COST Action

D32-Chemistry in High-Energy Microenvironments

D30-High Pressure Tuning of Chemical and Biochemical Reactions

BOOK OF ABSTRACTS

UNIVERSITA' DEGLI STUDI DI TORINO
Dipartimento di Scienza e Tecnologia del Farmaco

Working Group Meeting on:

New Synthetic Applications of High-Intensity Ultrasound, Microwave and High Pressure Environment

Turin 18-19 February 2005

PROGRAMME

Thursday 17

20.00 **Welcome Cocktail**
⇒ Deliveries reimbursement form

Friday 18

8.15-8.30.1 Welcome and Introductions

Chair: Cristina Leonelli

8.30-9.15 Organic Sonochemistry: Current Status, Unsolved Problems, and Challenges. *Pedro Cintas (Spain)*
9.15-10.00 Microwave effects in organic synthesis. *André Loupy (France)*
10.00-10.20 Criteria for the industrial application of "non classical" methods. *Werner Bonrath (Switzerland)*
10.20-10.40 High Pressure & Microwave reactors: problems and new opportunities. *Witold Lojkowski (Poland)*

10.40-11.10 coffee break

Chair: Bernd Ondruschka

11.10-11.30 Fabricating nanomaterials by sonochemical and microwave techniques for the elimination of hazardous materials from waste water. *Aharon Gedanken (Israel)*
11.30-11.50 Combinations of Wittig olefinations with Pd(0) catalysed C-C coupling reactions under ultrasound. *Thies Thiemann (Japan)*
11.50-12.10 High intensity US reactor operating under pressures up to 1 GPa of helium or argon: applications to nanopowders technology. *Andrzej Morawski (Poland)*
12.10-12.30 *In situ* and *ex situ* studies of processes in microwave irradiated materials. *Gavin A. Whittaker (UK)*
12.30-12.50 Transition element doped mesoporous silicas as catalyst for fine chemical synthesis. *Michael A Morris (Ireland)*

13.00-15.00 Lunch – Visit to the US and MW laboratory

Chair: Aharon Gedanken

15.00-15.20 High-Intensity Ultrasound assisted reactions of organic molecules. *George Heropoulos (Greece)*
15.20-15.40 Hydrogen from chemical hydrides by microwave or ultrasound assisted steam hydrolysis. *Bernd Ondruschka (Germany)*
15.40-16.00 Ultrasonic detection of hydrophobic effects in water-ethanol solutions. *Ants Tuulmets (Estonia)*
16.00-16.20 One-pot preparation of ionic liquids. *Jean-Marc Lévêque (France)*
16.20-16.40 Chemical composition effect on microwave assisted nanoparticles production. *Cristina Leonelli (Italy)*

16.40-17.00 coffee break

Chair: Pedro Cintas

17.00-17.20 Reactors combining high-intensity ultrasound and microwave irradiation. *Giancarlo Cravotto (Italy)*
17.20-17.40 Characterisation of structure and grain size distribution of nanoparticles. *Tomasz Wejrzanowski (Poland)*
17.40-18.00 The application of high energy electric and magnetic fields to process fly ash and ceramics. *Michael La Robina (Australia)*
18.00-18.20 MW-assisted heterogeneous gas phase catalysis - temperature measurement in dependence on the particle size and the catalyst mass. *Peter Scholz (Germany)*

18.20-18.50 Poster session

20.30 Dinner

Saturday 19

8.45-8.50.1 Session introduction

Chair: Witold Lojkowski

8.50-9.10 Conventional versus microwave hydrothermal synthesis of silico aluminates. *Carlo Mazzocchia (Italy)*
9.10-9.30 How Solvothermal reactions can be involved in the synthesis of novel materials as fine particles. *Gerard Demazeau (France)*
9.30-9.50 Synthesis of ceria doped by rare earth elements in high-energetic fields. *Jaroslav Cihlar/Klara Castkova (Czech Republic)*
9.50-10.10 Development of new pressure and temperature sensitive paints for high energy field characterization. *Uwe Beifuss (Germany)*
10.10-10.30 Hydrothermal synthesis - a system for controlling the nano-particulate product. *Ed Lester (UK)*

10.30-10.50 coffee break

Chair: Werner Bonrath

10.50-11.20 Simple and fast preparation of high surface area LaMnO3 perovkites via nitrates-mediated microwave synthesis. *Hakim Kaddouri (France)*
11.20-11.40 Thermodynamics and kinetics of hydrothermal synthesis. *Robert Piticescu (Romania)*
11.40-13.00 Separate WG Meetings (Presentation of cooperation plans in COST Action D32 and D30)

13.30 Lunch

ORGANIC SONOCHEMISTRY: CURRENT STATUS, UNSOLVED PROBLEMS, AND CHALLENGES

Pedro Cintas

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Since the early 1980s, sonochemistry has attracted a considerable attention as an innovative method for accelerating organic and organometallic reactions in a wide variety of solvents and conditions, often accompanied by unexpected selectivity patterns. Some pioneers made the very significant observation that sonochemistry could further be subdivided into reactions susceptible of real chemical effects induced by cavitation and those mainly sensitive to the mechanical impact of bubble collapse.[1] Despite our modest understanding of cavitation and sonoluminescence, this nonclassical high-energy technique is heavily applied in organic synthesis, the fine-tuned fabrication of micro- and nanosized particles, interfacial phenomena, and the environmental degradation of pollutants.[2] Sonochemistry also offers stimulating challenges such as the role of ultrasound in homogeneous reactions, in unusual media (low-vapor pressure media, e.g. RTILs and gels), or the enhancement of certain key effects in controlling reactivity (e.g. hydrophobic interactions).[3]

This talk highlights a succinct overview of sonochemistry, intended for those non-familiarized with this technique, and a series of current problems and challenges found by other groups and ourselves in recent years.[4] This COST meeting, encompassing three accelerating and far-reaching techniques, is certainly timely and welcome not only for discussions of the underlying phenomena involved in every case, but also for stimulating further collaborative efforts.

1. Luche, J.-L. In *Advances in Sonochemistry*; Mason, T. J., Ed.; JAI Press Ltd.: London, 1993; Vol. 3, pp 85-124.
2. a) Cintas, P.; Luche, J.-L. *Green Chem.* **1999**, *1*, 115-125. b) Mason, T. J.; Cintas, P. In *Handbook of Green Chemistry and Technology*; Clark, J., Macquarrie, D., Eds.; Blackwell: Oxford, 2002; pp 372-396. c) Cintas, P. In *Transition Metals for Organic Synthesis, 2nd Ed.*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim; Vol. 2, pp 583-596.
3. a) Oxley, J. D.; Prozorov, R.; Suslick, K. S. *J. Am. Chem. Soc.* **2003**, *125*, 11138-11139. b) Tuulmets, A.; Salmar, S.; Hagu, H. *J. Phys. Chem. B* **2003**, *107*, 12891-12896. C) Höfinger, S.; Zerbetto, F. *Chem. Eur. J.* **2003**, *9*, 566-569.
4. Recent work from our group: *Tetrahedron Lett.* **2000**, *41*, 4101-4104; *Ultrasonics Sonochem.* **2003**, *10*, 25-31; *J. Org. Chem.* **2003**, *68*, 7193-7203.

MICROWAVE EFFECTS IN ORGANIC SYNTHESIS

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Accelerations of organic reactions by microwaves (MW) are largely exemplified. They result from material-wave interactions leading to thermal effects (connected to dipolar and charge polarizations and inversion in alternance of electric field) and specific (non-purely thermal) effects resulting from variations in activation parameters, enhancements in molecular impacts and possibly localized microscopic temperatures.

In order to get some experimental evidences for specific effects, and consequently to underline the wide interest of this technology, there is a need for cautious and reliable results under microwaves and conventional heating. To this purpose, we can use reactors especially dedicated to chemistry with accurate control of temperature, emitted power and pressure all along the reaction with similar profiles of raising in temperature under both kinds of activation.

The specific MW effects will be considered according to reaction media and mechanisms. They could be essentially involved in the case of non-polar solvents, as they are transparent to the radiation. They could be evident in the case of polar mechanisms where the transition states are more polar (and therefore more sensitive to MW) than the ground states of the reactions. They could be more pronounced in the case of late transition states along the reaction coordinates.

The case of solvent-free reactions is by far the more propitious to observe specific effects as no masked by solvents. Three types of solvent-free methods under MW can be involved : -reactions between neat reagents in quasi equivalent relative amounts as interfacial reactions, - solid-liquid Phase Transfer Catalysis, in the presence of tetraalkylammonium salts, for anionic reactions, - reactions using supported reagents on mineral oxides (aluminas, silicas, clays). Several typical examples will be described. These methods consist furthermore in ecofriendly chemistry (Green Chemistry) as no solvents are involved and purity of products enhanced under very simplified and safe conditions.

1.Loupy, A. (edit), " Microwaves in Organic Synthesis ", Wiley-VCH, Weinheim, **2002**.

2. Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P.; Mathé, D. **1998**, *Synthesis*, 1213-1231.

3. Perreux, L.; Loupy, A. *Tetrahedron* **2001**, *57*, 9199-9225.

4. Loupy, A. *C.R. Chimie* **2004**, *7*, 103-112.

CRITERIA FOR THE INDUSTRIAL APPLICATION OF "NON-CLASSICAL" METHODS

Werner Bonrath

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There is a big interest in the implementation of new processes as well as new synthetic strategies. So-called "non-classical" methods, e.g. the application of ultrasound and microwaves, were viewed as convenient techniques [1].

