



Specific Support Action  
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**Workshop on  
Size-Dependent Effects  
in Materials for Environmental Protection  
and Energy Application**



*May 25 – 27, 2006, Varna, Bulgaria*

*Organised by the*

**Centre of Competence on  
Multifunctional Materials and New Processes with  
Environmental Impact  
at the Institute of General and Inorganic Chemistry,  
Bulgarian Academy of Sciences**

**<http://sizemat.igic.bas.bg>**

## Supporting organizations

### **Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences**

*Acad. G. Bonchev Str., bldg. 11, 1113 Sofia, Bulgaria, <http://www.igic.bas.bg/>*

The Institute of General and Inorganic Chemistry is one of the principal and oldest chemical institutes of the Bulgarian Academy of Sciences. The activities of the institute include basic and applied research, consultancy, industrial practice and teaching in three main research areas:

- ✓ inorganic materials science;
- ✓ chemical analysis;
- ✓ adsorption and catalysis.

### **Centre of Competence on Multifunctional Materials and New Processes with Environmental Impact (MISSION)**

*Acad. G. Bonchev Str., bldg. 11, 1113 Sofia, Bulgaria, <http://mission.igic.bas.bg/>*

The Centre of Competence MISSION, funded by the European Commission, was established on May 1, 2005 at the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences. The aim of this project is to establish an innovative leading Centre for the development and management of advanced materials for clean energy production and multifunctional materials for environmental protection. Attention will also be paid to the natural chemical resources as regards mainly their utilization and management. An important part of the efforts will be the development of a new strategy for evaluation and certification of environment friendly multifunctional materials.

Workshop on

**Size-Dependent Effects in Materials  
for Environmental Protection and  
Energy Application**

May 25 - 27, 2006, Bulgaria

Recreation and Conference House of  
the Bulgarian Academy of Sciences,  
Golden Sands resort near Varna

Dear Colleagues

On behalf of the Organizing Committee, it is my pleasure and honor to welcome all participants in the SIZEMAT workshop.

The SIZEMAT workshop is devoted to the size-dependent phenomena as a promising way to control the materials properties. The thematic area of the workshop comprises materials forming the basis of modern technologies, particularly with regard to clean energy production and environmental protection. Two classes of advanced inorganic materials will be covered: materials for clean energy storage and catalysts/sorbents for environmental protection. The workshop program is divided into presentations on a number of key topics followed by specific case studies and discussions. We hope that the program and diversity of the topics will be a basis for an exciting meeting and thought-provoking discussions.

We would like to thank the European Commission for the support of the SIZEMAT workshop.

We look forward to welcoming you to Varna – the sea capital of Bulgaria.

Yours sincerely

Dr. Radostina Stoyanova  
Scientific Secretary of  
the SIZEMAT workshop

## **Workshop Topics**

- A.** Effect of Synthesis Method on Particle Properties;
- B.** Nanostructural Design of Composite Electrode Materials for Lithium-ion Batteries;
- C.** Materials for Hydrogen Storage at a Nano-Scale Level;
- D.** Microstructural Effects in SOFC's;
- E.** Size Effects in Supported Metal Catalysts;
- F.** Catalysts Activation & Deactivation Caused by Re-dispersion or Sintering;
- G.** Novel High Surface Area Sorbents.

## **Workshop Organizers**

Assoc. Prof. Dr. Radostina Stoyanova	(Scientific Secretary)
Assoc. Prof. Dr. Dimitar Radev	(Technical Secretary)
Prof. DSc. Konstantin Hadjiivanov	
Assoc. Prof. Dr. Ekaterina Zhecheva	
Assoc. Prof. Dr. Anton Naydenov	

## Invited Speakers

- Topic A** Prof. Jan Šubrt – Institute of Inorganic Chemistry, Prague, Czech Republic  
*“Homogeneous precipitation as a way to uniform oxide based nanoparticles”*
- Topic B** Dr. Erik Kelder – Delft University of Technology, The Netherlands  
*“Synthesis of Nanopowders for Li-ion Battery Anodes and Cathodes”*
- Topic C** Dr. Martin Dornheim – Institute for Materials Research, GKSS, Research Center Geesthacht GmbH, Germany  
*“Hydrogen Storage in Light Weight Metal Hydrides and Reactive Hydride Composites”*
- Topic D** Dr. Hans Peter Buchkremer – Institute for Materials and Processing in Energy Systems, Research Centre Jülich, Germany  
*“How Processing and Durability of Microstructure Determines SOFC Performance”*
- Topic E** Prof. Michel Che – Pierre & Marie Curie University, Paris, France  
*“The Importance of Nuclearity in the Design and Properties of Catalysis-Related Nanomaterials”*
- Topic F** Prof. James A. Anderson - Surface Chemistry and Catalysis Group, Department of Chemistry, University of Aberdeen, Aberdeen, AB24 3UE, Scotland, UK.  
*“Regeneration of Supported Monometalic and Bimetallic Catalysts by Redispersion”*
- Topic G** Prof. Angel Linares Solano - University of Alicante, Spain  
*“The importance of developing micropore volume and controlling micropore size distribution to improve performance applications of high surface area activated carbons”*

## Scientific Programme (Preliminary)

### 24.05.2006 (Wednesday)

10:00 - 23:00      **Registration**  
20:00 - 22:00      **Welcome Party**

### 25.05.2006 (Thursday)

8:00 - 12:00      **Registration**  
9:00 - 9:10        **Opening Ceremony**

Chairman - Prof. Angel Linares-Solano

9:10 - 9:50        **Prof. Jan Šubrt** (Institute of Inorganic Chemistry, AS CR, Rez near Prague, Czech Republic) - *Homogeneous precipitation as a way to uniform oxide based nanoparticles*

9:50 - 10:10      **Prof. Yanko Dimitriev** (University of Chemical Technology and Metallurgy, Bulgaria) - *History of sol-gel science and technology*

10:10 - 10:30     **Prof. Margarita Kantcheva** (Bilkent University, Turkey) - *Spectroscopic Characterization of Modified Zirconias Prepared from Molybdenum (VI) and Tungsten (VI) Peroxo Precursors*

10:30 - 10:40     **Panel Discussion**

10:40 - 11:10     **Coffee Break**

Chairman - Prof. James Anderson

11:10 - 11:50     **Prof. Sefik Suzer** (Bilkent University, Turkey) - *Charging/Discharging of Metallic Nanoparticles as Revealed by XPS*

11:50 - 12:10     **Dr. Petco Stefchev** (CLSENEs, BAS, Bulgaria) - *LPD TiO<sub>2</sub> coatings on anodized aluminum*

12:10 - 12:30     **Dr. Lorentz Jantschi** (Technical University of Cluj-Napoca, Romania) - *Molecular Descriptors Family on Structure-Activity and Structure-Properties Relationships: Results*

12:30 - 12:40     **Panel Discussion**

12:40 - 14:00     **Lunch**

Chairman - Dr Hans Buchkremer

- 14:00 - 14:40**      **Dr. Erik Kelder** (Delft University of Technology, The Netherlands) – *Synthesis of nanopowders for Li-ion batteries anodes and cathodes*
- 14:40 - 15:20**      **Dr. Martin Dornheim** (GKSS, Research Center Geesthacht GmbH, Germany) - *Hydrogen Storage in Light Weight Metal Hydrides and Reactive Hydride Composites*
- 15:20 – 15:40**      **Dr. Rudy Wagemans** (Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, The Netherlands) – *Hydrogen Storage in Magnesium Clusters*
- 15:40 – 15:50**      **Panel Discussion**
- 15:50 - 16:30**      **Coffee Break**
- 16:30 - 18:30**      **Poster Session**
- 19:00 - 21:00**      **Dinner**

