactor. The best catalysts for soot combustion are optimized in composition spreads. The combustion temperature minimum in the compositional response surface, as so-called hit, is the starting point for the next generation of materials. With this combinatorial workflow the T_{50} value of soot combustion could be minimized to a temperature lower than 400°C.

References:

[1] http://eur-lex.europa.eu/LexUriServ/site/en/com/2005/com2005_0683en01.pdf.
[2] N.E. Olong, K. Stöwe, W.F. Maier, *Appl. Catal. B* **2007** *74* 19-25.
[3] N.E. Olong, K. Stöwe, W.F. Maier, *Catal. Today* **2008** *137* 110-118.

Characterization of titania precursors on heating in air

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The precursors of titanium dioxide (titania) to be used as photoactive materials [1, 2] were prepared from $TiOSO_4.xH_2O$ using subsequent precipitation by ammonia at the temperature of 0 °C. Two samples of titania precursors studied were prepared at slightly different laboratory conditions: the pH of both preparation solutions was equal pH ~ 3.5; the time of the precipitation differed (105 and 35 minutes for the samples No. 1 and 2, respectively).

The thermal behavior of the titania precursors was characterized by methods of thermal analysis on air heating from 25 to 1200 °C (differential thermal analysis, thermogravimetry, evolved gas analysis by mass spectrometry, emanation thermal analysis, ETA). The non-traditional method of ETA [3, 4] made it possible to indicate temperature intervals of microstructure changes during heating of the precursors and to evaluate the microstructure development of the samples in the conditions used for the heating.

The results of thermal analysis methods (Figs. 1 and 2) were used to characterize processes taking place on heating the precursors and to optimize laboratory conditions for the preparation of titanium dioxide (titania) of requested properties.

Acknowledgments

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References

[1] Y. Gao, Y. Masuda, W.-S. Seo, H. Ohta, K. Koumoto, *Ceramics International*, **2004**, *30*, 1365.
[2] P. Pulišová, J. Boháček, J. Šubrt, L. Szatmáry, P. Bezdička, E. Večerníková, V. Balek, *Proc. of CCTA10 held in Zakopane, J. Therm. Anal. Cal.,* accepted for publication.
[3] V. Balek and M. E. Brown, *Less common techniques, in: Handbook on Thermal Analysis and Calorimetry*, *Vol. 1 Chapter 9*, Edited by M. E. Brown, Elsevier Science B. V., **1998**, p. 445.
[4] V. Balek and J. Tölgyessy, *Emanation thermal analysis and other radiometric emanation methods, in Wilson and Wilson's Comprehensive Analytical Chemistry, Part XIIC*, G. Svehla Ed., Elsevier Science Publishers, Amsterdam **1984**, p. 304.

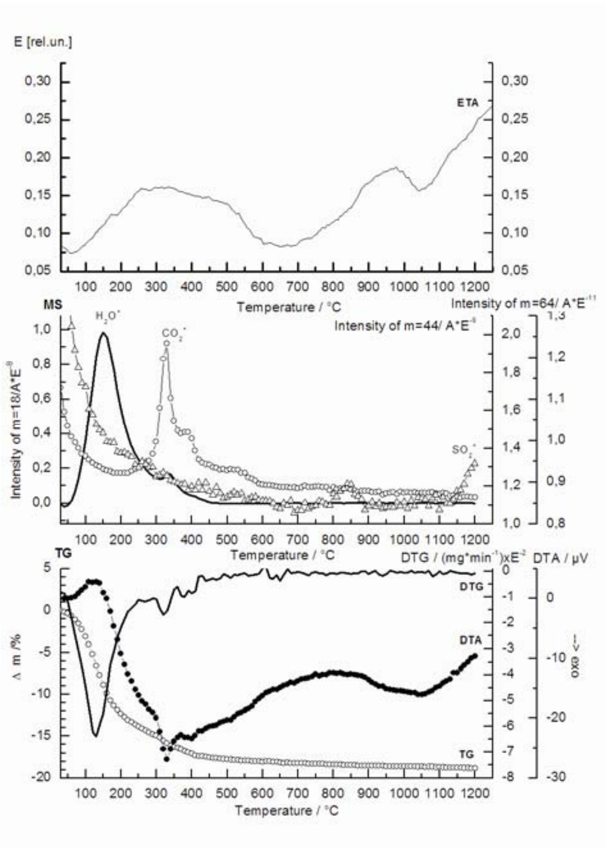

Fig. 1 *ETA, DTA and TG results measured in air – precursor No.1*

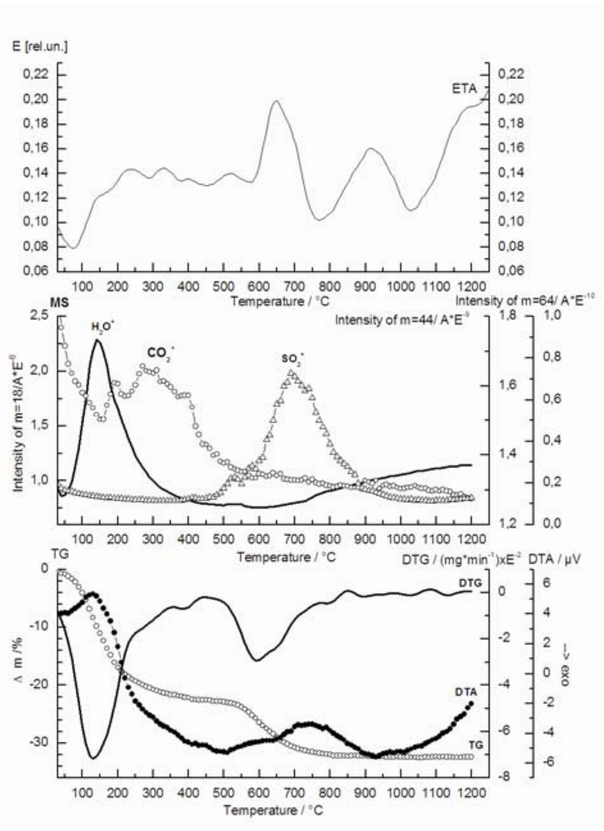

Fig. 2 *ETA, DTA and TG results measured in air – precursor No.2*

Thermodynamische Modellrechnungen zum Chemischen Transport von Zr–*Pn*–*Q* (*Pn* = P, As; *Q* = Se, Te)