For new synthetic methods criteria based on the atom economy and the E-factor are established. Atom economy means the number of atoms in the starting material, which are found in the product [2]. The E-factor is based on the amount of waste in kg per kg product [3].

We were interested in the application of "non-classical" methods, in chemical transformations or new process solvents, in order to use such types of methods as tool to influence selectivity and yield of reactions.

During the presentation several applications of "non-classical" methods will be presented and criteria for scale-up will be discussed. Especially aspects of reproducibility of laboratory scale (g-scale) experiments, which are later on transferred into large scale, will be presented. Furthermore aspects of the reactor design are discussed.

Another part of the presentation deals with the equipment factor, which gives information's about the restrictions of availability of a technology [4]. These facts are the most important criteria for the implementation of a new technology in industrial processes.

References

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[2] B. Trost, *Angew. Chem.* **1995**, *107*, 285.

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[4] W. Bonrath, *Ultrasonics Sonochemistry,* **2004**, *11*, 1.

HIGH PRESSURE & MICROWAVE REACTORS: PROBLEMS AND NEW OPPORTUNITIES

Witold Lojkowski

Institute for High Pressure Physics, Polish Academy of Sciences

There are many claims that microwave energy accelerates chemical reactions or change its course. Providing evidence for such effects requires that the reaction is carried out using conventional heating and microwave heating at the same temperature. Some of these experiments can be questioned in respect to scientific rigidity, because it is virtually impossible to have the same temperature field in a sample heated conventionally and using microwaves.

Carrying out chemical reactions using stronger than achievable till now electromagnetic fields could permit to better understand the effect of microwaves on chemical reactions. However, increasing the microwave power leads to plasma formation. Increasing the pressure in the microwave cavity permits to prevent plasma formation. Besides that high pressure permits to increase the temperature of boiling of liquids or to change phase equilibrium, so that the range of chemical reactions possible to investigate increases and nanopowders can be produced in solvothermal conditions. On this reason we started to develop high pressure microwave reactors. At present we operate two such devices, one operating at pressures up to 10 MPa, and the other at pressures up to 50 MPa. The average power densities possible to achieve reach 3 W/ml in the first case and may reach 30 W/ml in the second case.

We compared nanopowders of ZnO and Zirconia produced in the 10 MPa reactor during hydrothermal synthesis using conventional heating and microwave heating. We did not find measurable differences between powders produced by the two methods. In this kind of reactions it seems that the main advantage of microwave heating is of technical character: a volume of liquid can be quickly heated and cooled in very clean conditions. An issue is to ensure reproducibility of the conditions when a relatively small volume is rapidly heated in a cold environment.

In the case of the 50 MPa reactor, the highest reached temperature was limited by the transition of water into a supercritical fluid. We are open for collaboration with groups willing to exploit the new opportunities for chemistry in high energy environment using high pressure reactors.

FABRICATING NANOMATERIALS BY SONOCHEMICAL AND MICROWAVE TECHNIQUES FOR THE ELIMINATION OF HAZARDOUS MATERIALS FROM WASTE WATER.

Aharon Gedanken

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A few examples by which nanoparticles produced by sonochemistry, and by microwave dielectric heating are employed in the treatment of hazardous wastes. We have prepared sonochemically nanoRu, nanoPt inserted into (MSP) TiO_2, MSP CeO_2, and MSP ZrO_2. These catalysts were employed in the wet air oxidation of various acids (succinic, coumaric, and acetic). The coumaric acid is a model compound for the wastes of the manufacturing of olive oil. The comparison with well-known commercial catalysts will be presented.

We will show how MgO nanoparticles are able to kill gram positive and gram negative bacteria. This effect is strongly dependent on size.

Another example that will be presented is the use and aquatic plants in combination with microwave radiation for the elimination of heavy metal ions (Pb^{+2}, Ag^{+1}, and Ru^{+3}) from aqueous solutions. The aquatic plants were placed in an ethylene glycol solution and irradiated with microwave radiation. After burning the aquatic plants in argon or nitrogen nanoparticles of the corresponding metals were obtained.

Finally, early experiments conducted by Dr. Andreas Tiehm on the elimination of PCE using air-stable iron nanoparticles show that this is a promising material fro the elimination of hazardous chloro aliphatic compounds.

COMBINATIONS OF WITTIG OLEFINATIONS WITH Pd(0) CATALYZED C-C COUPLING REACTIONS UNDER ULTRASOUND

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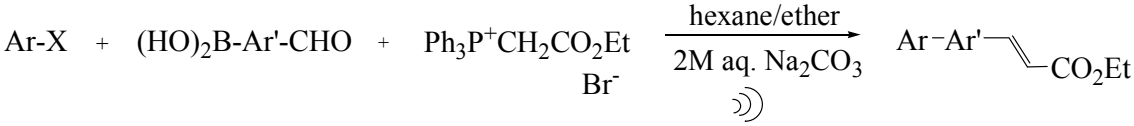
Mixtures of carbaldehydes and stabilized and semi-stabilized ylides or their phosphonium precursors give Wittig olefination products in very good yields, when the reactions are run in a two phase system under ultrasonication. A screening of Suzuki reactions with a number of haloarenes and arylboronic acids quickly showed that cross-coupling reactions also proceed successfully in such biphasic media, when ultrasound is used (eg., 1-iodonaphthalene and phenylboronic acid in hexane/ether 95/5 [*v*/*v*] / 2M aq. Na_2CO_3 gives 1-phenylnaphthalene in 98%). This led to the idea of combining the two processes with formylarylboronic acids, with haloarylcarbaldehydes or with substituted 3-haloalk-2-enals as substrates. The use of ultrasound allows for such reactions even to be carried out in a mixture of aq. Na_2CO_3 and ether and hexane. The bulk reaction temperature is lower than in most previously described experiments regarding such transformations. Meanwhile, the investigation of one pot Wittig-olefination/C-C cross coupling protocols under ultrasonication has broadened to include Heck- and Sonogashira reactions. Where *o*-haloaryl/hetarylcarbaldehydes or 3-haloalk-2-enals have been used as substrates in the one pot transformations, the products obtained could be submitted to ring closure reactions to obtain derivatives of natural products with interesting biological activity. Currently, an alternative possibility of carrying out one pot Wittig olefination/C-C-coupling protocols under microwave irradiation using supported metal catalysts is also being studied.



O-07

HIGH INTENSITY US-REACTOR OPERATING UNDER PRESSURE UP TO 1 GPA OF HELIUM OR ARGON: APPLICATION TO NANOPOWDERS TECHNOLOGY.

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High energy ultrasonic vibrations meat considerable attention in a wide range of applications: electronics, pharmacy, biotechnology, chemical technologies, ceramic and other applications.
Here we show our recent results of use the high energy supersonic wave applied in an exceptional medium: gas in viscous state. The ultra high gas pressure of up to 1.5 GPa causes an increase of gas density to that of liquids. In that presentation we show the effects obtained with using of the noble gases. The active gases, by their high chemical activity at high pressure and with high ultrasonic energy dissipation, may induce a rapid nitrogenization or oxidation processes; for example in nanopowders of ceramics. The use of very high ultrasonic energy in conditions of very high gas medium pressures activate intensive cavitation, analogue to that observed in liquids.

Our present application of this new combined technology is preparation of the nano-components for sintering and annealing of the new generation of MgB_2 superconductors. The material is doped with nanopowders of other phases (as pinning centers important for superconducitng properties), and subsequently subjected hot pressing (HP), hot isostatic pressing (HIP), as well as hydroextrusion (HE). The high-pressure ultrasonic technology permits very effective cleaning of the substrates, their homogenization and refinement with densification of the reactive pulp before the subsequent densification procedures are applied.

The preliminary results of our new technology adapted to the superconducting nanopowders, doped by SiC and diamond in aim of maximization of critical superconducting parameters (T_c, J_c) of new generation MgB_2, are presented. The exceptional properties of obtained samples of superconducting materials are shown: the microstructure, the highest known Tc of (42,6 K), as well as the received due to of above mentioned technology high mass densities of samples and fine structure.. Unusually high superconducting critical parameters have been obtained.

Treatment by high energy ultrasound under high gas pressure can be used for: mixing of submicron and nano size powders, milling, degradation of complexes, desorbtion of undesirable active gases or inversely saturation by the desirable active gases.

O-08

"*IN SITU* AND *EX SITU* STUDIES OF PROCESSES IN MICROWAVE-IRRADIATED MATERIALS"

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Microwave radiation may be used to accelerate synthesis and processing of a wide range of materials, particularly where migration of ions is involved. In order to follow such processes, and perhaps elucidate mechanisms, we have designed apparatus to enable us to perform X-ray diffraction experiments on a sample held on a conventional goniometer during microwave radiation. One central problem with most microwave heating devices in these circumstances is the requirement to contain the microwaves within a metal enclosure, whilst still providing access to X-rays. We describe systems suitable for use with a laboratory X-ray diffractometer and outline preliminary diffraction studies.

In contrast to X-rays, Neutron diffraction has fewer materials constriants in the construction of the microwave applicator, but still presents some technical problems in the space available. One solution to this problem has been to use a parallel-plate applicator, in which the electromagnetic radiation is brought close to the sample through a co-axial cable, then applied to the sample across two plates connected to the two conducting components of this cable. This allows the scattered beam to pass from the sample without attenuation over a significant solid angle. Preliminary results of scattering in lipid systems is described.