**26.05.2004 (Friday)**

Chairman: Dr. Eric Kelder

- 9:00 - 9:40**      **Dr. Hans Buchkremer** (Research Centre Juelich GmbH Institute for Materials and Processes in Energy Systems, Germany) - *How Processing and Durability of Microstructure Determines SOFC Performance*
- 9:40 – 10:00**      **Dr. Konstantin Petrov** (Institute of Electrochemistry and Energy Systems, BAS, Bulgaria) – *Bifunctional Catalysts and Electrodes for Oxygen Reduction and Evolution*
- 10:00 – 10:10**      **Panel Discussion**
- 10:10 – 10:30**      **Coffee Break**

Chairman: Prof. Jan Šubrt

- 10:30 - 11:10**      **Prof. Michel Che** (Pierre & Marie Curie University, Paris, France) - *The importance of nuclearity in the design and properties of catalysis-related nanomaterials*
- 11:10 – 11:30**      **Prof. Joaquim Faria** (Laboratory of Catalysis and Materials, University of Porto, Portugal) - *Size-Dependent Effects in Supported Metal Catalysts for Liquid Phase Hydrogenation Reactions*
- 11:30 – 11:50**      **Prof. Georgi Tyuliev** (Institute of Catalysis, BAS, Bulgaria) - *Peculiarities in the W4f photo-emission line shape of NiW catalysts supported on alumina*
- 11:50 – 12:00**      **Panel Discussion**
- 12:00 - 13:00**      **Lunch**
- 13:30 - 22:30**      **Excursions and Dinner**

## 27.05.2006 (Saturday)

Chairman: Prof. Michel Che

- 9:00 - 9:40**            **Prof. James Anderson** (Department of Chemistry, University of Aberdeen, UK) - *Regeneration of supported monometalic and bimetallic catalysts by redispersion*
- 9:40 - 10:00**        **Dr. M. Newton** (ESRF, Grenoble, France) - *Temperature dependent structural variation in alumina supported Rh nanoparticles: in what way is it reactively deterministic?*
- 10:00 – 10:20**      **Prof. Sefik Suzer** (Bilkent University, Turkey) - *X-ray induced reduction of Au and Pt ions on silicon substrates and production of nanoclusters*
- 10:20 – 10:30**      **Panel Discussion**
- 10:30 - 11:00**      **Coffee Break**

Chairman: Dr. Martin Dornheim

- 11:00 - 11:40**        **Prof. Angel Linares-Solano** (University of Alicante, Spain) - *The importance of developing micropore volume and controlling micropore size distribution to improve performance applications of high surface area activated carbons*
- 11:40 - 12:00**      **Dr. Sladjana Matic** (Faculty of Technology and Metallurgy, University of Belgrade, Serbia and Montenegro) - *Heavy metal removal by adsorption using diatomite*
- 12:00 – 12:10**      **Panel Discussion**
- 12:10 - 14:00**      **Lunch**
- 14:00 - 16:00**      **Poster Session**
- 16: 00 - 16:15**      **Closing**



*Topic A.*

**Effect of Synthesis Method on Particle Properties**



## Homogeneous Precipitation as a Way to Uniform Oxide Based Nanoparticles

Jan Šubrt

Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež,  
Czech Republic. *E-mail*: subrt@iic.cas.cz

The metal oxide based nanoparticles are among the most important materials with broad application area (catalysts, magnetic materials, phosphors, sorbents, etc.). Their application area depends very often on their size and shape. Many physical and chemical synthetic methods have been used recently to synthesize this class of materials. These methods often lead to particles with excellent characteristics, however, such procedures are mostly expensive and in some cases also environmentally harmful. On the contrary, precipitation is generally cheap and environmentally acceptable procedure leading sometimes to uniform particles with surprisingly valuable properties.

Homogeneous precipitation is considered as cheap and readily controllable method providing uniform metal oxide particles [1]. Contrary to the heterogeneous precipitation in which two different reactant solutions are mixed in solution so that a macroscopically heterogeneous liquid state is present for some time, in the homogeneous precipitation nucleation and precipitation starts in an initially homogeneous liquid, containing all the reactants and the liquid state remains homogeneous during reaction [2]. A central requirement to this aim is that supersaturation must be attained without causing significant concentration gradients, i.e., by perturbing metals salts solutions in such a way that either the activity of hydroxide ions or the activity of the metal ions is increased homogeneously [3].

Homogeneous precipitation of aqueous solutions of various metal salts with urea leads to oxide or hydrated oxide nanoparticles [4, 5]. Depending on the details of the procedure, particles of various size and shape can be easily synthesized. At presence of suitable supporting material, nanocrystalline layers can be deposited on its surface [6]. The materials were tested with positive results as photocatalysts, anticorrosive barrier pigments, agents for decomposition of chemical warfare agents, as well as in some other applications.

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## History of Sol-Gel Science and Technology

Yanko Dimitriev<sup>1</sup>, Yordanka Ivanova<sup>1</sup>, Reni Iordanova<sup>2</sup>,

<sup>1</sup>University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria,  
*E-mail: yanko@uctm.edu*

<sup>2</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113  
Sofia, Bulgaria

The objective of this review article is to summarize some of the most significant research achievements in the sol-gel science and technology. Comprehensive review papers have been made regularly in the past three decades by outstanding scientists such as Mackenzie, Sakka, Zarzycki, Schmidt, Uhlmann, Livage, Ulrich, Dislich. The main sources for the scientific information are the Journal of Sol-Gel Technology started in 1993 and the International Sol-Gel Workshops periodically held from 1981 up to now. In the beginning the studies have been centered mainly on silica and silicate glasses but they progressively have been extended to many other oxide and non-oxide ceramics and composites. It has been shown that the sol-gel methods have great potential in producing important materials in forms of bulk, fibers, sheets, coating films, and particles at relatively low temperatures. It is also possible to produce materials of new compositions with high purity, high homogeneity, and to control particle size distributions in a nano-scale. From fundamental point of view it was very important the development of models by which it is possible to explain and to predict the competitive reactivity of different precursors and to select most stable clusters in solutions. The understanding of phase separation in sol-gel systems has led to successful preparation of porous gel solids. The theoretical analysis of drying mechanisms contributed essentially to overcome the shrinkage of bulk and film samples. One of the most important advances of sol-gel science is the preparation of inorganic-organic hybrids. They started with the development of ormocers based on the formation of chemical bonds between the constituents and nonocomposites, containing organic molecules incorporated into porous gel matrix. That is why the sol-gel method is a representative nanotechnology. Specific examples are presented that have been carried out in leading universities and laboratories. Some our results in this field will be also discussed briefly. A classification was made of sol-gel derived materials according to their functions: optical (solar collector, fibers, waveguide), electronic (piezoelectric transducer, non-volatile memory, solid electrolyte), thermal (refractory and low expansion ceramics, aerogel), chemical (catalyst, membrane, corrosion protection), biomedical (entrapment of enzyme and living tissue, implant). It was emphasize the crucial role of starting precursors and the processing routes to the final structure and the impact on technological functions.