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Im PbFCl-Typ kristallisierende Pniktid-Chalkogenide aus den Systemen *M*–*Pn*–*Q* (*M* = Th, U, Zr, Hf; *Pn* = P, As, Sb; *Q* = S, Se, Te) zeigen ein ungewöhnliches Verhalten im temperaturabhängigen elektrischen Widerstand, welches als nichtmagnetischer Kondo-Effekt interpretiert wird [1-3]. Zur Verknüpfung der Zusammenhänge zwischen der chemischen Zusammensetzung, der Kristallstruktur und den physikalischen Eigenschaften ist es notwendig, alle relevanten Untersuchungen an einem Kristallindividuum durchzuführen. Hierfür wurden große Einkristalle ($\geq$ 1 mm^3) der entsprechenden ternären Phasen über Chemischen Transport gezüchtet. In diesem Zusammenhang wurde das thermochemische Verhalten ausgewählter Phasen der Systeme Zr–P–S, Zr–As–Se und Zr–As–Te mit DTA–TG, TG–MS und KE–MS untersucht. Diese Untersuchungen zeigen, dass sich die Verbindungen unterhalb ihrer Schmelztemperatur zersetzen. Da chemische Transportreaktionen mit thermodynamischen Gesetzmäßigkeiten zu beschreiben sind, ist eine Vorhersage des optimalen Transportmittels, der Reaktionsbedingungen und der transportierten Stoffmenge möglich. Zur Simulation der Transportexperimente müssen die kondensierten und gasförmigen Spezies mit ihren thermodynamischen Daten (Enthalpie, Entropie, Wärmekapazität) bekannt sein. Über entsprechende Modellrechnungen wurden die Transportbedingungen optimiert und die beim Chemischen Transport ablaufenden Reaktionen beschrieben.

Literatur

[1] M. Schmidt, T. Cichorek, R. Niewa, A. Schlechte, Yu. Prots, F. Steglich, and R. Kniep, *J. Phys.: Condens. Matter* **2005**, *17,* 5481–5488.

[2] A. Schlechte, R. Niewa, M. Schmidt, G. Auffermann, Yu. Prots, W. Schnelle, D. Gnida, T. Cichorek, F. Steglich, and R. Kniep, *Sci. Technol. Adv. Mat.* **2007**, *8*, 341–346.

[3] A. Czulucki, Dissertation, TU-Dresden **2010**, *eingereicht*.

Untersuchungen zum Hydrolyseverhalten von $BiCl_3$ in Argon mittels TG-MS

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In einer TG-MS-Apparatur (NETZSCH STA409CD), die in einem mit Argon gefüllten Handschuhkasten (MBraun) installiert ist, wurde die Reaktion von festem $BiCl_3$ mit Wasserdampf unter definierten experimentellen Bedingungen untersucht. Ausgangspunkt waren die kürzlich durchgeführten in-situ Röntgenbeugungsexperimente an festem $BiCl_3$, welches Kontakt mit Luft hat. Dabei wurde eine intermediäre Phase beobachtet, die sich im weiteren Reaktionsverlauf in bekanntes BiOCl umwandelt. Aus den gemessenen Röntgenpulverdaten konnte die Struktur des zwischenzeitlich gebildeten $BiCl_3{*}H_2O$ erstmalig bestimmt werden [1].

Wird dem über die Probe geleiteten Argon Wasserdampf bei 27 °C hinzugesetzt, so kann die oben beschriebene Reaktion anhand des TG-Signals verfolgt werden. Es gelingt durch Abbruch der Messung, $BiCl_3{*}H_2O$ zu isolieren. Beim Aufheizen des so erhaltenen Produktes in trockenem Argon (10 K/min) setzt bei 50 °C eine Gewichtsabnahme ein unter gleichzeitigem Anstieg des Ionenstromes $m/z = 18$ (H_2O^+). Diese Stufe entspricht der Abgabe des Kristallwassers. Bei etwa 250 °C beginnt $BiCl_3$ zu sublimieren, einerseits angezeigt durch einen weiteren Masseverlust und andererseits belegt durch die massenspektroskopische Registrierung der charakteristischen Gasspezies $BiCl_x^+$ ($x = 1, 2, 3$). Gebildetes $BiCl_3{*}H_2O$ kann bei 27 °C in der Thermowaage wieder in $BiCl_3$ umgewandelt werden, indem es trockenem Argon ausgesetzt wird.

References

[1] A. Wosylus, S. Hoffmann, M. Schmidt, M. Ruck, *Eur. J. Inorg. Chem.*, **2010**, accepted.

The Thermal Properties of ST/UP and ST/UEP Copolymers

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In this study, the unsaturated polyesters (UP) as well as the unsaturated epoxy polyesters (UEP) [1-4] prepared from tetrahydrophthalic anhydride (THPA), maleic anhydride and the mixture of suitable glycols: ethylene glycol/1,4-butanediol (EG/BDO), ethylene glycol/1,6-hexanediol (EG/HDO) or 1,4-butanediol/1,6-hexanediol (BDO/HDO) were used as a component of low styrene content copolymers. The thermal properties of benzoyl peroxide (BPO) and BPO/THPA cured styrene copolymers have been studied by means of DSC, TGA and DMA analyses.

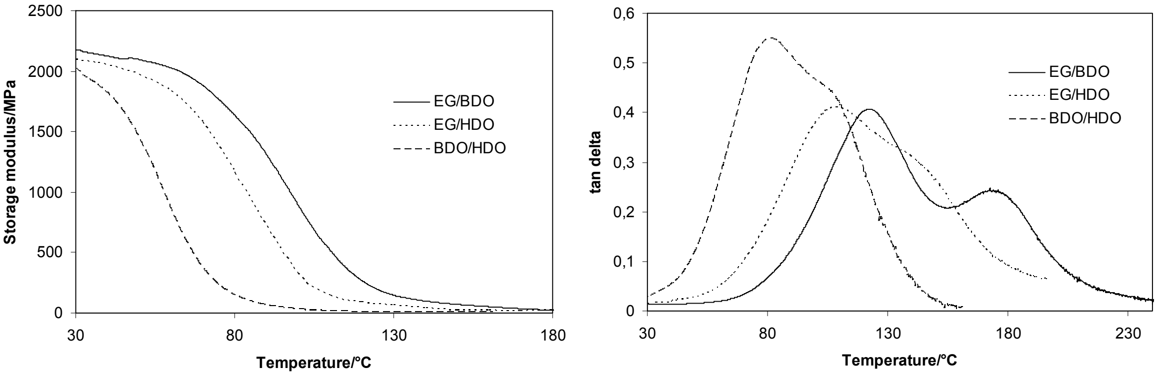

Figure 1. Storage modulus (E') and tan delta (tanδ) vs. temperature for BPO/THPA cured copolymers based on UEP.