Finally, the question of ion migration in solid systems is addressed in a series of ex-situ experiments. Whilst the argument is plausible, the extant experimental evidence for an enhancement that has an influence on the rate of reaction is open to criticism. By employing a polarised microwave field to heat a sample containing two isostructural compounds for a period of several days, the diffusion rates at various angles to the electric field may be compared by slicing and polishing of the samples. Mapping of ion concentrations at the interface between the two materials using a scanning electron microscope allows relative diffusion rates in each direction to be calculated, thus giving a direct comparison of the rate of ion diffusion in relation to the angle to the electric field. We have now compared the time dependence of the ratio of the relative diffusion rates. It is proposed that the time-dependence of the enhanced diffusion may be explained in terms of ponderomotive enhancement effects.

TRANSITION ELEMENT DOPED MESOPOROUS SILICAS AS CATALYST FOR FINE CHEMICAL SYNTHESIS

Mark P. Copley, Trevor R. Spalding, Michael A. Morris, Justin D. Holmes

Materials Chemistry, University College Cork, Ireland

Modified mesoporous silicas have recently been shown to have great potential as catalysts. Doping of mesoporous silica is the most common approach but other oxide and metal systems can be prepared. They are thought to have considerable potential impact in catalysis due to their novel physiochemical properties, including high surface areas and tunable pore size. At UCC we have pioneered methods of in-situ modification of mesoporous silicas. We have employed a method involving the co-condensation of the silicon alkoxide and appropriate transition element precursor. Extensive work has been carried out by us using the elements iron, zirconium and titanium to produce highly efficient catalysts for use in specific areas of fine organic chemistry.

Iron doped mesoporous silica has been previously shown to be catalytic for reactions such as hydroxylation and degradation. Zirconium and titanium modified mesoporous silicas demonstrate high activity for rearrangement and ring opening reactions.

All catalysts synthesized in UCC demonstrate high ordering, thermal and hydrothermal stability. They are also found to be reusable for a number of reaction cycles with no leaching of the transition element dopant been noted during reactions. The iron modified samples demonstrated high activity for the acylation of phenol while the zirconium and titanium modified silicates were highly active for the alcoholysis of styrene oxide. Reactions were carried out using both reflux conditions and in a controlled microwave environment. Products of all reactions were identified using ^{1}H NMR, C, H and N microanalysis and GC-MS.

All modified mesoporous silicas were characterized using the following analytical techniques; x-ray diffraction, BET/BJH surface analysis, x-ray fluorescence spectroscopy and transmission electron spectroscopy. Iron modified silicas were also characterized by Mössbauer spectroscopy. In certain cases NH_3 adsorption techniques (NH_3 TPD) were used to quantify the Lewis and Brönsted acid sites.

HIGH INTENSITY ULTRASOUND ASSISTED REACTIONS OF ORGANIC MOLECULES

Georgios A. Heropoulos*, Spyros Georgakopoulos, Maria Micha-Screttas, Barry R. Steele

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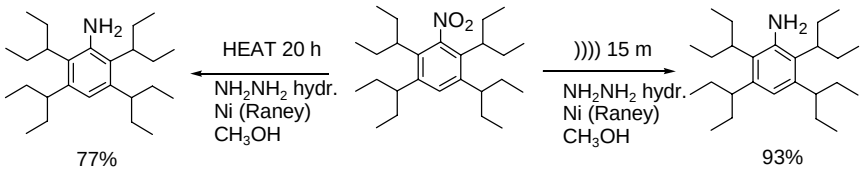
Sterically demanding molecules are of great interest in many applications, while an additional useful property often associated with the presence of bulky organic groups is increased lipophilicity, which makes for more amenable handling with organic solvents.[1] In our laboratory we have developed a simple procedure for the production of certain crowded aromatic molecules using a catalytic system for the clean addition of ethylene to a series of alkylaromatics, and we are now actively developing the chemistry of these compounds further.[2] We report here the preparation of a series of nitroaromatics and their reduction to the corresponding anilines.

Ultrasound techniques have been applied to many reactions involving metals, and we therefore examined the use of high intensity ultrasound to the reduction of our nitro-compounds. These reactions were solvent, catalyst quality and ultrasound intensity dependent and, in comparison to their silent reactions, proceeded much faster and afforded higher yields.[3]



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3) This work has been submitted for publication.

HYDROGEN FROM CHEMICAL HYDRIDES BY MICROWAVE OR ULTRASOUND ASSISTED STEAM HYDROLYSIS

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The paper reports on our recent investigation of a gas/solid chemical reaction between steam and chemical hydrides that liberates pure hydrogen gas. Our aims are to obtain fundamental kinetic, chemical, and thermodynamic data on the reaction so that sufficient information is known to evaluate this technology rigorously for its potential as a means of delivering hydrogen for fuel cells and internal combustion engines. We report on our results and conclusions of the a.m. reaction under different conditions and the characterization of the hydrated by-products. Well-known is that simple hydrides (CaH_2) as well as complex hydrides ($LiAlH_4$, $LiBH_4$, $NaBH_4$) react with liquid water or steam to produce hydrogen. For example, $NABH_4$ has been extensively studied:

$$NaBH_4 + (2+x)\ H_2O \rightarrow 4\ H_2 + NaBO_2\ x\ H_2O + heat$$

"x" is the "excess hydration factor", representing the fact that the solid by-products can exist in varying degrees of hydration. The liquid-phase reaction has some disadvantages. Excess water reduces the mass efficiency of the system. Recent discoveries (1999, 2004) show that by vaporizing water prior to contact with the hydride, hydrogen yields in excess of 90 % may be obtained without the need for a catalyst. Thermodynamic considerations show that, in principle, the heat liberated by the reaction is more than sufficient to vaporize the stoichiometric water required for the steam.

Three steam hydrolysis systems used in this work consist of a quartz tube reactor. The energy input was realized under thermal heat, microwave irradiation, and ultrasound conditions. The hydrolysis of sodium borohydride is, as expected, feasible with non-classical forms of energy, such as ultrasonic and microwave energy. However, huge quantitative differences become apparent: the hydrolysis in the microwave field has been investigated using two methods; the physical separation of the source of the water vapour from the place of the hydrolysis has shown obvious advantages when compared to the hydrolysis in boiling water. The possible reasons for these differences were investigated in selected experiments. In conclusion, the following results were obtained:

- Sodium borohydride dissolves immediately in boiling water and condensing water vapor while dihydrogen develops.
- The quality of the sodium borohydride only plays a subordinate role. The batches obtained from different manufacturers gave comparable results.
- When the hydrolysis is carried out following method II, the temperature achieved is, at least over some periods of time, much higher than the boiling point of the mixture in the reaction flask. During these times, relatively more dihydrogen evolves.
- The position of the frit in the glass connection piece is irrelevant for the control of the power input, when regulated via the temperature in the flask.
- A continuous addition of sodium borohydride during the hydrolysis is feasible, and it allows for the short-term evolution of larger amounts of dihydrogen. A continuous basic out-put is maintained.

The main problems are due to the regulation of temperature and energy input. A possible regulation of the energy input in small steps and avoidance of the congestion at the frits, *e.g.* by including some kind of a by-pass, would allow the use of higher pressures, thus making the process even more effective.

Acknowledgment: This work was supported by DaimlerChrysler AG, Ulm.

ULTRASONIC DETECTION OF HYDROPHOBIC EFFECTS IN WATER-ETHANOL SOLUTIONS

Ants Tuulmets

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The hydrophobic interaction (**HI**) is the tendency of apolar groups to aggregate in aqueous solutions, in order to minimize unfavourable interactions with water. HI is a principal force determining the structures of proteins and nucleic acids, and the binding of substrates to enzymes. Also some rather simple organic reactions can show hydrophobic effects when carried out in aqueous solutions.[1] Reaction rates are frequently dominated by HI between the reactants and/or the transition state with water or with a cosolute.. HI can stabilize the reactants thus diminishing the reaction rate. Accordingly, stabilization of the transition state by HI brings about a rate enhancement.[1]

We have shown that ultrasonication (**US**) can cause changes in the translational energy of species, thus leading to a solvent structure break or to a shift of solvation equilibria, HI included.[2] In aqueous ethanol solutions, hydrophobic reagents can be hidden in the clusters formed of ethanol molecules and thus made inaccessible for the reaction. Ethyl, n-propyl, and n-butyl acetates were used as probes of the inclusion of a reagent in the clusters. Indeed, the US effect on the acid-catalyzed hydrolysis of esters correlated with the order of hydrophobicity of the esters. Butyl acetate should be the most powerfully held by clusters, and US was the least efficient in this case. A logical interference from that was an unfavourable effect of US upon the reactions promoted by HI, e.g. Diels-Alder reaction, the benzoin condensation, etc.[1] Indeed, we observed slowing down of the benzoin condensation reaction of benzaldehyde by US in water and in water-ethanol solutions.[3]

In conclusion, if breaking down the stabilization of the encounter complexes between the reagents, US suppresses the reaction rate, while perturbation of the solvent-stabilization of the reagents accelerates the reaction. Thus, US may become a useful tool for the investigation of reactions in solutions.

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3. Tuulmets, A.; Hagu, H.; Salmar, S. *J.Am. Chem. Soc.,* (submitted).