## Spectroscopic Characterization of Modified Zirconias Prepared from Molybdenum(VI) and Tungsten(VI) Peroxo Precursors

Cevriye Koz, Mahmut Ali Ermeydan and Margarita Kantcheva

Laboratory for Advanced Functional Materials, Department of Chemistry, Bilkent University, 06800 Bilkent, Ankara, Turkey. *E-mail*: margi@fen.bilkent.edu.tr

Zirconia-supported M(VI) oxides (M = Mo, W) are usually prepared by impregnation of hydrous zirconia with solutions of the corresponding oxometallates. In general, equilibrium adsorption procedures allow better dispersion of the active phase. In the case of zirconia, the adsorption of M(VI) anionic species is favored in solutions with a pH below 6.7 (the PZC of zirconia). However, the nuclearity of the M(VI) species in aqueous solutions increases with a decreasing pH value. This can limit the diffusion of the polyoxoanions into the micropores of the amorphous hydrous zirconium oxide. Therefore, it is of interest to investigate the possibility of the application of molybdenum- and tungsten-containing anionic precursors with reduced nuclearity for synthesis of  $\text{MO}_x/\text{ZrO}_2$  catalysts by equilibrium adsorption at low pH.

In this study, modified zirconias are obtained by adsorption from aqueous solutions of dimeric oxodiperoxo complexes of molybdenum(VI) and tungsten(VI),  $[\text{M}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ , at pH 1.8 using hydrated zirconia. The concentrations of the solutions range from 0.025 to 0.75 mol  $\text{M}^{6+}/\text{L}$ . The samples are characterized by XRD, DR-UV-vis, Raman and FT-IR spectroscopy. The M(VI) uptake depends on the concentration of the peroxo solutions and approaches a plateau value for concentrations larger than 0.50 mol  $\text{M}^{6+}/\text{L}$ . The maximum uptake obtained under these conditions corresponds to 16 and 32 wt % of molybdenum and tungsten, respectively. According to the Raman spectra, no crystalline  $\text{MO}_3$  phases are detected after calcination at 550°C (Mo-containing samples) and 600°C (W-containing samples). Using the approach of Weber [1] and Barton et al. [2], the number of nearest neighbors in the  $\text{MoO}_x$  and  $\text{WO}_x$  domains is estimated as 3 and 4, respectively. The localization of the supported  $\text{MO}_x$  species on zirconia is studied by FT-IR spectroscopy of adsorbed CO. The comparison with samples having identical molybdenum and tungsten loading obtained by impregnation leads to the conclusion that the equilibrium adsorption from the peroxo complexes results in an increase in the number of anchoring sites on the surface of zirconia. As a consequence, the dispersion of the  $\text{MO}_x$  species is higher for the materials obtained by equilibrium adsorption of the  $[\text{M}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$  precursors than that of the samples prepared by impregnation.

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## Molecular Descriptors Family on Structure-Activity and Structure-Property Relationships: Results

Lorentz Jäntschi<sup>1</sup> and Sorana Bolboacă<sup>2</sup>

<sup>1</sup>Technical University of Cluj-Napoca, Romania, 15 Constantin Daicoviciu Street, 400020 Cluj-Napoca, Romania. *E-mail*: lori@chimie.utcluj.ro

<sup>2</sup>University of Medicine and Pharmacy, 13 Emil Isac Street, 400023 Cluj-Napoca, Romania

### Introduction

The aim of the paper is to present the results of utilization of molecular structure in modelling of structure-property (SPR) and structure-activity relationships (SAR) on classes of chemical compounds, as precursors of models elaboration of new chemical compounds with better activities and properties.

### Material and Method

The methodology use in modelling of property and activity of chemical compounds by integration of complex structural information, called Molecular Descriptors Family (MDF), follows the steps: sketching the compounds, generating the MDF members, finding the SAR's/SPR's models based on compounds measured activity and property, validating the SAR/SPR models and comparing them with previous reported models, and analyzing the selected models [1]. The MDF SPR/SAR methodology was applied on a number of sixteen sets and the results are present here.

### Results and Discussions

The results obtained on studied sets, express as squared correlation coefficient ( $r^2$ ), cross-validation leave-one-out (loo) scores ( $r^2_{cv(loo)}$ ),  $n$  the sample size,  $v$  the number of variables are in the next table:

No.	Set name	Previous reported SAR				MDF SAR								
		$r^2$	n	V	Ref.	$r^2$	$r^2_{cv(loo)}$	n	v	Ref.				
1	IChr10	0.9	10	2	[2]	0.999	0.999	10	2	[3]				
2	PCB_rrf	-	-	-	[4]	0.628	0.619	209	1	[5]				
						0.693	0.682	209	2					
						0.737	0.717	209	4					
3	PCB_lkow	-	-	-	[6]	0.873	0.870	206	1	[6]				
						0.890	0.885	206	2					
						0.917	0.909	206	4					
4	36638	0.967	16	?	[7]	0.994	0.991	16	3	[8]				
5	23159	0.388	18	1	[9]	0.755	0.684	18	1	[10]				
		0.839	18	3		0.982	0.974	18	2					
6	23159e	-	-	-	[11]	0.899	0.758	8	1	[12]				
						0.968	0.898	8	2					
7	Ta395	0.87	13	2	[11]	0.977	0.961	15	2	[12]				
8	Tox395	0.8	13	2	[11]	0.957	0.934	14	2	[12]				
9	41521	0.913	8	3	[13]	0.999	0.998	8	2	[14]				
		0.985	8	5										
10	26449	0.9911	10	1	[15]	0.961	0.954	10	1	[16]				
		0.9982	10	2							0.990	0.988	10	2
		0.9929	10	4							0.998	0.997	10	4

11	MR10	0.9755	10	2	[17]	0.999	0.999	10	2	[18]
12	23151	0.741 0.985	16 13	4 4	[19]	0.997	0.995	16	3	[20]
13	52344	0.78 0.71 0.81 0.97	8 8 8 8	1 1 2 4	[21]	0.904 0.999 0.999 0.999	0.832 0.999 0.999 0.999	8 8 8 8	1 2 2 2	[22]
14	52730	-	-	-	[23]	0.966 0.998	0.947 0.996	10 10	1 2	[24]
15	Triazines	0.97	30	3	[25]	0.951 0.975 0.983 0.989	0.946 0.971 0.976 0.985	30 30 30 30	1 2 3 4	[26]
16	22583	0.888 0.885 0.883	37 20 57	5 5 5	[27]	0.783 0.835 0.900 0.918	0.766 0.809 0.884 0.900	57 57 57 57	2 3 4 5	[28]

The performances of obtained models are always better comparing with the previous reported models, which sustain the usefulness of the MDF SAR/SPR methodology in understanding the relationships between compounds structure and activity/property, in prediction of the activity/property and in discovery, investigation and characterisation of new chemical compounds.

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## LPD TiO<sub>2</sub> Coatings on Anodized Aluminum

Katia Ivanova<sup>1</sup>, Petco Stefchev<sup>1</sup>, Petko Vitanov<sup>1</sup>, Hristosko Dikov<sup>1</sup>, Christos Trapalis<sup>2</sup> and Velichka Lazarova<sup>3</sup>

<sup>1</sup>Central Laboratory for Solar Energy and New Energy Sources at Bulgarian Academy of Sciences, Tzarigradsko chaussee 72, 1784 Sofia, Bulgaria.

<sup>2</sup>Institute of Materials Science, National Centre for Scientific Research “Demokritos”, Ag. Paraskevi, 153 10, Greece.

<sup>3</sup>Institute of Solid State Physics at Bulgarian Academy of Sciences, Tzarigradsko chaussee 72, 1784 Sofia, Bulgaria.