It was proved, that the presence of different glycol's chain length in polyester's structure had a considerably influence on the studied properties of cured low styrene content copolymers. The use of unsaturated (epoxy) polyesters containing shorter aliphatic glycol's chain lengths (EG/BDO) allowed to produce more stiff and thermally stable network structure of obtained copolymers compared to those based on EG/HDO and BDO/HDO.

References

[1] Z. Bończa-Tomaszewski, P. Penczek, A. Bańkowska, *Surf. Coat. Int. Part B, Coat. Trans.*, **2006**, *89*, 157.

[2] Z. Piotrowska, J. Kiełkiewicz, *Int. Polym. Sci. Technol.*, **1996**, *23*, 96.

[3] M. Worzakowska, *J. Appl. Polym. Sci.*, **2008**,*109*, 2973.

[4] M. Worzakowska, *J. Appl. Polym. Sci.*, **2008**, *110*, 3582.

Curing Reaction of DCPD Terminated Unsaturated Polyesters with Styrene and Methyl Methacrylate

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Dicyclopentadiene (DCPD) is the Diels-Alder reaction dimmer of cyclopentadiene (CPD) and is also a byproduct in the olefin cracking process. DCPD due to their availability, low coast and reactivity can be used as a modifier of unsaturated polyester's structure thus producing the resins ideal for e.g. boat construction, shower applications, etc. [1]. In this paper, DCPD was used to modify the unsaturated polyester's structure (UP) obtained in polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), maleic acid (MA) and suitable glycol: ethylene glycol (EG), 1,4-butanediol (BDO) or 1,6-hexanediol (HDO). The influence of unsaturated polyester's structure as well as different vinyl monomer content (20 - 80 wt%) on the course of benzoyl peroxide (BPO) initiated cure reaction with styrene (ST) or methyl methacrylate (MM) were estimated by differential scanning calorimetry (DSC) and discussed.

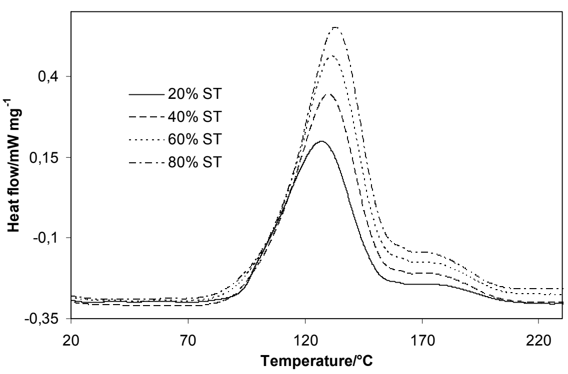

Figure 1. Curing reaction of DCPD terminated UP based on HDO with ST.

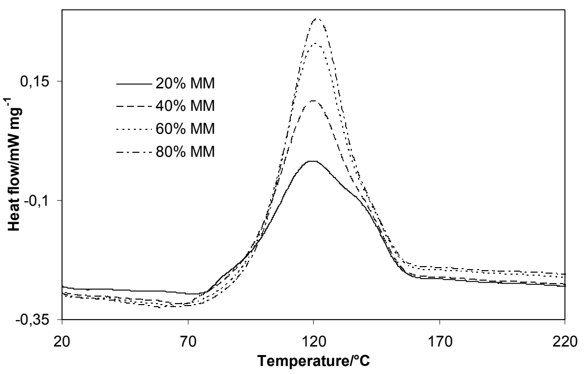

Figure 2. Curing reaction of DCPD terminated UP based on HDO with MM.

References

[1] K. G. Johnson, L. S. Yang, *Preparation, properties and applications of unsaturated polyesters*, Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters, John Wiley & Sons, Ltd, **2003**.

Thermal Study of $Ce_{0.9}Tb_{0.1}O_2$ Compound

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The new inorganic pigments having the general formula $Ce_{1-x}Tb_xO_2$ give the colour shades from cream to orange after application into ceramic glaze. These pigments have been synthesized by classical ceramic methods, i.e. solid state reaction, as very promising alternative to the pigments containing the toxic elements such as Pb, Cd, Cr, Cu and etc.

The colouring mechanism is based on the charge – transfer band from O_{2p} to Ce_{4f} in the semiconducting CeO_2. The band gap between the anionic O_{2p} valence band and cationic Ce_{4f} conduction band can be modified by the formation of solid solutions, which introduces an additional electronic level between the valence and conduction bands [1]. The success of CeO_2-based materials is mainly due to unique combination of an elevated oxygen transport capacity coupled with the ability to easily shift between reduced and oxidized states, i.e. the sesquioxide $CeO_{1.5}$ and the dioxide CeO_2 [2]. In the connection of element cerium-terbium, the Ce exist in a two oxidation state 3+ and 4+, which contribute to the very good ionic and electronic conductivity and catalytic properties [3].

The $Ce_{0.9}Tb_{0.1}O_2$ pigment was prepared with using of agent of mineralization Li_2CO_3 which works like flux. The mixture of the starting precursors and fluxing agent was submitted to the thermal analysis which provides the important information about the temperature region of the pigment creation and its thermal stability. The simultaneous TG-DTA measurement was using as a method of thermal analysis. The temperature region for analysis was from 35 °C to 1200 °C with heating rate 10 °C/min and α-Al_2O_3 like reference material.