ONE-POT PREPARATION OF IONIC LIQUIDS

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The development of practical methodologies using "greener" or more environmentally benign media is one of the topical leading concerns of any chemical synthesis. In recent years, the use of ionic liquids as recyclable reaction medium to replace volatile organic compounds has received considerable attention. [1,2] They are, for most of them, cationic species derived from amines among them imidazolium salts that are widely studied and used. Their high thermal stability and relative inertia due to their pure ionic structure confer them a promising future. Two steps are necessary to synthesise these salts. The first step, (Menschukin reaction[3]) is the quaternisation of the imidazole and the second step, (Finkelstein reaction[4]) is the metathesis of the counter-anion as shown in the figure 1 below.

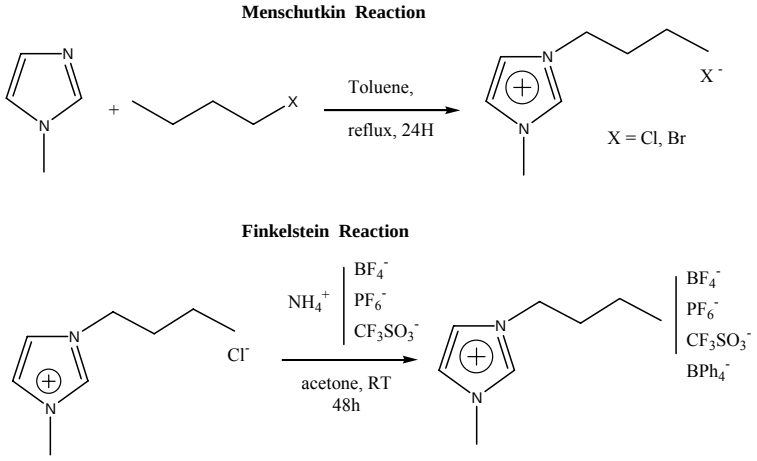

Figure 1

The generally admitted time to synthesize the BF_4^-, PF_6^- or $CF_3SO_3^-$ derivatives, vary between 3 to 7 seven days with large amounts of volatiles solvents compared to the amount of synthesized material.[1,2] Our preliminary experimental campaign was the occasion for us to foresee the potential of ultrasound by dramatically accelerating the Finkelstein step leading to the desired product in 1h compared to 72h on mechanical stirring without further purification. The first step, Mentschukin reaction, occurring in a homogeneous phase is strongly thermally dependent. Even if these conditions are not favourable for ultrasonic irradiation, we studied the possibility to produce through a neat "one-pot" synthesis under ultrasonic irradiation at 20kHz and under pressure the hexafluorophosphate 1-alkyl-3-methylimidazolium, leading to a reasonable conversion yield. An overall of this system will be presented with the study of key parameters such as the influence of acoustic power and reaction temperature.

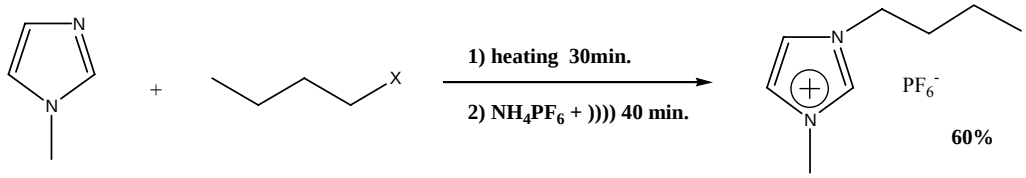

Figure 2

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CHEMICAL COMPOSITION EFFECT ON MICROWAVE ASSISTED NANOPARTICLES PRODUCTION

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The effect of microwave, MW, and solution chemistry on the transformation of $[Zr_4O_{(8-x)}(OH)_{2x}]$ to $ZrO_{(2-y/2)}$ amorphous $(OH)_y$ and to crystalline m-/t-ZrO_2, where m- and t- indicates respectively monoclinic and e tetragonal, phases have been investigated in low pressure MW hydrothermal process.

Microwave accelerate treatment times due the efficient dielectric heating of the water content of the pressurised vessel. A commercial pressurised reactor, CEM Mod. MDS-2000, was used at 250 W, 2.45 GHz, output power at 200 psi (194°C) for 2 hrs treatment time.

Full conversion of hydroxides to oxide, 98%, was reached in a neutralised, pH 9, solution whereas the conventional treatment requires times of about 20 hrs. The predominant crystalline phase for the particle range dimension produced (5-10 nm) is the tetragonal.

The monoclinic phase is more dependent upon chemical concentration, with respect to the tetragonal one: changing from 38 to 12 nm when NaOH concentration varies from 0.1 to 10.0 M, whilst the tetragonal varies from 17 to 21 for the came NaOH concentration range. Zirconia starting compounds also affect monoclinic phase size, varying from 15 to 30 nm when $ZrOCl_2.8H_2O$ solution varies from 0.1 to 1.0 M. One more effect of the chemical composition was found on the synthesis of pure zirconia nanoparticles: agglomeration appear to be influenced either by the zirconia raw material or the alkali concentration.

When common stabilising oxides are added to the starting zirconia solution, 3-6-8at% Y_2O_3, 3-6-12at% Bi_2O_3, and 5-10-15-20at% Pr_2O_3, 2-3-4 at% NH_4VO_3. Their effect was not only an increase in the tetragonal phase, but also a reduce particle size recorded as surface area increase (i.e. for Bi surface area from 84.53 (3%at) to 114.39 (12%at) m^2/g).

Reaction time has been evaluated on the crystallinity and crystal size f the powders, and it was noticed to have higher effect on the first parameter, crystallinity, rather than on the second.

It has so far proved that chemical parameters, additives and the synthesis parameters, mainly irradiation time, can affect phase partitioning and crystallite size in hydrothermal low pressure microwave assisted processes for nanopowder preparation. The problem to attain larger nanoparticles production was faced by designing a new large scale reactor. Its development and construction will be realised during the COST activity jointly with other laboratories.

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REACTORS COMBINING HIGH-INTENSITY ULTRASOUND AND MICROWAVE IRRADIATION

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In the last decade non-conventional energy sources such as microwave (MW)[1] and high-intensity ultrasound (US)[2] have been increasingly exploited in organic synthesis because they bring reactions to completion in minutes or even seconds rather than hours or days. They can also induce reactions that would otherwise prove very laborious and may bring out peculiar chemoselectivities, opening up new synthetic pathways. Although the application domains of US and MW do not overlap, they both have a great potential towards developing environment-friendly synthetic methods; moreover their combined use seems to be extremely promising. In a study of chemical modifications of cholic acids, we showed that either technique could considerably improved yields and reaction times compared to conventional methods[3].

Few synthetic reports have appeared in the literature involving a simultaneous irradiation with both energy sources; among them some notable applications are esterification[4], condensation, *O*-allylation, synthesis of ethers, aromatic SN, the Knoevenagel-Doebner reaction[5]. Because of technical hurdles the potential of combined US/MW irradiation has not been systematically investigated as yet.

In our laboratory two types of US/MW combined reactors have been developed:
- type A features two reaction cells (one for each kind of irradiation) joined by short lengths of tubing to allow circulation of the reacting liquid between them
- type B features a single reaction cell placed in a MW oven; simultaneous irradiation with US is carried out by means of a horn tip machined from a rod of fused quartz.

In both types temperature control proved the greatest hurdle, which was met by an appropriate selection of silicone oil and tubing.

The advantages offered by combined irradiation have been brought out in experiments with several reactions, particularly with Pd-catalyzed aryl-aryl couplings[6].

Acknowledgement. COST Action D32 is gratefully acknowledged. The present work was supported by MIUR (COFIN - project: "Sviluppo di processi sintetici eco-compatibili nella sintesi organica").

Combined US/MW reactors have been developed in collaboration with NTS srl Arcugnano (Vicenza, Italy).

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CHARACTERISATION OF STRUCTURE AND GRAIN SIZE DISTRIBUTION OF NANOPARTICLES

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Nanomaterials exhibit distinctly different mechanical and physical properties. This requires development of characterisation methods for nanopowders. The added value of nano-powders in applications results from "size effects" where the properties change under a critical dimension [1]. For optimising the synthesis process of nanopowders and their further applications, it is important to perform quantitative characterisation of the powders. Besides the commonly used techniques, such as X-ray diffraction (XRD), specific surface characterisation and laser diffraction, direct imaging techniques including Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) could be used. The computer image analysis method enabled complete characterisation of the average grain size, grain size distribution, grain morphology, structure of agglomerates and surface structure [2÷6]. In the present work the TEM techniques were combined with advanced image analysis techniques, to obtain precise quantitative data about analysed nanopowders. The obtained results were compared with a new advance method of XRD pattern analysing. The experimental technique also included Zeta potential measurements.

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THE APPLICATION OF HIGH ENERGY ELECTRIC AND MAGNETIC FIELDS TO PROCESS FLY ASH AND CERAMICS

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ANSTO's development of waste forms for nuclear waste has lead to the development of equipment and methodologies that allow us to control the properties of materials like titanate ceramics. The complex compositions of waste streams in the nuclear industry have resulted in the design of a wide range of chemical compositions of ceramics, glass and glass-ceramics to immobilize specific radioisotopes. Concurrently with the science of the waste form design, processing strategies had to be designed to study the effects of atmosphere [1], melting conditions and precursor particle size on the microstructure and durability of the final phases formed. The work reported here highlights the problems encountered and potential solutions.