A new process for preparation of LPD TiO<sub>2</sub> coatings on anodized porous aluminum substrate has been developed. The influence of the porous anodized aluminum substrate and the parameters of the LPD process on the TiO<sub>2</sub> coatings are determined by electron microscopy and XRD investigations. At room temperature beta crystalline structure of TiO<sub>2</sub> coatings is formed. Heating the LPD TiO<sub>2</sub> coatings on anodized Al at temperatures > 300 C° transform beta TiO<sub>2</sub> to the anatase crystal modification. This new process for LPD preparation of TiO<sub>2</sub> coatings on anodized Al is applicable in photocatalysis and sensors. The photocatalytic activity of TiO<sub>2</sub> film surfaces, irradiated with UV black light lamp, was investigated by salicylic acid decomposition.



## **Nano-/Amorphous TiFe Alloys Prepared by Mechanical Alloying**

Borislav Abrashev<sup>1</sup>, Stoyan Bliznakov<sup>1</sup>, Tony Spassov<sup>2,1</sup> and Alexander Popov<sup>1</sup>

<sup>1</sup>Institute of Electrochemistry and Energy Systems, Acad. G. Bonchev, bl.10, 1113 Sofia, Bulgaria. *E-mail*: babrashev@abv.bg

<sup>2</sup>Department of Chemistry, University of Sofia “St. Kl. Ohridski”, 1126 Sofia, Bulgaria

TiFe alloys have been prepared by high energy ball milling for different time under high purity argon and tested as hydrogen storage electrodes in 6 M KOH. The morphology of the powders milled for various times differs significantly. X-ray diffraction analysis showed that after 20 hours of milling the starting mixture of the elements (in ratio 1:1) had transformed into an amorphous phase. It was found that the discharge capacity significantly increases with increasing the milling duration. The electrode prepared from powder milled for 15h showed 70 mAh/g discharge capacity, whereas that produced from the 20h milled alloy - 140 mAh/g. Generally, different electrochemical characteristics were found with the materials having different microstructures.

## **Plasma-Chemical Treatment of Systems Consisting of Natural Phosphate, Phosphogypsum and Flotation Waste through Thermodynamic Investigations**

K. Ouzounov, G. Vissokov, I. Grancharov and L. Brakalov

University of Chemical Technology and Metallurgy, Dept. of Technology of Inorganic Substances 8, Kl. Ohridski Blvd 1756 Sofia; Bulgaria. *E-mails*: kalu@abv.bg, vissokov@abv.bg, ivan@uctm.edu, Aklab@uctm.edu

A plasma chemical treatment is inherently more expensive in most cases. Therefore, research activities in this area have been restricted to special wastes destruction problems, where thermal plasmas offer unique advantages, such as: 1\ high temperatures and energy densities allowing fast and complete decomposition of wastes.; 2\ very high quenching rates allowing the formation of non-equilibrium compositions and preventing undesirable recombination; 3\ easy control over the chemistry of processing.

The subject of the present investigations is the thermodynamic study of the possibilities for plasma chemical treatment (PCT) of the specified two- and three-component systems of wastes-mineral raw materials. In the conditions of Low-Temperature Plasma\LTP\ \air, nitrogen and argon plasma in the temperature range 1000-3700 K \is carried out thermodynamic analysis of the systems: natural phosphate \NPh\ - phosphogypsum \PhG\ - flotation waste\FW\ : 30 % NPh+70 % FW; 90 % NPh+5 % PhG+5 % FW; 70 % NPh+15 % PhG+15 % FW; 50 % NPh+25 % PhG+25 % FW; 30 % NPh+35 % PhG+35 % FW.

The results from thermodynamic calculations allow assessing the thermal dissociation of the components in condensed and gaseous phases and respective to take hold of useful products in the temperature range. The possibility to obtain different products desired has been proved. Data obtained by thermodynamic analysis made can be used to plan investigations on plasma-chemical treatment (PCT) of the systems considered.

## Oxidation of n-Hexane Over Supported Pt Catalysts on a Thin-Film Zirconia/Stainless Steel Supports

Nenad Radić<sup>1</sup>, Boško Grbić<sup>1</sup>, Tsvetana Marinova<sup>2</sup>, Plamen Stefanov<sup>2</sup> and  
Dimitar Stoychev<sup>3</sup>

<sup>1</sup>ICTM, Department of Catalysis and Chemical Engineering, 11000 Belgrade, Serbia and Montenegro. *E-mail*: nradic@nanosys.ihm.bg.ac.yu

<sup>2</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria.

<sup>3</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria.

The typical catalysts for VOCs deep oxidation are based on well dispersed active noble metals within a thin film of washcoat supported on ceramic or metallic monolith. Stainless steel (SS) substrates offer a significant advantage with regard to the ceramic monolith because of its better thermal conductivity and resistance to thermal shock, shorter light off time and higher mechanical strength. The thin films of ZrO<sub>2</sub> are a promising material for washcoat of the stainless steel foils due to its high mechanical and corrosion stability.

Within this work we have synthesized SS/ZrO<sub>2</sub>/Pt catalysts by two methods. In the first method, ZrO<sub>2</sub> film was obtained by electrochemical deposition of ZrO<sub>2</sub> on stainless steel foil [1] and subsequent wet impregnation of Pt. In the second method, spray pyrolysis technique was used. The ZrO<sub>2</sub> thin film and Pt were supported on SS in two consecutive steps. The catalyst samples were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

Comparison of the SS/ZrO<sub>2</sub>/Pt catalysts, synthesized by different method, was based on catalysts activities in the complete oxidation of n-hexane in air.

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## Characterization of Mesoporous Structure of SiO<sub>2</sub>

V. Fruth<sup>1</sup>, F. Papa<sup>1</sup>, L. Sarbu<sup>2</sup>, E. Tenea<sup>1</sup>, G. Voicu<sup>3</sup>, C. Andronescu<sup>1</sup>,  
C. Nistor<sup>2</sup> and A. Sarbu<sup>2</sup>

<sup>1</sup>Institute of Physical Chemistry, Romanian Academy, 060021 Bucharest, Romania

<sup>2</sup>INCDCP ICECHIM, 060021 Bucharest, Romania

<sup>3</sup>Politehnica University of Bucharest, 1-7 Polizu Str., 011061 Bucharest, Roumania

Highly porous materials such as mesoporous oxides are of technological interest for catalytic, sensing, optical and remediation applications: the mesopores (of size 2-50 nm) permit ingress by molecules and guests that are physically excluded from microporous materials. Their use is in constant progress as demonstrated by numerous published papers in this field.

The performances and the capacity of these systems to absorb a liquid are directly related to their mesoporous structure and their high specific surface area. Mesoporous structure of SiO<sub>2</sub> were obtained, using a chemical route, from a natural mineral (serpentine) which is present as waste on the left side of Danube river.

The specific surface areas of the samples were determined according to the methods of Brunauer-Emmett-Teller (BET). The mesopore size distribution curves were plotted by using the desorption data. The specific micropore and the specific micropore-mesopore volumes were determined by the extrapolation of these curves. The SiO<sub>2</sub> nanopowder was characterized using X-ray diffraction spectroscopy, DTA/TG analysis, IR spectrometry and SEM observation.

The correlation between the specific surface areas and the specific micropore-mesopore volumes is discussed.