This work is supported by project of Grant Agency of Czech Republic (No. 104/08/0289) and IGA University of Pardubice (SGFChT04)

References

[1] T. Masui, S. Furukawa, N. Imanaka: *Chem. Lett.*, **2006** ,*35*, 1032.
[2] S. Huang, L. Li, O. Van der Biest, J. Vleugels, *Solid State Sci.*, **2005**, *7*, 539.
[3] M.A. Perin, E. Wimmer: *Phys. Rev. B.*, **1996**, *54*, 2428.

The Synthesis and Study of $PrFeO_3$ Compound

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The research is focused on the preparation of pigments, which are widely used not only to colour different materials. The perovskit with general formula ABO_3 belongs among these pigments, which representing the interesting group of compounds in the term of substitute possibilities.

The attention was paid to synthesis of $PrFeO_3$ pigment when the influence of temperature of calcination on the colour properties was followed. The pigment has been synthesized by classical dry process from the starting oxides, i.e. Pr_6O_{11} and Fe_2O_3. The prepared reaction mixtures were calcinated in electric furnace at different temperatures 1000, 1100 and 1200 °C for 2 hours.

The samples were applied into organic matrix in a mass tone and the colour properties were measured. The powder pigments were submitted to the measure of particle size distribution and their structures were also observed.

The methods of thermal analysis, exactly the simultaneous measurement TG-DTA, were used for verification of calcination temperature for synthesis of $PrFeO_3$ compound. Several endothermic effects on the DTA curve of reaction mixture were detected which are related to changes in the starting oxide Pr_6O_{11}. The exothermic effect with maximum at 995 °C corresponds to formation of $PrFeO_3$ compound which was also confirmed by the X-ray diffraction analysis. At temperature above 1000 °C the last endothermic effect on the DTA curve was identified that is connected with partial reduction of Fe^{3+} ions.

This work is supported by project of Grant Agency of Czech Republic (No. 104/08/0289) and MSM (No. 0021627501).

Thermal Study of the $(Bi_2O_3)_{0.5}(Ln_2O_3)_{0.5}$ Compounds

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The compounds based on Bi_2O_3 seem to be interesting for their yellow and orange colour hues because they can substitute the problematic pigments (especially chromate yellows) with regard to the environmental point of view. Intense colours of these pigments are based on incorporation of ions of lanthanides into the host lattice of Bi_2O_3. These pigments are described by the formula $(Bi_2O_3)_{0.5}(Ln_2O_3)_{0.5}$. This type of pigments is prepared by medium temperature calcination of the basic starting oxides (Bi_2O_3 and Ln_2O_3).

The formation of these pigments was followed by thermal analysis using the STA 449C Jupiter (NETZSCH, Germany) which allows evaluation of data and simultaneous registration of the thermoanalytical curves TG and DTA. Starting raw materials and prepared starting mixtures were studied by thermal analysis in the corundum crucible in air at temperature region from 30 to 1000°C.

The results of thermal analysis of the starting mixtures for synthesis of $(Bi_2O_3)_{0.5}(Ln_2O_3)_{0.5}$ pigments show the temperature region of the pigment formation. At the temperature about 730°C the cubic modification of □-Bi_2O_3 starts to appear from the monoclinic modification □-Bi_2O_3. Dy_2O_3 dissolves in Bi_2O_3 during the heat treatment of the starting mixture forming the solid solution of both oxides. For this reason starting mixtures were calcinated at temperature of 800°C in the electric furnace. This fact is also in accordance with results of X-ray diffraction analysis.

Prepared pigments indicate the increase of their melting temperatures even above 1000°C, although melting temperature of pure Bi_2O_3 was only 820°C. This fact can give a direction for colouring of ceramic glazes. The experiments perform hopeful results for application into ceramic glazes.

The work was supported by Grant Agency of Czech Republic (No. 104/08/0289) and the Ministry of Education, Youth and Sports of Czech Republic (No. 0021627501).

Synthesis and Colour Properties of $Lu_2Zr_{1,5}V_{0,5}O_7$ Pigment

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The present study is focused on the preparation of ceramic colour pigments namely pyrochlores. These compounds have many good properties such as low thermal conductivity, high melting point, high thermal expansion coefficient, high stability and ability to accommodate defects [1]. The yellow pigment $Pb_2Sb_2O_7$ is basic representative of the pyrochlores but it contains problematical Pb and Sb.

This contribution deals with the pyrochlore compounds of $Lu_2Zr_2O_7$ type with introduction of vanadium (V) as chromophore that can be used as ceramic pigments. The compound with formula $Lu_2Zr_{1,5}V_{0,5}O_7$ was prepared by the traditional ceramic method for the first time. This method involves homogenization of the mixture of the corresponding oxides, their calcination at very high temperature (1300 – 1500°C). The same compound was also prepared by precipitation and two step process. The formation of these pigments was followed by thermal analysis using the STA 449C Jupiter (NETZSCH, Germany).

All samples were studied systematically using X-ray diffraction analysis, particle size distribution and colour properties. Fired pigments were apllied into organic matrix and ceramic glaze and measured by ColorQuest (HunterLab, USA) in the visible region of light. The colour properties are described in terms of CIE L*a*b* system.

The goal was to develop conditions for the synthesis of this type of pigments and to determine the influence of preparation method on the colouring effects of these compounds. Our results indicate that precipitation gives dark rich yellow hues and two step method needs lower calcination that clasical ceramic method (1300 °C).

This research is supported by Grand Agency of Czech Republic (104/08/0289) and IGA University of Pardubice (SGFChT04).

References

[1] R. Vassen, X. Cao, F. Tietz, D. Basu, D. Stover, *J. Am. Ceram. Soc.* , **2000**, *83*, 2023.

Calibration of 3-Layer-Calorimeters for Determination of Storage Capacity of PCMs

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Phase change materials PCM have an increasing meaning for example for air conditioning of rooms, storage of solar heat for the winter or keep warm of meals. The storage capacity is an important parameter for the characterization of PCMs. It results as the sum of latent heat during the phase change and sensible heat for the relevant temperature interval. Heat of transformation and latent heat are normally determined by DSC for small size of sample, usually less than 100µl. Such small samples are not representative for inhomogeneous materials like the most PCMs. For measurements on inhomogeneous materials, a method with much larger volume of samples is necessary. Such a method is the T-history method [1]. With such instruments it is possible to determine the enthalpy as a function of temperature during melting and crystallization of 10 to 100g of PCM.