Radio Frequencies (RF) have been used extensively to melt metals and alloys [2,3]. In contrast with joule melting, RF heating is a more efficient technique for melting and preparing high-density materials. Typically ceramics and glasses of interest are difficult to melt using RF, as the majority of these materials are very good electrical insulators and do not couple with an electromagnetic field. This means that in order to melt the material with an electromagnetic field, one must resort to the use of a high melting point conductor to initially couple with the field. The powder is then heated indirectly by contact with the conductor and convection until it becomes conductive. Also, poor electrical conductors tend to be poor thermal conductors, and large heat loses can be expected. A way of overcoming these problems was needed, but it was necessary to make sure that the solution was not detrimental to the microstructure of the ceramic or glass and that its final properties were the same as one would obtained by melting it using conventional joule heating.

Two methods of melting fly ash and titanate ceramics were used; 1) a standard cold crucible melter (CCM) with a conductor and 2) a CCM without a conductor but with an additional coil to generate a high voltage electric field to encourage dielectric heating. In the second method, the high voltage field was applied using a graphite rod that allowed a corona discharge to occur when the temperature of the powder was high enough for the insulator to conductor transition to occur. Once this occurred, the discharge produced localised plasma which further heated the powder. In both methods, it was found that once the bulk of the material was hot enough to be conductive, i.e., the Mott transition temperature had been reached, eddy currents formed due to inductive coupling and easily sustained the heating till the melting point was reached. It was found that the high energy electric field made it easier to melt fly ash, Fig 2, whereas in the standard cold crucible it was more problematic Fig 1. Synroc C, was also melted by the two methods. The mineral phases present in synroc all formed in both methods showing that the ceramic can be formed by either method Fig 3 and Fig 4.

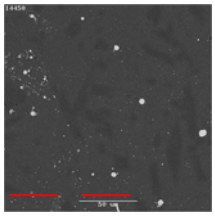

Fig 1. Flyash conductor used.

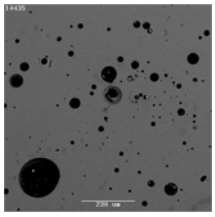

Fig 2. Flyash no conductor but with an additional electric field.

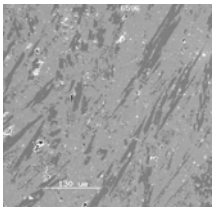

Fig 3. Synroc C conductor used (130μm).

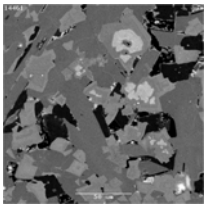

Fig 4. Synroc C with no conductor but with an additional electric field (50μm).

Melting of ceramics and glass-ceramics is possible with and without using an initiator. The absence of an initiator does result in more oxidising conditions that in the case of the titanate ceramics can cause segregation of volatile components such as Mo and Cs.

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MW-ASSISTED HETEROGENEOUS GAS PHASE CATALYSIS - TEMPERATURE MEASUREMENT INDEPENDENCE ON THE PARTICLE SIZE AND THE CATALYST MASS

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To date, only few literature sources report on heterogeneous gas phase catalysis in the multimode microwave field. The most prominent reasons for this fact are unresolved problems such as precise temperature measurements under microwave radiation. In our previous work, we were able to show that we obtained good power control and precise temperature measurement with a modified gastronomy microwave oven. This oven was equipped with a switching power supply and a pyrometer for temperature measurements [1]. The pyrometer was used in order to measure the temperature at the catalyst surface and to control the power input. The determination of the temperature inside the catalyst bed was performed with a thermocouple by recording and evaluating cooling curves after the microwave oven was switched off. In this way, radial and axial temperature profiles could be obtained as well [2]. A series of technically interesting patents tries to employ the advantages of the microwave technology for three-way-catalysts and diesel soot filters [3,4,5]. Scientific oriented investigations have only been published scarcely so far [6]. In our multimode microwave reactor [1], we initially investigated the catalytic propane oxidation for $La_{1-x}Sr_xBO_3$ (with B: Co, Mn) catalysts and found that the dielectric properties of the manganates by far surpassed those of the cobaltates, whereas the catalytic properties of these catalysts behaved completely diametrically. We investigated the microwave absorption behavior of perovskite–type catalysts in dependence on particle size. In the range between 2 mm and 250 µm it is similar. If the particle size is smaller much less power is necessary to heat the catalysts. From an industrial point of view, the behavior of a higher catalyst mass in the multi-mode microwave applicator is very interesting for a possible scale-up. Therefore, different catalyst masses under equal space velocities were investigated. The mass was varied from 1.5 - 12 g and the flow rate adjusted from 5.25 – 42 L h^{-1}. The inlet temperature, measured by Irpyrometer in the catalyst bed, was kept constant at 270 °C. As a result the catalyst bed temperature, measured in the middle of bed, increases strongly with increasing catalyst mass. Hence, the conversion also increases from 50 to 100 %. It is remarkable that the necessary microwave power to reach a desired temperature (measured by IR-pyrometer at the entrance of the catalyst bed) is nearly constant.

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CONVENTIONAL VERSUS MICROWAVE HYDROTHERMAL SYNTHESIS OF SILICO ALUMINATES

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A feasibility study on the synthesis of sodalite ($Na_8(Al_6Si_6O_{24})Cl_2$) from kaolinite ($Si_2Al_2O_5(OH)_4$), metakaolinite (dehydroxylated kaolinite), NaOH and NaCl using a microwave process has been carried out by comparing the heating time and reaction temperature with the same operating conditions both under microwave irradiation and under conventional thermal process.

Experiments have been conducted using the hydrothermal method at atmospheric pressure. The results show that the reaction is more significantly hastened under microwave irradiation than under conventional heating. The synthesis of sodalite ($Na_8(Al_6Si_6O_{24})Cl_2$) has been performed using natural starting compounds, such as silica and alumina sources (kaolinite and metakaolinite). The following reagents have been employed; kaolinite ($Si_2Al_2O_5(OH)_4$), metakaolinite (dehydroxylated kaolinite), sodium hydroxide and sodium chloride. While kaolinite is a crystalline compound, metakaolinite, which is obtained by dehydroxylation of the former, is amorphous. Two types of kaolinite have been studied. The thermal stability of both low (Kao-well) and high (Kao-bad) defect kaolinite together with the transformation of kaolinite into metakaolinite have been investigated using the thermogravimetric technique.

Sodalite synthesis has been carried out under conventional heating and phase identification, depending on the heating time and the nature of starting materials and has been studied, using powder X-ray diffraction technique (XRD).

No diffraction peaks have been observed in the XRD diagrams of the solids prepared from metakaolinite, after a heating period of 90 min at 80°C, indicating the amorphous nature of the sample. After a heating time of 180 minutes, a crystalline product formed. The observed XRD patterns are characteristic of Zeolite A. Once the heating time reached 300 minutes, several XRD patterns attributable to sodalite appeared, while those of zeolite A decreased. Finally, after *ca.* 6 hours heating sodalite formation was completed. No sensible change has been registered when heating was prolonged to 24 hours under the same operating conditions.

Under MW heating crystalline compounds form after 90 minutes: they are characterised by their XRD patterns which are mainly assigned to Zeolite A, with a few ones ascribed to sodalite. Finally when the heating time is increased up to 180 minutes, the XRD patterns of the resulting product mostly indicate the presence of natural sodalite together with some traces of Zeolite A.

In the present study, also kaolinite was used to synthesise sodalite. The kaolinite was purified from other compounds. In this case it was possible to obtain sodalite in 180 minutes at 90°C using MW irradiation and 24 hours at 90°C using conventional heating. No zeolite A intermediate was detected in both cases. The purification of starting material was fundamental to increase yield in sodalite (from 30% to 75%).

The efficiency of the microwave process over the conventional thermal process has been proved by the yield in sodalite.

HOW SOLVOTHERMAL REACTIONS CAN BE INVOLVED IN THE SYNTHESIS OF NOVEL MATERIALS AS FINE PARTICLES.

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Solvothermal reactions concern all the reactions at high pressures involving a non-aqueous solvent. The temperature can be lower or higher than the critical temperature T_c (subcritical or supercritical domain). The precursor can be soluble or unsoluble in the solvent.In the first case the reaction can be initiated in the liquid phase and then the final product can precipitate.In the second case it is possible to control the thermal decomposition of the precursor in suspension in the liquid phase. In both cases ,it is necessary to select the nature of the solvent versus (i) the chemical composition of the final material, (ii) the required temperature for initiating the reaction and (iii) the selected domain (sub- or supercritical) in function of the objective of the reaction.

Solvothermal reactions can be used both in Solid State Chemistry (in particular for the synthesis of novel materials (1-2) or for developing new processes (3)) or in Materials Science in different ways: (i) preparation of small crystallites (4), (ii) deposition of thin films (5), (iii) low temperature sintering of functional materials (6), (iv) crystal growth(7).

During these last five years, solvothermal reactions have been particularly improved in the elaboration of finely divided materials (micro- or nanocristallites) and of novel materials (oxides, sulphides,borides,carbides…). This important development has led to initiate a specific chemistry in non-aqueous solvents.

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SYNTHESIS OF CERIA DOPED BY RARE EARTH ELEMENTS IN HIGH-ENERGETIC FIELDS

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Cerium oxide has a wide range of applications: thin ceramic layers for solid oxide fuel cell and for oxygen membranes, nanostructured ceramic for electroapplications, ceria nanoparticles for catalytic processes etc. Its chemical and physical properties are dependent, besides others, upon particle size and surface area. The material characterisation can be affected by the preparation method. Synthesis of ceria under nonconventional conditions (hydrothermal conditions, ultrasound or microwave field etc.) can lead to nanocrystalline products that needs no calcination (which causes the growth of particles).