## Effect of Synthesis Method on the Catalytic Properties of Silver-Modified Zeolites and MCM-41 for Environmental Applications

Petya Konova<sup>1</sup>, Anton Naydenov<sup>1</sup>, Fredrik Klingstedt<sup>2</sup>, Narendra Kumar<sup>2</sup>, Plamen Nikolov<sup>1</sup>, Penko Nikolov<sup>1</sup> and Dimitar Mehandjiev<sup>1</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: petya\_konova@abv.bg

<sup>2</sup>Laboratory of Industrial Chemistry, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, 20500 Åbo/Turku, Finland

Different silver modified mesoporous molecular sieves and zeolite catalysts were synthesized using five different preparation methods. The metal modification was carried out through in-situ, impregnation and ion-exchange techniques. Effect of acidity, metal dispersion and concentration on the selective catalytic reduction of NO<sub>x</sub> (HC-SCR) and ozone decomposition was studied. To correlate catalytic activity with preparation parameters, the catalysts were characterized by XRD, SEM, N<sub>2</sub>-physisorption, octane/propene-TPD, EPR and ICP techniques. Pore size distribution was obtained from the adsorption curve of the isotherm, using the procedure developed by Orr and Dalla Valle [1]. In order to investigate possible synergetic effects metal modifiers such as Cu, Zr and Ce were introduced together with silver.

The experiments on heterogeneous catalytic decomposition of ozone [2] were performed in an isothermal plug-flow reactor. A very high activity of the Ag modified ZSM-5 and MCM-41 catalysts was observed even at ambient temperature (conversions exceeding 90 %) and at the same time the catalysts remained active for a long time. The prepared catalysts were also tested for their activity in selective catalytic reduction of NO<sub>x</sub> emissions into nitrogen [3] using a simulated diesel exhaust gas in the temperature range 150-600°C. The most active catalyst, 5wt.%Ag-H-ZSM-5, showed a maximum activity of 52% at approximately 450°C using propene as a reducing agent. As a summary regarding the HC-SCR application, the MFI structure showed the highest activity and the catalyst performance could be correlated with the catalyst structure, acidity, metal state and dispersion.

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## Study of the Complexation of Some Heavy Metals in Sight of Their Elimination by Ultrafiltration

Zohir Nedjar, A. H. Meniai, M. Chikhi and A. Khelfaoui

Engineering laboratory of Processes and Environment, Industrial Chemistry Department,  
Mentouri Constantine University, Algeria. *E - Mail:* znedjar10@yahoo.fr

In Algeria, the water becomes more and more rare, more and more assaulted; this country suffers for several decades from the aridity and from the pollution, the industries directly throw out in the natural environment without a preliminary treatment their waste water that volume and degrees of concentration are very variable what disrupts ecological balance and returns the treatment of industrial refusals necessary.

The objective that we had settled by beginning this study was to determine the best conditions of complication of heavy metals, namely the pH of environment the complexant power of some ligands, the temperature, the speed of agitation, etc., in order to have a better separation by ultrafiltration [1].

The analysis of the various metals in solution was realized by the volumetric method (Titration by the EDTA, Citric and Nitric Acid). The experimental study of the reaction of complexation of heavy metals by the EDTA allowed us to say that elimination will be more important for the group of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ );

1. If the concentration of the ligand increases  $[\text{Y}]_{\text{opt}} = 10^{-3} \text{ M}$
2. If the speed of agitation increases  $V_{\text{agi (opt)}} = 750 \text{ tr / min}$
3. If the temperature of environment increases  $T_{\text{opt}} = 50^\circ \text{ C}$
4. If the pH of environment increases  $\text{pH}_{\text{opt}} = 7$  (neutral Environment) [2].

In our team of search, we were interested to change the ligand ( EDTA) by other ligands (Citric Acid and Nitric Acid), we can directly say that volumetric method does not give results because reaction environment becomes acid and the (Titling) EDTA reacts with protons and there will be also a *destruction* reaction of the least stable complex. We drew the curves of return on ultrafiltration according to the concentration of the perméat (free cation) supposing that the quantity of the complexed cation is retained with the membrane [3].

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## Effect of a Modified Support on the Catalyst Activity in NO Reduction with CO

Daniela Stoyanova<sup>1</sup>, Nikoleta Kassabova<sup>2</sup> and Mariana Khristova<sup>1</sup>

<sup>1</sup> Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail:* dsto@svr.igic.bas.bg

<sup>2</sup> University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria.

The presence of a modifier in the alumina support stabilizes the dispersion of the supported active phases. Binary oxide systems, Al<sub>2</sub>O<sub>3</sub>–CaO and Al<sub>2</sub>O<sub>3</sub>–MgO, were synthesized and calcined at 1000<sup>0</sup>C to be used as supports. The active phase supported was Cu-Co with a Cu/Co ratio corresponding to that of the stoichiometric CuCo<sub>2</sub>O<sub>4</sub> spinel. The catalysts were calcined at T= 550<sup>0</sup>C for 3h and investigated with respect to NO reduction with CO and poisoning by SO<sub>2</sub>. The synthesis of the aluminocalcium precursor was performed by deposition - precipitation of boemite on water suspension of CaCO<sub>3</sub> at a Al<sub>2</sub>O<sub>3</sub> : CaO ratio of 90:10 wt%. The aluminomagnesium support was obtained by the method of mechanical dry mixing of boemite and Mg hydroxy carbonate at a Al<sub>2</sub>O<sub>3</sub> : MgO ratio of 92-96 : 8-4%. Activity test was carried out on a flow apparatus in the feeding a NO+CO+Ar gas mixture at a velocity of W=26000h<sup>-1</sup>. The presence of the modifier in the support affects both the catalyst activity and the active components ratio. This can be attributed to the formation of spinel structures in the support depending on the presence of Mg or Ca in Al<sub>2</sub>O<sub>3</sub>. This concerns also the physicochemical characteristics and phase composition of the catalyst samples.

The highest activity and recovery after poisoning was demonstrated by the catalysts with Mg-containing alumina support (8 wt% MgO). This indicates that the support is applicable to catalysts for high temperature processes such as purification of motor gases and technological waste gases. The formation of the structure and texture of supported oxide catalysts is strongly affected by the genesis of the support. The complete regeneration after poisoning is of great importance for these catalysts as it prolongs their exploitation time interval.

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## Electrochemical Behaviour of the Ni-Nanocomposites

Toma Stankulov<sup>1</sup> and Dessislava Kostadinova<sup>1,2</sup>

<sup>1</sup>Institute of Electrochemistry and Energy systems (CLEPS), Bulgarian Academy of Sciences, Acad.G.Bonchev Str., bl. 10, 1113 Sofia, Bulgaria. *E-mail*: [tstankulov@gmail.com](mailto:tstankulov@gmail.com)

<sup>2</sup>Laboratoire de Materiaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS-ENSCM-UM1, Institut C. Gerhardt FR 1878, 8 Rue Ecole Normale, 34296 Montpellier Cedex 5, France

This work aims at electrochemical investigation of Ni-nanocomposites. The influence of the quantity of Ni in the structure on electrochemical performance of the nanocomposite was examined in galvanostatic mode.

The samples were prepared by intercalation of negatively charged Ni-based nanoparticles in Mg/Al layered double hydroxide (LDH) and following anion exchange route. The quantity of the Ni in the structure is proven by chemical analysis. [1]

Suspensions of Ni-nanoparticles were prepared by controlled hydroxylation of Ni<sup>2+</sup> cations in presence of citrate ions. Pre-calcinated samples were reduced in the atmosphere of 25%H<sub>2</sub>/Ar at 1000°C.

Preliminary experiments have shown that sample with maximum quantity of Ni in the composite show low capacitance.