We use a 3-Layer-Calorimeter supplied by the company w&a (wärme- und anwendungstechnische Prüfungen / Fürstenberg). Construction and measurement technology are explained. The instrument is calibrated in the temperature range between 10°C and 30°C with water. We extended the calibration to 80°C using water and to 100°C using Al_2O_3 for temperature jumps of 20 K. A calibration function is determined for any temperature. The calibration was tested by comparing the measured specific heats with the literature.

For two different alkenes $C_{16}H_{34}$ (T_m = 18°C) and $C_{36}H_{74}$ (T_m = 76°C) specific heat and storage capacity for melting and crystallization are determined with water and Al_2O_3 as calibration substance, respectively. The results are compared with data from literature. With a 3-Layer-Calorimeter it is possible to determine storage capacities with an accuracy of 5…10%, comparable with the T-history method [2].

References:

[1] Zhang et al., Measurement science & technology, 10 (1999) 201.
[2] Lázaro et al., Measurement science & technology, 17 (2006) 2168.

Synthesis of Cr-doped $SrSnO_3$

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The compound $SrSnO_3$ belongs to the family of analogous alkaline-earth stannates, $MSnO_3$ (where M=Ca, Sr and Ba). Stannates are currently being investigated for their attractive dielectric characteristics which are important in ceramic and electronic industry where they are finding application as thermally stable capacitors [1]. The main interest of our research group was to prepared strontium stannate and find out whether the doped stannates by chromium can be used in ceramic industry as the high-temperature inorganic pigments.

The compound of general formula $SrCr_xSn_{1-x}O_{3-x/2}$ was prepared by solid state reaction among Cr_2O_3, SnO_2 and $SrCO_3$ (95% of purity). Raw materials were mixed in a porcelain mortar in order to obtain homogenous reaction mixture which was calcined at high temperatures 1300, 1400 and 1500 °C.

All prepared pigments were applied into the organic matrix in a mass tone. The colour of pigments was measured in the visible region of light (400 – 700 nm) using a spectrophotometer ColorQuest XE (HunterLab, USA). Simultaneous TG/DTA measurements were performed by STA Jupiter 449 equipment (NETZSCH, Germany). The crystal structures of the powder materials were studied by X-ray diffraction analysis using a diffractometer D8 Advance (Bruker, GB).

The main aim of the research was to prepare new stannate compounds which can be used as inorganic pigments. One-phase systems have already been identified at the diffractograms of samples prepared by calcining at 1300 °C. The most interesting colour properties were provided by the compound $SrCr_{0,05}Sn_{0,95}O_{2,975}$ prepared by firing at 1300 °C, producing a reddish brown colour hue.

This research is supported by the Grant Agency of Czech Republic (104/08/0289) and IGA University of Pardubice (SGFChT04).

References

[1] A.M. Azad, L.L.W. Shyan, T.Y. Pang, *Journal of Alloys and Compounds*, **1999**, *282*, 109-1 24.

Study of Colour Properties of Ni Doped Titanium Dioxide

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The rutile pigments can be classified into the group of ceramic pigments. For these pigments high chemical and thermal resistance is characteristic. The great advantage of rutile pigments is their easy preparation and good availability of raw materials. In view of the fact, that these pigments are thermal stable up to the melting point (≈ 1800°C), it opens many possibilities for using. One of the possibilities is a production of solid solution with the introduction of chromophore. Industrial ceramic pigments are manufactured from anatase and chromophore elements (Cr, Mn, Ni or V) and counterions (Nb, Sb or W).[1]

The preparation of these pigments is based on the traditional ceramic method. Anatase titanium paste ($TiO_2.xH_2O$) and titanylsulfate ($TiOSO_4.xH_2O$) were choosen as starting materials, both of them can be obtained from the production of titanium dioxide. All starting materials were thoroughly homogenized in a porcelain mortar and then were calcinated at temperatures 800, 900, 1000, 1100 and 1200 °C and were maintained for 2h. Raw materials of titanium and a mixture of starting oxides were studied by DTA-TG analysis using STA Jupiter 449 (NETZSCH GmbH, SRN).

The main aim of the research was to prepare solid solution with rutile structure that was obtained by conventional solid-state reaction. The goal was to develop conditions for the synthesis of this type of pigments and to determine the influence of chromophore on the colouring effects of these compounds. The pigments prepared are characterized by yellow-green and khaki green colour.

This research is supported by the Grant Agency of Czech Republic (104/08/0289) and IGA University of Pardubice (SGFChT04).

References

[1] F. Matteucci, G. Cruciani, M. Doni, M. Raimondo: Ceramics International *32,*385 (2006).

Water Vapor TA Experiments for Mathematic Modelling of Combustion Processes

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The aim of this project is to gain accurate initial values by thermoanalytical (TA) experiments for mathematic modelling of combustion processes. Major parameters of the technical process are to be varied. One major parameter is the water vapor content in the combustion atmosphere. In power plants (using organic fuels like coal, refused derived fuel or biomass) the atmosphere contains up to 30% water vapor. Water vapor is continuously produced. However, in conventional TA experiments, continuous high water vapor contents can't be established by the release of water from the sample. Inherent to the TA system, water vapor evolving from the sample is transported out of the thermobalance immediately after release. In temperature ranges, in which no water is formed, the sample is treated in "dry" conditions.

TA – High Resolution FTIR experiments fulfill almost all prerequisites for gaining data, which allow the mathematic modelling of combustion processes. By simulating distinct condition zones of the combustion chamber, parameters like temperature, heating rate, oxygen content and gas mixtures are varied. While adding water vapor to the transfer gas, the limitations of the TA systems arise. It is limited to very low water vapor concentrations, since condensation has to be excluded thoroughly and the humid transfer gas should adapt to the sample temperature before contacting the sample. Hence, we implemented a purpose-built Netzsch water vapor furnace into our TA - HR FTIR system.