In the present study, an ultrasound field, hydrothermal conditions and mechanochemical method were used for synthesis of nanocrystalline ceria doped by Sm, Gd and Y. The aim of this work was study of the effect of reaction conditions on phase composition, microstructure, particle size distribution, surface area and agglomeration of ceria particles. Ultrasound synthesis were performed with ultrasound intensity of 20-100W/cm^2, frequency of 20 kHz, at temperatures of 25-60°C and reaction time of 30-120 min. Hydrothermal conditions for ceria synthesis: temperature of 160°C-200°C and reaction time 4-5 hours. Mechanochemically was ceria synthesized at rotation speed of 200-900 rpm and reaction time of 2-48 hours.
Nanocrystalline powders of Gd-, Sm- and Y doped ceria helt traces of unreacted -OH groups and Ce3+ ions without respect to a synthetic method.

Doped ceria powders prepared by ultrasonic sonochemical method were crystallite size about 2-4 nm, particle size up to 50 nm and specific area was 50-100 m2/g. Particle agglomeration decreased with increasing ultrasound intensity, while size and shape of particles were not affected by US.
Acoustic field localised namely in cavitation zone resulted in acoustic streaming and physical modifications of ceria particles. Chemical action of US had probably weak effect on reactions because of low influence of US on oxidation of Ce^{3+}. Similar properties of doped ceria powders prepared sonochemically and mechanochemically promotes concept of physical mechanism of disintegration of agglomerates by acustic pressure of ultrasound.

DEVELOPMENT OF NEW PRESSURE AND TEMPERATURE SENSITIVE PAINTS

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Pressure Sensitive Paint (PSP) is a unique optical non intrusive experimental method in the field of aerodynamics to obtain the pressure distribution on a models surface in much less time than any other experimental pressure measurement technique, giving detailed information about the pressure distribution.

Our group has a strong interest in the synthesis of pressure sensors. We have developed a PSP system that has been introduced successfully for the measurement of pressure distributions in the field of wind tunnel research. The optical sensing of pressure is based on the change of phosphorescence intensity of newly developed oxygen sensitive dyes. For this purpose the dye is embedded in a polymer silicon matrix or is applied directly to metal or metal oxide surfaces. This approach allows the development of stable optical oxygen sensors. In a similiar way we have developed a TSP (*Temperature Sensitive Paint*) system allowing the measurement of temperature on surfaces. The talk will highlight an overview of PSP, intended for those who are not familiar with this new technique, as well as some current problems and challenges.

In addition our group has a strong interest in the development of microwave assisted chemical reactions in the field of organic synthesis. The focus is on transition metal catalyzed reactions as well as cyclization reactions for the synthesis of libraries of heterocycles.

O-23

HYDROTHERMAL SYNTHESIS – A SYSTEM FOR CONTROLLING THE NANO-PARTICULATE PRODUCT

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Nanoparticulate metal oxides and metals are finding increasing applications in areas as diverse as sun blocks, electro-conductive printing inks, electronic displays, pigments and catalysts.Many of the routes to such particles involve relatively noxious chemicals, are not easily scalable, have a complex and time-consuming sequence of stages, or may require expensive precursors. These methods include sol-gel (aerogels and xerogels), metal-atom aggregation in cryogenic inert gas matrices, thermal or ultrasonic decomposition of metal carbonyls, reduction of metal ions, semiconductor particles, zeolites and inverse micelles. By contrast, Supercritical Water Hydrothermal Synthesis (scWHS) offers a relatively simple route which is inherently scalable and chemically much more benign.

The approach at Nottingham has been two-fold:

(i) we have shown that scWHS techniques, originally developed in Japan[1, 2] for formation of pure metal oxides can be used to generate scientifically much more valuable mixed-metal oxides[3, 4]

(ii) we have combined our expertise in chemistry and chemical engineering to devise a much more efficient reactor [5, 6] (Figure 1) which has greatly increased the scope of reactions which can be tackled in this way.

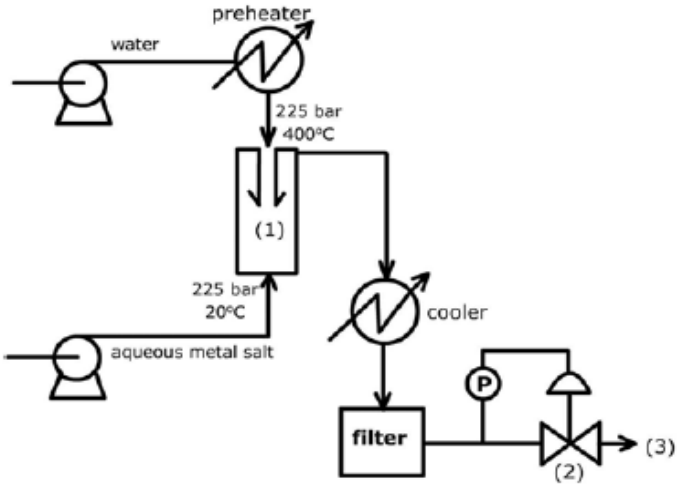

Figure 1 – a schematic of the supercritical water rig

The talk will explain how the reactor geometry was devised, and how operating parameters such as metal salt concentration, temperature and pressure can be used to control particle size and morphology with different metals/metal oxides.

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SIMPLE AND FAST PREPARATION OF HIGH SURFACE AREA $LAMNO_3$ PEROVSKITES VIA NITRATES-MEDIATED MICROWAVE SYNTHESIS

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Lanthanum manganates have attracted much attention as cathode materials for high temperature solid oxide fuel cell (SOFC) and also as catalysts for several reactions such as oxidation of hydrocarbons, CO, oxygenated compounds, reduction of NOx, etc. Owing to the scarcity and high cost of noble metals, worldwide efforts are being made to replace noble metal by non-noble metal catalysts, particularly ABO_3 type perovskites (where A = rare earth and B = transition metal such as Cr, Mn, Fe, Co.....) with or without partial substitution of A by other element, such as Sr, Ce..etc. The potential of perovskite-type oxides in catalysis was first reported by Parravano in 1952 [1] for CO oxidation. Since this early work numerous publications relevant to the application of these oxides in catalysis appeared.

Despite their numerous and interesting properties, perovskites suffer from some restrictions that limit their applicability in industrial processes. One of the most disadvantages is their specific surface area. Among the several methods analysed to prepare high temperature methane combustion catalysts, the most important are: co-precipitation, sol-gel processing [2], combustion synthesis, reverse micelle-mediated synthesis [3], etc. The latter was claimed to be one of the most promising route for obtaining high BET surface area of the solids. Although such method is valuable for production of materials with relative high surface area, it is typically both multistep procedure and it involve costly reagents.

In the present work we have investigated the effects of microwave irradiation in the synthesis of lanthanum manganates catalysts with high specific surface area. The activity of these catalysts was evaluated in the catalytic combustion of methane at high temperature.

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THERMODYNAMIC AND KINETICS OF HYDROTHERMAL SINTHESIS

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Nanocrystalline ceramic and composite materials present a set of highly improved and novel mechanical, electronic, optical, catalytic or bioactive properties over the traditional materials. The implementation and utilisation of these new materials is strongly dependant on the microstructural and surface nanochemistry characteristics investigation and modelling. New processes for the synthesis and sintering are required to be developed to control and optimize the chemical composition, component distribution, crystalline and grain sizes.

The present paper describes the basic methods regarding thermodynamic and kinetic modelling the hydrothermal synthesis from aqueous solutions of complex oxide ceramic nanopowders and process optimization. The advantages of the hydrothermal synthesis in terms of free energy required to obtain crystalline materials are discussed.

Starting from the thermodynamic and kinetic predictions some original results on the hydrothermal synthesis are presented. Yttria-doped zirconia nanopowders with crystallite size in the range 4-22 nm for solid state ionic with enhanced conductivity at lower temperatures, lead zirconate titanate (PZT) powders and films with crystallite sizes below 40 nm for piezoelectric applications, barium titanate powders, zinc oxide nanopowders and new hybrid biocompatible nanopowders in the system hydroxyapatite – maleic copolymers have been prepared.

The authors acknowledge the cooperation and financial support in the frame of three RTD projects and the first Romanian Virtual Center of Excellence in Nano-bio-technologies CENOBITE in the frame of National Programme for New Materials, Micro and Nanotechnology, two European RTD projects and cooperation with partners from COST D30 WG “High Pressure synthesis of nanomaterials” and COST 525 “Grain Boundary Engineering”.

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THE STATE OF ART OF THE X-RAY DIFFRACTION METHODS ON NANOSTRUCTURES IN THE RESEARCH CENTER FOR ADVANCED MATERIALS

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The main activities of the Research Center for Advanced Materials in the field of structure characterization of nanomaterials were presented. Nanomaterials in different forms (powder or thin films) prepared for different applications and especially by *hydrothermal and hydrothermal/electrochemical procedures* were investigating in order to obtain the phase compositions (qualitative and quantitative) and the microstructural properties (crystallites sizes, micro strains and fault probability). To provide the microstructural properties, two different methods for pattern analysis were performed. One of them is based on the facility of the new function, called Generalized Fermi Function (GFF), that allow to determine these properties from the single peak profile analysis in the case of small crystallite sizes. Another method of analysis is based on the whole pattern fitting and provides the average values for micro structural parameters. In this paper we present the powerful of these two methods applied in the global structure characterization of oxides thin solids films (ZnO, TiO2, WO_3) doped or no doped with active metals (Au, Ag, Pt), biocompatible thin solids films, composite nanomaterials based on montmorillonite.