The crystal structure underwent transformation leading ultimately to formation of a spinel structure. This change was studied by XRD.

The different quantity of the Ni is proven by chemical analysis. The mean size of 5nm is obtained.

The final reduced materials were characterized by TEM in order to compare the size distribution of metal particles at various Ni contents.

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## Nickel-Titanium Nanosized Alloys obtained by Mechanically Assisted Synthesis

Dimitar Radev

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: d\_dradev@abv.bg

The alloys in Ni-Ti system find large application in a contemporary technique and medicine due to the unique combination of high mechanical properties, chemical stability shape-memory effect of these alloys. Nanocrystalline nickel-titanium alloys NiTi and NiTi<sub>2</sub> were prepared using the method of mechanically assisted synthesis. The method consists of two steps: mechanical treatment of stoichiometric amounts of nickel and titanium powders in a planetary ball mill for 30 hours and annealing of activated reagents under protective atmosphere of pure Ar. The products were investigated by SEM, TEM and XRD methods. It was shown that the alloying of activated reagents proceeds at 550°C and nanosized products with average particle size of 50 nm were obtained. In comparison with other methods for synthesis of nanosized products, the method of mechanically assisted synthesis allows obtaining of a large scale product using simple technique and significantly reduced synthesis temperatures. It was also shown that the alloying process and formation of NiTi and NiTi<sub>2</sub> proceeds completely at 1200 °C when the same reagents without mechanical activation were used. The high sinterability of nanosized NiTi powders is a precondition for obtaining of articles with easy controlled structural peculiarities such as grain and pore size, presence and kind of porosity.

## Size-Dependent Properties of Semiconducting AgBiS<sub>2</sub> Quantum Dots in Thin Film Form Synthesized by Chemical and Sonochemical Routes

Biljana Pejova and Ivan Grozdanov

Institute of Chemistry, Faculty of Natural Sciences and Mathematics, St. Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia. *E-mail*: biljana@iunona.pmf.ukim.edu.mk

Chemical and sonochemical methods for deposition of quantum dots of AgBiS<sub>2</sub> in thin film form were developed and its size-dependent optical and electrical properties were investigated. The synthesis is based on controlled precipitation reaction which gives colloidal particles with narrow size distribution. The low concentrations of relevant ionic species in a reaction system were achieved using sodium thiosulfate with double role: as a precursor of sulfide ions and as a complexing agent. In the case of sonochemical deposition, the reaction system was sonicated using high-intensity ultrasonic probe (100 W/cm<sup>2</sup>) with frequency of 20 kHz based on direct-immersion ultrasonic horn. The crystal size was controlled by chemical (controlling experimental conditions during deposition process) and physical (post-deposition annealing) mean. Besides for identification of synthesized quantum dots, the experimental XRD patterns were utilized for calculations of some structural parameters such as: average crystal radius, lattice parameters, dislocation density and crystal strain. Due to heterogeneous sonochemical effects, which result in formation of microjets and shock waves, the synthesized quantum dots of AgBiS<sub>2</sub> are smaller in comparison with those prepared by conventional chemical route. Due to three-dimensional confinement effects, the prepared quantum dots manifest pronounced size-dependent properties. The optical band gap energy of as-deposited quantum dots in thin film form (calculated on the basis of spectral dependence of absorption coefficient in the framework of Fermi's golden rule and parabolic approximation for dispersion relation) is blue shifted in comparison to macrocrystal and exhibits red shift upon annealing treatment. The increasing trend of crystal size upon annealing is followed by decrease of grain boundary effects.

## Liquid Phase Separation in the $\text{MoO}_3\text{-La}_2\text{O}_3\text{-B}_2\text{O}_3$ System

Lyubomir Aleksandrov<sup>1</sup>, Reni Iordanova<sup>1</sup>, Yanko Dimitriev<sup>2</sup>, Elena Kashchieva<sup>2</sup> and  
Tzvetoslav Iliev<sup>3</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail:* reni@svr.igic.bas.bg

<sup>2</sup>University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria.

<sup>3</sup>Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

Rare earth molybdates have been extensively studied due to their interesting ferroelectric, ferroelastic, nonlinear and fast oxide-ion conducting properties. That is why it is important to get more information about phase diagrams and the structure of these compounds. Object of the present study is  $\text{MoO}_3\text{-La}_2\text{O}_3\text{-B}_2\text{O}_3$  system. Subsolidus phase equilibrium in this system was investigated and the formation of only one three component  $\text{LaMoBO}_6$  phase was established [1]. The fields of coexisting of the stable crystalline phases were determined as well. The problem for liquid phase separation was not discussed irrespective of the appearance of this phenomenon in the binary  $\text{MoO}_3\text{-B}_2\text{O}_3$  [2] and  $\text{La}_2\text{O}_3\text{-B}_2\text{O}_3$  systems [3]. The aim of this investigation is to verify the tendency for liquid phase separation in the three component compositions that is very significant for the preparation of materials using melt cooling. It was found that the slow cooled samples (cooling rate  $10^2$  K/s) containing small amounts of  $\text{La}_2\text{O}_3$  (5-10 mol%) were separated in two liquid phases: a black layer and milk greenish one. Droplet like and more complex microheterogenities were found by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) in the compositions situated inside and outside of the immisibility region. It was proved that depending on the composition and preparation different macro- and microstructure were obtained. Heating of the mixtures from room temperature up to monotectic temperature leads to the establishment of the equilibrium between three crystalline phases. The cooling of melts with the same compositions enhances the formation of microheterogeneous structures. By this way it is possible to design amorphous and polycrystalline materials with controlled particle size distribution.

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## Nano Particles in Low Melting Selenite Amorphous Materials

Albena Bachvarova-Nedelcheva<sup>1</sup>, Reni Iordanova<sup>1</sup>, Yanko Dimitriev<sup>2</sup> and Elena Kashchieva<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: albenadb@svr.igic.bas.bg

<sup>2</sup>University of Chemical Technology and Metallurgy, “Kl. Ohridsky” blv., 1756 Sofia, Bulgaria.

Selenite glasses and glass-ceramics are a new class of materials, which are not yet fully investigated. Nano particles formation in these low melting materials provokes the possibility for modification of optical and electrical properties. Depending on the methods of preparation it is possible to obtain different microheterogeneous structures as a consequence of the crystallization, phase separation and reduction processes.

The aim of the present investigation is to establish the appropriate road of nano particles formation during the heat treatment. It has been selected multicomponent glass compositions containing SeO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, TeO<sub>2</sub>, MoO<sub>3</sub>, ZnO and Ag<sub>2</sub>O oxides. Different methods of preparation of the initial glass samples were applied:

- a) Melting of the oxide batches in sealed silica ampoules evacuated at a pressure  $P=0.1$  Pa;
- b) Mixing of low-melting oxide glasses with selenite compounds (ZnSeO<sub>3</sub>, Ag<sub>2</sub>SeO<sub>3</sub> and PbSeO<sub>3</sub>) and their melting in air;
- c) Melting of the oxide batches at high oxygen pressure ( $P = 35$  to  $36$  MPa).

The heating of the obtained amorphous materials was performed at 200-250<sup>0</sup>C at different time of exposure. By TEM and SEM was proved the separation of nanosized particles, randomly distributed in the amorphous matrix volume. The heat treatment influences on the optical properties of the glasses. Nano-glass-ceramic materials were obtained during the long thermal treatment.