This study shows results using complex fuel samples to demonstrate the relevance of water vapor as parameter for the combustion process. The investigation emphasizes on evolved low volatile nitrogen products which are produced from wooden RDF (refused derived fuel). These waste fractions are widely used in alternative power plants and for co-combustion. Gaseous N-products are formed mainly from urea-formaldehyde and melanin-formaldehyde resins in the RDF sample. The results show significantly different quantitative product relations in comparison to "dry" results. E.g. the ammonia release is higher in water vapor atmosphere, whereas the release of HNCO is reduced. Only part of that effect can be explained by hydrolysis of HNCO in the humid gas phase. In fact, the results indicate different reaction mechanisms of the product formation during thermal treatment.

These first results with RDF fuel samples show the importance of water vapor as reaction partner in the combustion atmosphere. Water vapor has to be taken into account as parameter in TA experiments in order to gain accurate initial values for mathematic modelling of continuous processes with humid atmosphere.

The Chemical Structure and Thermal Properties of Polymeric Microspheres Obtained from Multifunctional Methacrylate Monomers

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Recently, micro-sized, monodisperse polymer particles have been applied in biomedical materials, microelectronics, chromatography, and other fields. According to Okubo et al. [1] a number of monomers having functional groups required for the mentioned above applications, is limited. Most researchers focus their attention on typical monomers used mostly in preparation of monosized polymeric microspheres: nonpolar styrene and divinylbenzene (ST and DVB) as well as medium polar methyl methacrylate (MMA). In this work we present new group of methacrylate monomers applicable for synthesis of polymeric microspheres.

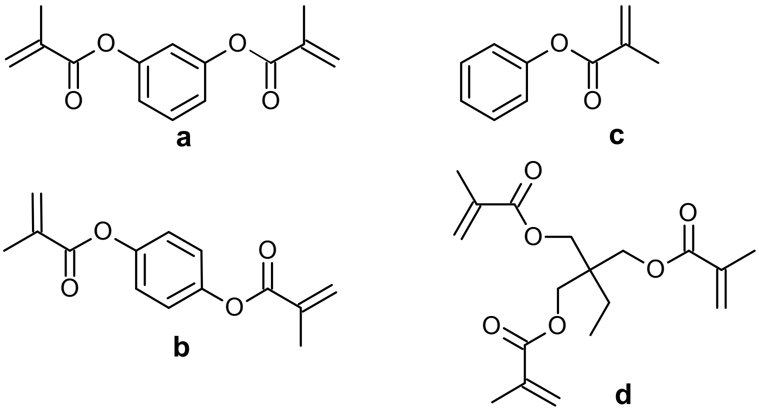

Figure 1. Chemical structure of used monomers: a) 1,3-dimethacryloiloxybenzene (1,3DMB); b) 1,4-dimethacryloiloxybenzene (1,4DMB); c) methacryloiloxybenzene (MB) d) trimethylolpropane trimethacrylate (TRIM).

The aim of this work was to study the influence of the chemical structure of monomers on the thermal properties of porous methacrylate microspheres. Polymeric microspheres were prepared by suspension polymerization of three aromatic monomers: MB, 1,3DMB and 1,4DMB with cross-linking agent –TRIM (Figure 1). As a pore forming diluents chlorobenzene and dekan-1-ol were used. To determine chemical structures and thermal properties of studied microspheres differential scanning calorimetry (DSC) and Raman spectroscopy measurements were used.

References

[1] M. Okubo, T. Miya, H. Minam, R. Takekoh, J Appl Polym Sci **2002**, 83, 2013.

The Use of High Heating Rates to Characterize Flame Retardant Materials by Thermogravimetric Analysis

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Thermogravimetric Analysis is used extensively in the flame retardant industry to study the decomposition of materials and formation of char which is indicative to the level of flame retardant behavior. However, one issue arising from TGA methods were the relatively rates available when compared to a typical fire situation. Standard TGA testing is typically carried out at 10 or 20 K/min, where as a within a fire scenario, heating rate of the advancing flame front could potentially be one or two orders of magnitude greater. The Q5000IR TGA includes on approach to furnace heating which provides high controlled and ballistic heating rates. When this is combined with high sensitivity balance, they lend themselves to the study of high heating rate decomposition behavior.

Whilst it is understood that the decomposition of flame retardant and the substrate are kinetically driven and will, therefore, depend on the heating rate, the problem arises when the decomposition of the flame retardant resulting in the formation of char with the substrate and the decomposition of the substrate forming flammable volatiles.

The ability to observe the decomposition of the flame retardant at high heating rates will allow the manufacturer to gain a better insight into the performance of new flame retardants at the development stage.

Thermoanalytical Investigations During a Car Fire

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A fire was set on a car in BAM's test field Horstwalde, near Berlin, to investigate the evolution of temperature and of gaseous fire products in the passenger compartment. The aim was to identify the conditions for self-rescuing of passengers. The investigation of smoke gas temperatures and smoke gas composition during this car fire are presented in this work. The car was put on fire by an ignited mixture of diesel and petrol in a small pan under the front tires. The fire went from the engine compartment over to the passenger cabin up to a complete range of car fire. The fire lasted 50 minutes. A dummy was placed on the driver's seat, which was equipped with several thermocouples. The resulting temperatures during the fire show the actual temperatures directly on the dummy. In addition, a thermal imaging camera was used to monitor the car temperatures during the fire at a distance of 15 m. The smoke gases were analysed using FTIR spectroscopy. The gases were collected through a removable probe sensor, corresponding to the nose of the dummy in the passenger compartment. The gases were continuously collected and analyzed during the whole period of the car fire. The composition of the gases changed during the fire, depending on the temperature in the passenger compartment. The various experimentally determined parameters (temperature, smoke gas composition) were integrated into different numerical simulations. Both, the experimental data and the numerical simulations on the car fire are presented and discussed.