INFLUENCE OF ZIRCONIUM OXIDE INCLUDING RARE – EARTH ELEMENTS ON STRUCTURE AND PROPERTIES OF POLYURETHANE NANOCOMPOSITES

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Transparent polyurethane elastomers offer many interesting benefits to users. Their optical clarity, high tensile strength and good energy absorption make them ideal to use in many areas, such as: optoelectronics, layers in laminates, shatter – proof coatings for glass and in medical applications [1]. In order to receive new properties of transparent thermoplastic elastomers the nanofillers with luminescence properties are introduced to polyurethane matrix, which enables to obtain polymer nanocomposites that are widely used in optoelectronics. Special properties of nanocomposites are connected with highly developed surface of nanofiller, which has a great influence on increasing interfacial affect between filler and single macromolecular particles of matrix. Additionally, introduction of rare – earth elements to nanofiller give us high luminescence properties in obtained nanocomposites. Nanofiller's dimentions are smaller than light wave – length, so it doesn't have influence on nanocomposite's optical properties.

The aim of this study was to evaluate the influence of zirconium oxide including rare – earth elements on polyurethane matrix properties for applications in optoelectronics.

Components used for PUR synthesis were: polycaprolactone diol (PCL) Mn=2000, 4,4'-dicyclohexymethane diisocyanate (H'MDI), chains extenders (DIOL A, DIOL B). As nanofiller zirconium oxide including rare – earth elements was used. The filler was added to the chosen polyurethane matrix in 1,0% wt. respectively to the hole weight of polymer. Samples for research were synthesized from a mixture of substrates in prepolymer method.

Study of section structure of obtained materials was performed by Atomic Force Microscopy, samples were investigated by Tapping Mode technique. Microscope observations of brittle fracture and section structure of obtained materials were performed using Scanning Electron Microscope. Grain size analysis of nanofillers was performed with SEM and TEM. Physical properties of nanofillers (specific surface and density), physical and mechanical properties of obtained composites were studied.

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P-03

INFLUENCE OF THE INCORPORATION METHODS OF NANOFILLER ON STRUCTURE AND PROPERTIES OF POLYURETHANE NANOCOMPOSITES FOR OPTOELECTRONICS APPLICATION

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The basic method of synthesis of transparent polyurethane elastomers is polyadditions of diizocyanate and polyols. It could be described as a sequence reaction of monomers and oligomers containing isocyanate and hydroxyl groups [1]. Chains of these copolymers are composed of rigid and flexible segments, which can be arranged in hard and soft domains. Incorporation of nanoparticles to the polymer matrix with special luminescence properties allows to obtain nanocomposites used in optoelectronical sub-assemblies Elastomer's properties depends on both ingredients (polyurethane and nanofiller): chemical constitution, their interaction and concentration, size and shape nanofiller particles and the way the filler was incorporated to polymer [2]. Inorganic nanofillers have a strong inclination to agglomerate in polymers because of physical interaction between organic polymer matrix and inorganic filler. That is why the aim of this study was to define the influence of the method of incorporating the nanofiller on structure and properties of obtained polyurethane nanocomposites

Components used for PUR synthesis were: polycaprolactone diol (PCL) Mn=2000, 4,4'-dicyclohexymethane diisocyanate (H'MDI), chains extenders (DIOL A, DIOL B). As nanofiller zirconium oxide including rare – earth elements was used. The filler was added to the chosen polyurethane matrix in 0,5% wt. respectively to the whole weight of polymer. Nanofiller was added to polymer as a concentrate and suspension of powders. Samples for research were synthesized from a mixture of substrates in prepolymer method.
Microscope observations of the structures of brittle fracture and section of obtained materials were done using SEM. Study of sections structure of obtained materials was performed by Atomic Force Microscopy. Samples were investigated by Tapping Mode technique. Physical properties of nanofillers (specific surface and helium density), physical and mechanical properties of obtained composites were studied.

Additionally examination of transmittance before and after the process of rendering amorphus for 2h at 80˚C of obtained samples was carried out.

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INFLUENCE OF TEMPERATURE ON SONOCHEMICAL SYNTHESIS OF CADMIUM SULPHIDE

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Ultrasonic waves are commonly used in chemistry for the preparation of materials with new (or enhanced) properties. Sonochemical procedures have been exploited for the preparation of solid particles characterised by small (≅ nm) sizes. These outcomes arise from acoustic cavitation that is the formation, growth and implosive collapse of bubbles in liquid, which generates transient temperatures of ~ 7000 °K, pressure ~ 2000 atm and cooling rate of 10^9 °K/s [1]. These extreme conditions induce chemical reactions such as oxidations, reductions, dissolutions and decompositions, which can be employed to prepare metals, metal carbides, oxides[2], sulphides[3], etc. In this work the synthesis of CdS is reported. The effects of the experimental conditions of the synthesis, as the temperatures or the chemical composition of the precursor bath, are debated. Moreover the synthesis of highly dispersed CdS particles into the voids of a mesoporous silica (MCM-41) is reported. The samples have been charaterised by XRD, FESEM, TEM and photoluminescence measurements.

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A SIMPLE CONTROLLER FOR DOMESTIC MICROWAVE OVENS

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Almost twenty years have passed since the first attempts to run organic syntheses in domestic multimode microwave ovens. Today the market offers a number of dedicated monomode instruments, which allow accurate MW focussing on the reaction vessel, power and temperature control, thus providing the highest degree of reproducibility of the experimental procedures.[1] Nevertheless, modified domestic ovens are still very appealing for their low cost, especially for researchers who don't use microwaves routinely in their synthetic work; some examples of such modifications can be found in literature.[1-4] Here an inexpensive homemade electronic controller, which can be easily interfaced with any microwave cooker, is described. With this device it is possible to produce microwave pulses of fixed power (depending on the magnetron characteristics) and variable length, according to a programmable "on/off" pattern. Temperature control can be accomplished through a Teflon-lined MW-shielded diode probe especially designed for this purpose, which can be dipped in the reaction medium and, differently from bulky shielded thermocouples, can fit also small reaction vessels. The controller allows temperature monitoring during the "off" periods and can be programmed to block any further MW emission after a certain temperature has been reached, and until it has not dropped under a given value.

It should be clear that this system is not supposed to compete with the commercial laboratory ovens equipped with fibre-optic sensors in terms of accuracy of temperature monitoring and thermostatization; it rather represents an interesting tool for those who are looking for an economically convenient way to improve the reproducibility of their syntheses with respect to a common domestic MW cooker.

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MICROWAVE DRIVEN HYDROTHERMAL SYNTHESIS OF ZNO, ZRO2, AND IRON OXIDES UNDER PRESSURES UP TO 10 MPA

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Microwave driven hydrothermal synthesis proved to be attractive method of nano-powders fabrication. A broad range of oxides can be produced by this method under slightly elevated pressures. In this contribution we report results of investigations of hydrothermal synthesis of zirconia, zirconia doped with rare earth elements, zinc oxide and iron oxides. These materials have been processed in a microwave reactor for hydrothermal synthesis operating at pressures up to 10 MPa.

In the investigations no special effects related to the use of microwave energy has been observed. However, the significant advantage of microwave reactors is fast heating and cooling rates and thus short reaction times. These reactors offer also possibility for clean reaction environment.

The short reaction times in the present study permitted made it possible to study in an efficient way the effect of a variety of factors on the properties of powders. In particular, the study covered the influence of grain size, grain size distribution, phase composition and powder agglomeration on the final products. This approach is particularly suited when powders have to be produced for specific applications (e.g. magnetic properties, luminescence, sintering) and the optimum synthesis method has to be selected.

SIMPLE, MICROWAVE ASSISTED AMIDATION OF NON-PROTECTED PHENOL CONTAINING 2- ALKENOIC ACIDS

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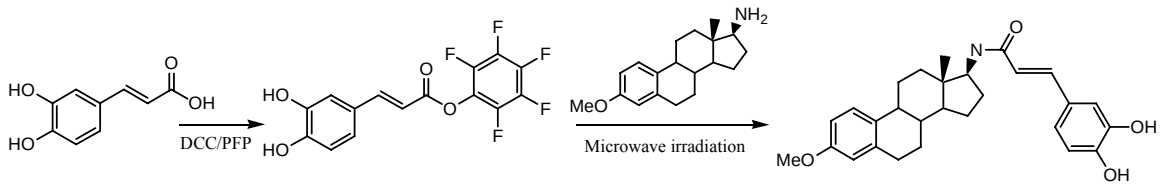
Hydroxycinnamic acid derivatives are interesting because of their antioxidant properties. Linking hydroxycinnamic residues to steroids may give the opportunity to utilize the steroidal components as a delivery system for the antioxidants. In the following, a simple way of preparing steroidal and non steroidal hydroxycinnamides under microwave irradiation is described. A number of different methods for the amidation of unsaturated carboxylic acids are known. Most of these, however, have the drawback that they cannot be used with non-protected hydroxycinnamic acids as the phenolic function itself reacts with the coupling reagents used, such as with diphenylphosphinic chloride. Initially, the authors carried out an activation of the acids with dicyclohexylcarbodiimide (DCC) and pentafluorophenol (PFP) providing the pentafluorocinnamate as an intermediate and reacted it with amines. Under normal conditions this reaction afforded the desired products in low yields due to the presence of a cinnamic acid by-product formed during the activation step. When the same reaction mixture was submitted to microwave irradiation, the yield increased dramatically, where the by-product formed in the first step also underwent the reaction to afford the desired product. A series of amides were prepared with reaction times of 5 min – 13 min, in the case of liquid amines, in solventless systems. In must be stressed that there is no need to protect the phenolic groups when performing the reactions under microwave irradiation.