## Synthesis Method for Large-Crystal $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$

Stefka Tepavitcharova, Antonina Kovacheva, Diana Rabadjieva and Christo Balarew

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: antonina1975@abv.bg

Aqueous solutions containing  $\text{Mg}^{2+}$  ions are used for the preparation of  $\text{MgCO}_3$  and  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  by precipitation with alkali carbonates. The initial raw materials are: solutions of pure magnesium salts, solutions containing magnesium and calcium ions, suspensions of magnesium hydroxide or dolomite, solutions of natural magnesium brine etc. The main problem with all technologies is the resulting small-grain precipitate which is hard to filter and wash, this being the reason for obtaining a low-purity product.

We propose a method for preparation large  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  crystals. The initial raw material is waste brine from sea-salt production, a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  being used as precipitant. The effect of brine concentration, precipitant composition and concentration, temperature, presence of seeds and precipitate recrystallization time on the particle size of the  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  obtained has been investigated.

The optimum conditions of the formation process for preparation of  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  crystals with sizes of  $92.4 \times 9.9 \mu\text{m}$  have been established. Concentrated brine (71.39 g/l  $\text{Mg}^{2+}$ ) was used as initial raw material with a precipitant of  $\text{Na}_2\text{CO}_3$  (95 mass.%) and  $\text{NaHCO}_3$  (5 mass.%) at precipitation and recrystallization temperature of 30 C, recrystallization lasting 55 min,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  seeds being added at the end of the precipitation process. The crystals obtained were easy to filter and wash. Food grade quality  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  with magnesium carbonate impurities of a pharmacopoeia purity (X Pharmacopoeia of Russia) was obtained after 4-5 fold washing of the product with water (solid phase:water = 1:10).

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## **A Method for Preparation of Monodisperse Colloidal SiO<sub>2</sub> with Controlled Acidity and Particle Size**

D. Simeonov<sup>1</sup>, I. Uzounov<sup>1</sup> and Lubomir Spasov<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

<sup>2</sup>Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail:* [spasov@ic.bas.bg](mailto:spasov@ic.bas.bg)

The paper presents the results about preparation of monodisperse colloidal SiO<sub>2</sub> with controlled particles size. The ion-exchange method was used. Initial substance was 4% Na<sub>2</sub>SiO<sub>3</sub> (sodium metasilicate) water solution. The particles size of the obtained samples was within range 10 - 100 nm. They were determined by transmittance electron microscopy (TEM). It was established the influence of growing coefficient upon dispersity and stability of the system SiO<sub>2</sub> – H<sub>2</sub>O. The samples synthesized were stabilized with Na<sup>+</sup> ions at pH 9.5 and without Na<sup>+</sup> at pH 2.5.

The both types of colloidal silica are suitable for preparation of thin layers by electrochemical methods in spite of classical ones. The advantage of our product is absence of organic compounds in comparison the same product prepared by sol–gel method.

## Study of Synthesized Iron Oxide Catalysts by Thermal and Mechano-chemical Methods in the Methanol Decomposition

Daniela Paneva<sup>1</sup>, Tania Tsoncheva<sup>2</sup> and Ivan Mitov<sup>1</sup>

<sup>1</sup>Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

*E-mail:* daniela@ic.bas.bg

<sup>2</sup>Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Methanol has recently attracted strong interest as an alternative source for fuels and raw materials for the chemical industry. In previous studies [1,2] it was shown that iron oxide supported on various matrices presents a good activity in methanol decomposition and the reaction selectivity could be easily controlled varying the dispersity of the supported iron oxide or the nature of the support. In this study the physicochemical properties and catalytic behaviour of iron oxide, synthesized by thermal and mechano-chemical dehydration of iron hydroxides have been characterized and compared.

The iron oxide catalysts were obtained by thermal treatment of  $\alpha$ -FeOOH,  $\gamma$ -FeOOH and  $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ , (S1, S2, S3) respectively and by mechano-chemical method from  $\alpha$ -FeOOH (S4). The samples were characterized by X-ray powder diffraction, infrared and Mössbauer spectroscopy and methanol decomposition as a catalytic test. The catalytic reaction experiments were performed in a flow type of apparatus and at atmospheric pressure. All initial samples are monophasic - iron (III)-oxide, but they have different dispersity and morphology. The iron oxide particles, synthesized by different methods display antiferromagnetic or superparamagnetic behaviour and effect of collective magnetic excitation. All the samples are active in methanol decomposition above 550-600 K. The samples could be arranged according to their catalytic activity in methanol decomposition as follows:  $\text{S2} > \text{S3} = \text{S1} > \text{S4}$ . The main registered products of methanol decomposition are  $\text{CH}_4$ , CO and  $\text{H}_2$ . However some differences in the product distribution are observed. The methane selectivity is lower for S2 sample and passes through a maximum with the temperature increase. It is practically unchanged in the whole investigated temperature interval for S1 and S3. Higher  $\text{CH}_4$  selectivity is registered with S4. Transformation of  $\alpha$ - $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ ,  $\alpha$ -Fe,  $\text{Fe}_3\text{C}$  in reaction medium is observed with all samples. The different proportion between these phases and initial ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ) in each sample suggest layered model of particles.

In conclusion, the variations in the synthesis method and precursors affect the phase transformations in the reaction medium, which change the reductive and catalytic properties.

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## Dextran Secondary Raw-Material in Process of Industrial Waste Water Copper Valorization

Goran Nikolic<sup>1</sup>, Zarko Mitic<sup>2</sup> and Milorad Cacic<sup>1</sup>

<sup>1</sup>Faculty of Tecnology, University of Niš, 16000 Leskovac, Serbia.

*E-mail: goranchem\_yu@yahoo.com*

<sup>2</sup>Faculty of Medicine, University of Niš, 18000 Niš, Serbia.

*E-mail: zak\_chem2001@yahoo.com*

Some results of the low-molar dextran utilization as secondary raw-material from a production process of clinical dextran in pharmaceutical and chemical industry were presented in this paper. The secondary raw dextran was depolymerized and purified by corresponding methods [1]. Low-molar dextran fractions were used for copper ions separation, presented approximately 30% in waste water after copper cementation process. This complexing procedure of low-molar dextran with copper ions in alkali solution is a new waste water reprocessing method.

Many laboratory and pilot experiments in different conditions were carried out. It was concluded that the valorization of copper ions in the form of various commercial products is possible [2]. The obtained waste water is categorized as grade II, so it can be discharged into natural waters or returned to the process.

The priority of this copper valorization process from the waste water is in the possibility of obtaining commercial products, which can be used in pharmaceutical and cosmetic industry.

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## Synthesis of Metastable $\beta$ -MoO<sub>3</sub>

Reni Iordanova<sup>1</sup>, Angelina Soyanova<sup>2</sup> and Emil Rachin<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: reni@svr.igic.bas.bg

<sup>2</sup>Medical University-Pleven, Dept Chem&Biochem, 5800 Pleven, Bulgaria

MoO<sub>3</sub> and molybdenum oxygen compounds represent a very interesting class of materials in view of their application as catalysts, gas-sensors, electrochromic materials, semiconductors, ferroelectrics, electrolytes, end etc.

The properties of such materials strongly depend on their structure, morphology, crystallinity, particle size, synthesis methods and the precursors.

Molybdenum oxide exists in two polymorph phases: thermodynamically stable  $\alpha$ -MoO<sub>3</sub> with orthorhombic symmetry and metastable  $\beta$ -MoO<sub>3</sub> with monoclinic symmetry [1]. It has been shown that  $\beta$ -MoO<sub>3</sub> is a more active catalyst in the partial alcohol oxidation than  $\alpha$ -phase, and demonstrates good intercalation properties [2].