References

[1] N. Gude, *Studienarbeit*, *TU Berlin*, **2010**

Investigations of Smoke Emission and Smoke Gas Composition in the Smoke Density Chamber

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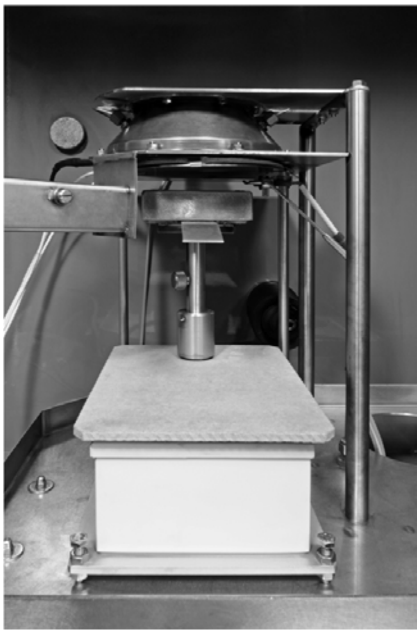

Fire prevention in structures is aimed at limiting the spread of fire and smoke for a certain time in order to give people the chance to escape from the fire. Due to the toxicity, the light absorption and the scattering properties of smoke are always one of the major hazards and affect the escape routes of persons who are exposed to the smoke.

Essential characteristic values on smoke gases can be obtained by using the smoke density chamber. The specific optical density of smoke gases, of flat material samples, is determined according to EN ISO 5659-2 and ASTM E 662. In a closed test chamber the sample is exposed to horizontal thermal irradiation of either 25 kW/m² or 50 kW/m² (EN ISO 5659-2), or to vertical thermal irradiation of 25 kW/m² (ASTM E 662), with or without a pilot flame. In order to evaluate the toxicity, determinations of smoke gases (qualitative and quantitative) are obtained by applying FTIR-spectroscopy. A FTIR-spectrometer is directly coupled with the chamber.

By investigating the measurable light transmission, values on the specific optical density Ds are determined. When tests, according to EN ISO 5659-2, are carried out, the mass referenced optical density MOD is determined too. After 4 and 8 minutes test time, gas samples are quantitatively analyzed by using FTIR-spectroscopy with respect to some acute inhalation-toxic smoke gas components. The smoke gas toxicity of a sample is thereby evaluated by the CIT-value (CEN TS 45545-2). In this work, various experiments and the resultant specific values are presented and discussed. Different wooden samples were smouldered under different experimental conditions. It will be presented the optical density, the mass loss over time and the smoke gas compositions during the smouldering of wooden samples. Furthermore, the temperature distribution in the Smoke Density Chamber will be presented. The collected values, of the different materials, are compared and evaluated in terms of their fire behaviour.

Three Distinct Binding Sites for Co(II) Ions in Human Serum Albumin – Thermodynamic Calculation

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Human serum albumin (HSA) is the most abundant protein of blood serum, involved in the transport of metal ions, including Co(II). Using isothermal titration calorimetry (ITC) we characterized the presence of three independent Co(II) binding sites in HSA and determined conditional binding constants for these sites at pH 7.4.

Using circular dichroism spectroscopic titrations we confirmed three distinct Co(II) binding sites in HSA and the assignment of NTS as the weakest binding site for Co(II) ions. We ordered these sites according to their binding affinities as cadmium site B > multi-metal binding site (MBS) > N-terminal binding site (NTS). These results are in full agreement with those obtained using other techniques [1].

References

[1] E. Mothes, P. Faller, Biochemistry, 46 (2007) 2267-2274.

Thermal Analysis of Nanostructured Calcite Crystals Covered with Phospholipid Layers

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The lipid self assembled monolayers or supported membranes have attracted great attention as functionalizing methods of inorganic particles. Such supramolecular structures combine the properties both from the particle core and lipid vesicle. As a result we obtain stabilized deposited membrane which takes the architectural advantages of particles and the properties of lipid. This explains wide range of applications of solids coated with lipid layers in biotechnology or biomedicine.

The main objective of this work is to obtain and characterize calcium carbonate particles covered with lipid layers (dilauroylphosphatidylcholine (DLPC) and dimyristoylphosphatidylcholine (DMPC)).

Nanostructured calcite crystals were obtained in the process of carbonation of calcium hydroxide slurry conducted in rotating disc reactor (RDR) [1]. This method allowed for obtaining very pure, thermodynamically stable single calcite crystals. Its surface purity was confirmed by the thermogravimetric analysis (TGA). The specific surface area of precipitated powder was highly developed (23 m^2/g from BET). The scanning (SEM) and transmission (TEM) electron microscopy showed nanostructured morphology of calcite. The single crystallite diameter was about 30 nm. Barret-Joyner-Halenda (BJH) pores size distribution revealed porous surface morphology with the highest number of 2-3 nm pores. The calcite surface coating with lipid layers was conducted by adsorption from the solution on *in situ* precipitated $CaCO_3$.

Calcite probes treated with different amounts phospholipids were investigated by thermogravimetric analysis (TGA) differential scanning calorimetry (DSC) and X-ray photoelectron microscopy (XPS). Those studies allowed for adsorbed lipid layers morphology studies, interface chemical composition and quantity examination as well as determination of interactions between molecules. TGA enabled also to distinguish between different lipid molecules species present on calcite surface (adsorbed/chemisorbed ones, interlocated between adsorbed to surface formed local bilayer) and free lipid molecules.

References

[1] K. Kędra-Królik, P. Gierycz, *J. Therm. Anal. Cal.,* **2006**, *83*, 579.

Assays of Complex Samples Using Mass Spectrometry with Soft Single Photon Ionisation Coupled to Thermal Analysis

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Combining mass spectrometry (MS) with a preceding analytical technique is well established. One common combination is MS and thermal analysis (TA), where evolving gases from TA are assayed using MS applying electron ionisation (EI) as ionisation method. As the kinetic energy of the electrons, typically 70 eV, is much higher than the ionisation energies of the assayed sample molecules, in particular organic compunds are fragmented due to the high excess energy. That hampers the correlation of the ion signals with sample components especially for complex mixtures and natural samples. Using so called soft ionisation techniques such as single photon ionsation (SPI) with vacuum UV photons or chemical ionisation (CI), fragmentation can be reduced. Nevertheless, EI has the advantage of being generic, having existing spectrum libraries, being easily applicable, affordable, simple and easy to combine with other vacuum-based ionisation methods. Therefore, the combination of the two generic and vacuum-based ionisation methods SPI and EI with TA is well suited for a non-targeted assay of organic or semi-organic samples.