MICROWAVE ASSISTED PREPARATIONOF INORGANIC MATERIALS MICROPARTICLES

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Microwave heating has been demonstrated to be a powerful tool to speed reaction rate and to accomplish difficult reactions in relatively short time (1). Microwave assisted heating has been already applied to the synthesis of small particles of GeS by sublimation (2) and by GeS_2 thermal decomposition. Using both multimode cavity type and monomode type microwave system some transition metal oxides have been prepared by oxidation of solid metal carbonyls under oxygen flow under microwave radiation. The reaction is rapid, violent in some cases, and the oxides can be easily collected from the reactor walls. In this way Fe_2O_3 (particle size from 10 to 500 nm) from $Fe_3(CO)_{12}$, W_2O_5 (particle size from 40 to 200 nm) from $W(CO)_6$ (3), and Mn_3O_4 from $Mn_2(CO)_{10}$ have been prepared. In similar conditions also silica can be prepared by oxidation of silicone compound. SiO_2 particles (particles size from 10 to 500nm) was prepared by microwave assisted oxidation of gas chromatography grade SE–30 silicone rubber. Using a monomode system, the reaction temperature, 1100–1200°C, can be reached in about 10 minutes using 500W power. Nano–sized, 35 m^2/g, XRD amorphous silica particles can be easily obtained by microwave assisted high temperature oxidation of a wide range of silicone grease and sealant (4). We believe that such oxidation technique may be also regarded as an "environment friendly" method for recovery of disposed silicone based materials. Alumina particles in the 1 to 5 μm size range have been obtained by microwave decomposition of $Al(NO_3)_3 \cdot 9\ H_2O$ to the nitrosyl oxide $Al_{22}O_{34}(NO)_2$ which has been then mixed with Na_2SO_4 and decomposed to Al_2O_3 by microwave assisted heating at 900°C (900W for 45'). The material shows a B.E.T. surface area of 135 m^2/g (5).

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A NEW FLOW REACTOR FOR SIMULTANEOUS IRRADIATION WITH MICROWAVE AND HIGH-INTENSITY ULTRASOUND: DEGRADATION OF 2,4-DIBROMOPHENOL BY FENTON'S REAGENT

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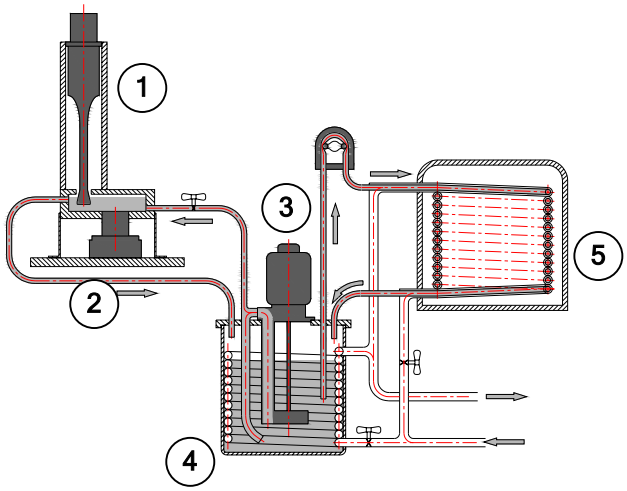
Microwave (MW) and high-intensity ultrasound (US) have emerged as powerful techniques for the elimination of persistent organic pollutants (POPs)[1,2] that constitute a major health hazard, whether by direct exposure or through accumulation in biota. In order to achieve decontamination, POPs should be completely mineralised to CO_2, H_2O and inorganic ions, or at least converted to less harmful chemical species. Fenton's reagent can be employed to treat a variety of industrial wastes containing a range of organic compounds[3,4] such as phenols, formaldehyde, pesticides, wood preservatives, plastic additives and rubber chemicals The Fenton catalyst causes the decomposition of H_2O_2 yielding highly reactive hydroxyl radicals (HO·) that attack and destroy organic pollutants. Owing to their high standard reduction potential they can oxidize almost any organic compound to carbon dioxide and water. However, being extremely short-lived, they must be continuously generated by chemical, photochemical or electrochemical reactions. Under US (20 kHz) or MW irradiation in water we had observed a rapid and complete degradation of aromatic halides, halogenated phenols and polychlorinated biphenyls in the presence of Fenton's reagent[5]. Compared to conventional conditions, reactions carried out under US and MW are faster and much more efficient. The present work extended that investigation to assessing the combined effect of US and MW in a new flow reactor developed in our laboratory. As shown in the following scheme, US irradiation was carried out simultaneously at 20 kHz and 300 kHz, while the MW irradiation took place in a modified domestic oven (700 W). Studying the degradation kinetics of 2,4-dibromophenol (0.1 g/l in water) by Fenton's reagent, we assessed the contribution of each energy source to the overall effect. We found that MW and 300 kHz US played the main role. Even if no Fenton's reagent was added, about 40-50% of 2,4-dibromophenol was destroyed after 2 h irradiation. Degradation was monitored by TLC, GC and NMR spectra.

1. US 20 kHz
2. US 300 kHz
3. Pump
4. Tank
5. MW oven



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EXTRACTION OF NATURAL PRODUCTS UNDER HIGH-INTENSITY ULTRASOUND: "THE CAVITATING TUBE"

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In our laboratory high-intensity ultrasound (US) are employed in organic syntheses, for the degradation of persistent organic pollutants and for the extraction of organic compounds from vegetal matrices[1]. In the present work US-assisted and conventional extraction were compared on two natural oil sources[2]. A newly devised US reactor (18.3 kHz) considerably improved extraction rates and yields. The effect of US is mainly due to the mechanical fragmentation of plant cell walls that increases direct exposition of cell contents to the solvent[3]. US can also facilitate the hydration and swelling of dried plant material, improving diffusion of soluble components[4].

For comparison we experimented with different US devices and frequencies (18.3, 20.6, 300 and 500 kHz) in the extraction of soybean germ (SG) and rice bran (RB), as shown in *Table 1*. Besides petroleum ether (PE), we also used as solvents several ionic liquids (ILs) (*Table 2*). We compared results with those obtained by conventional techniques (static extraction at room temperature and refluxing in a soxhlet). The new US device (*Fig.*) we call a "cavitating tube" (18.3 kHz) uniformly gave the highest yields. Most apolar ILs proved very efficient solvents for the extraction of SG under US at 20 KHz.

Table 1. PE extraction (oil as % of matrix weight).

Plant material	Funnel r.t., 12 h	Soxhlet rfx, 4 h	*H* 20.6 kHz, 50 W, 2 h*	*T* 18.3 kHz, 55 W, 2 h*	*CH* 300 kHz, 100 W, 2 h*	*CH* 500 kHz, 25 W, 2 h§
SG	3.2	8.2	9.5	22	6	10
RB	12.4	13.5	14	21	10	13

H= horn, CH = cup horn, T = cavitating tube; * T = 37°C. § T = 26°C

Table 2. Extraction of SG with ILs. (oil as % of matrix weight).

IL	*CH* 20 kHz, 40 W, 60°C, 2 h	*H* 500 kHz, 25 W, 35°C, 2 h
$[BMIM]N(Tf)_2$	25	11
$BMIMBF_4$	15	-
$OMIMBF_4$	11	13
$OMIMPF_6$	18	10

$[BMIM]N(Tf)_2$ = 1-butyl-3-methylimidazolium trifluoromethanesulfonimide.
$BMIMBF_4$ = 1-butyl-3-methylimidazolium tetrafluoroborate.
$OMIMBF_4$ = 1-octyl-3-methylimidazolium tetrafluoroborate.
$OMIMPF_6$ = 1-octyl-3-methylimidazolium hexafluorophosphate.

The "*Cavitating tube"*

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GRAIN SIZE AND GRAIN SIZE DISTRIBUTION OF PR-DOPED ZIRCONIA NANOPOWDERS OBTAINED IN HIGH PRESSURE MICROWAVE REACTOR

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Zirconia is an important ceramic material with useful mechanical, thermal, optical and electrical properties.

Luminescence properties of ZrO_2 and Pr-doped ZrO_2 nanopowders strongly depend on shape, grain size, grain size distribution and phase composition. The powders were synthesized via a hydrothermal method using a microwave reactor under pressure up to 8 MPa and temperatures up to 300^{o}C. The microwave driven hydrothermal synthesis permit to precisely control the reaction regime (time, power, pressure) and in consequence provide to expected properties of the resulting powders.

In this work we investigated the effect of process parameters on grain size and grain size distributions. It was determined using two methods. The first one was based on analysis of transmission electron microscopy (T1EM) images. The second one was based on analysis of the shape of X-ray diffraction (XRD) peaks. The two methods yielded similar results.

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