The coupling between thermobalance and mass spectrometer is done with a continously heated capillary; alternating EI and SPI mass spectra are recorded. For single photon ionisation of the organic compounds in the evolving gas from the thermobalance, an electron beam pumped rare gas excimer light source (EBEL) is used. In the EBEL, electrons are accelerated in a potential difference of 12 kV before entering an argon filled cell through a thin silicon nitride membrane. The electrons then partly ionise argon atoms, which subsequently react to argon excimers which decay emitting monochromatic vacuum UV photons (E = 9.8 eV). [1, 2]

References

[1] M. R. Saraji et al., *Anal. Chem.*, **2008**, *80*, 3393.
[2] R. Geissler et al., *Anal. Chem.*, **2009**, *81*, 6038.

Phase Formation in the System Hg/P/I Induced by Evaporation Pressure

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The potential of an optimised high temperature gas balance for in situ measurements of phase formation and phase transformation processes of highly volatile solids has been investigated.

Using the gas balance (see [1]) equilibrium pressure induced formation reactions in the range from 0.1 up to 10 bar can be examined. The model system Hg/P/I is feasible due to the components equilibrium pressure behaviour. Fig. 1 shows the formation and sublimation of mercury-(II) iodide followed by the formation of ternary phases $Hg_{16}P_8I_{12-x}$ (see $Hg_9P_5I_6$ [2], $Hg_8P_4I_5$ [3]) at □ > 300 °C.

Additionally, phase transformations under high equilibrium pressures are substantiated ($HgI_2(s) \rightarrow HgI_2(l)$; $T = 526$ K; $P_{red} \rightarrow P_{violet}$; $T > 700$ K).

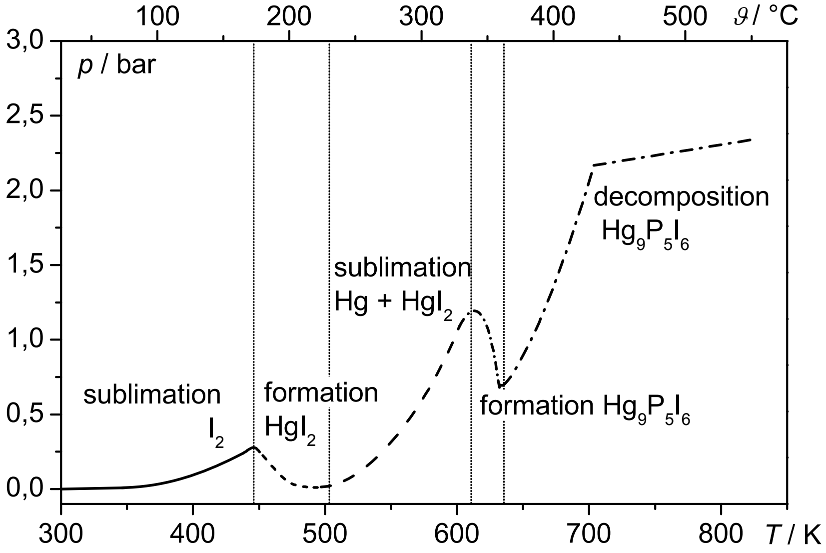

Figure 1. *p*-*T* curve of formation of $Hg_9P_5I_6(s)$.

References

[1] A. Hackert, V. Plies, *Z. Anorg. Allg. Chemie.* **1998**, *624*, 74-80.
[2] M. Ledesert, A. Rebbah, P.H. Labbe, *Z. Kristallogr.* **1990**, *192*, 223-231.
[3] M. Bawohl, Dissertation, Uni Münster, **2010**.

Some Remarks on ASTM E 2105-00: “Standard Practice for General Techniques of Thermogravimetric Analysis (TGA) coupled with Infrared Analysis (TGA/IR)”

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Thermoanalytical methods such as thermogravimetry (TG) are describing the temperature depending behaviour of a sample on a macroscopic scale. Fourier transform infrared spectroscopy (FTIR) is an identifiying method which is sensitive to molecular functional groups. They are somehow complimentary and therefore the online combination of both TG and FTIR is very useful in order to characterize the thermal processes such as decomposition, dehydration, pyrolysis or chemical reactions.

ASTM E 2105-00 is a guide-line for the coupled technique TG-FTIR which gives helpful advice about the aim of this technique, about how to realize the hardware combination and which parameters should be checked and reported in order to obtain comparable measurement results. Nevertheless, there are coupling equipments commercially available which offer more possibilities on both sides hardware and software.

This work presents some remarks on terms and definitions of the ASTM E 2105-00 as well as measurement results with which the improvement of both hardware technique and software capabilities of state-of-the-art equipments is demonstrated. A summary collects the most important issues which should be taken into consideration in order to improve the reliability of the measurements results. An additional work presents results obtained for samples suggested in the above discussed standard procedure for their use as standard materials [1].

References

[1] S. Eichholz, E. Füglein, annual conference of the german national thermoanalytical society (GEFTA), **2010**.

Zinc stearate a standard material for the TG-FTIR method? Related to ASTM E 2105-00: “Standard Practice for General Techniques of Thermogravimetric Analysis (TGA) coupled with Infrared Analysis (TGA/IR)”

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Thermoanalytical methods such as thermogravimetry (TG) are describing the temperature depending behaviour of a sample on a macroscopic scale. Fourier transform infrared spectroscopy (FTIR) is an identifiying method which is sensitive to molecular functional groups. They are somehow complementary and therefore the online combination of both TG and FTIR is very useful in order to characterize the thermal processes such as decomposition, dehydration, pyrolysis or chemical reactions.

ASTM E 2105-00 is a guide-line for the coupled technique TG-FTIR which gives helpful advice about the aim of this technique, about how to realize the hardware combination and which parameters should be checked and reported in order to obtain comparable measurement results. Nevertheless, there are coupling equipments commercially available which offer more possibilities on both sides hardware and software.

By means of measurement results this work discusses the use of the suggested test material zinc stearate. Beside this, other more common materials such as calcium carbonate or calcium oxalate monohydrate are used in order to prove the efficiency of the transportation of the released gases from the thermoanalytical unit to the flowcell of the spectrometer. An additional work collects the most important issues that should be taken into consideration for the setup of a TG-FTIR coupling unit and adds suggestions for further improvements of both hardware and software [1].

References

[1] E. Füglein, annual conference of the german national thermoanalytical society (GEFTA), **2010**.

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