The motivation for the present experiments is the suggestion for a higher reactivity of metastable  $\beta$ -MoO<sub>3</sub> in solid state reactions. Several methods for synthesis have been applied up to now: electrodeposition, mechanical activation, chemical vapor deposition (CVD) and sol-gel methods [2-4]. In this study a ion-exchange method was applied to verify the influence of experimental conditions (temperature, time, pH, and additives) on the structural peculiarities of the resulting products. It was confirmed the important role of nitric acid for the evaporation process of water. The observed change in color of the obtained samples with the change of the experimental conditions pointed to the formation of certain structural defects in  $\beta$ -MoO<sub>3</sub>. By scanning electron microscopy (SEM) was determined that the synthesis details contribute essentially to the particle size distribution and the morphology of the grains.

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## Methods for Synthesis of Nanocrystalline $ZrW_2O_8$ Phases

Maria Mancheva<sup>1</sup>, Reni Iordanova<sup>1</sup>, Yanko Dimitriev<sup>2</sup>, Kostadin Petrov<sup>1</sup>, Georgi Avdeev<sup>1</sup> and  
Dimitar Klissurski<sup>1</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: mancheva@svr.igic.bas.bg

<sup>2</sup>University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria.

Thermal expansion of materials is one of the factors which must be taken into consideration in the design of optical devices, materials with high mechanical and thermal stability, solid oxide fuel cell, electronic packages and so on.  $ZrW_2O_8$  belongs to a family of materials with negative thermal expansion (NTE) coefficient in wide temperature range. Several methods of  $ZrW_2O_8$  synthesis have been reported in the literature: solid state reaction between  $ZrO_2$  and  $WO_3$  [1], coprecipitation route [2], non-hydrolytic sol-gel method [3] etc.

The aim of this study was to compare the advantages of two new methods for the preparation of  $ZrW_2O_8$  phases: (i) melt quenching (rapidly solidified melts) and (ii) mechanochemical synthesis.

- (i) The mixture of  $ZrO_2$  and  $WO_3$  taken in molar ratio ( $1ZrO_2 : 2WO_3$ ), was melted at 1300 °C, and was fast cooled at a rate of  $10^4$ - $10^5$  K/s.
- (ii) A mixture of  $ZrO_2$  and  $WO_3$  in molar ratio ( $1ZrO_2 : 2WO_3$ ) was treated mechanically up to 10h in air, in planetary ball mill, followed by calcination at 1200 °C for 8h.

Phase composition and structural transformations were monitored by powder x-ray diffraction (XRD) and infrared spectroscopy (IR). Polyphase samples containing the main product  $ZrW_2O_8$  and traces of  $WO_3$  and  $ZrO_2$  were obtained. It was found that the mechanochemical method is a more appropriate one for the synthesis of nanocrystalline cubic ( $\alpha$ )  $ZrW_2O_8$ . The predominantly orthorhombic ( $\gamma$ )  $ZrW_2O_8$  phase was obtained after melt quenching method. The average particle sizes of the  $\gamma$  - and  $\alpha$  -  $ZrW_2O_8$  were 50 and 70 nm, respectively. The obtained materials are suitable for lowering the thermal expansion of various composite materials.

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## Mechanochemically Assisted Synthesis of Nanocrystalline NiWO<sub>4</sub>

Maria Mancheva<sup>1</sup>, Reni Iordanova<sup>1</sup>, Dimitar Klissurski<sup>1</sup>, Georgi Tyuliev<sup>2</sup> and Boris Kunev<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: mancheva@svr.igic.bas.bg

<sup>2</sup>Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

Nickel tungstate is an important inorganic material of metal tungstate families (MWO<sub>4</sub>, where M = Ca, Co, Ni, Cu, Fe) that have wide application in various fields, such as in photoluminescence, optical fibers, scintillator materials, humidity sensors and catalysts [1]

Different authors have prepared NiWO<sub>4</sub> by several methods: conventional solid-state synthesis [2], coprecipitation route [3], microwave – assisted method [1] etc.

The aim of the study was to obtain NiWO<sub>4</sub> by mechanochemical activation ensuring short reaction time at lower synthesis temperature.

A stoichiometric mixture of NiO and WO<sub>3</sub> in a 1:1 molar ratio was subjected to intense mechanical treatment in air using a planetary ball mill (Fritsch №7) up to 10 h. Phase identification and structural transformation were monitored by powder x-ray diffraction (XRD) and infrared spectroscopy (IR). The final product was analyzed by x-ray photoelectron spectroscopy (XPS). The single NiWO<sub>4</sub> phase was obtained directly during mechanochemical treatment. The average particle size of the resulting product is 30 nm. The surface area is 3 m<sup>2</sup>/g measured by modified BET method. The hydrodesulphurization of thiophene was used as catalysts test reaction and a promising activity was observed.

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## Synthesis of TiO<sub>2</sub>-SnO<sub>2</sub> Nanostructured Thin Films by Chemical Methods

Irina Stambolova<sup>1</sup>, Sasho Vassilev<sup>2</sup>, Miroslav Abrashev<sup>3</sup>, Tsenka Tsacheva<sup>4</sup>,  
Plamen Stefanov<sup>1</sup>, Vladimir Blaskov<sup>1</sup> and Pavel Peshev<sup>1</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: irinast@svr.igic.bas.bg

<sup>2</sup>Institute of Electrochemistry Energy Systems, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

<sup>3</sup>Faculty of Physics, University of Sofia, 1164 Sofia, Bulgaria

<sup>4</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

Thin nanocrystalline TiO<sub>2</sub>-SnO<sub>2</sub> (0-80 mol% SnO<sub>2</sub>) films are obtained by chemical methods: spray pyrolysis and sol gel (spin coating). The initial compounds are TiCl<sub>4</sub> and SnCl<sub>4</sub>. The films are characterized by XRD, XPS, Raman spectroscopy and EDX analysis. The size of the nanocrystallites were determined by XRD-LB measurements. It is established that the preparation conditions as: type of synthesis method, annealing temperature, the kind of substrate and concentration of SnO<sub>2</sub> affect both the phase composition and the crystallite size. The anatase phase is characteristic of the sprayed films on quartz substrates, annealed in temperature range 450-700°C for SnO<sub>2</sub> concentration up to 50 mol%. The increase of the SnO<sub>2</sub> content above mentioned leads to the formation of a rutile phase. The sprayed films, deposited on metal and treated at 450°C with 0- 10 mol% SnO<sub>2</sub> contain only anatase phase. Further enhancement of tin dioxide concentration brings about the crystallization of coexisting of Ti<sub>2</sub>O<sub>3</sub> and rutile modifications, besides anatase TiO<sub>2</sub>. A significant change in the phase composition is registered with the rise of the temperature (600°C). The undoped titania films are composed of anatase and Ti<sub>2</sub>O<sub>3</sub>. The introduction of SnO<sub>2</sub> in titania films leads to a formation of three coexisting phases: anatase, Ti<sub>2</sub>O<sub>3</sub> and rutile. The titania films with 0 to 5mol%, synthesized by sol gel method on quartz/glass substrates, treated at 450 °C contain only anatase phase. The enhancement of the SnO<sub>2</sub> concentration above 5 mol% brings about appearance of a rutile phase. The kind of the films deposition method influences also the dimensions of the crystallites. The crystallites size of the TiO<sub>2</sub>-SnO<sub>2</sub> films, obtained by spray pyrolysis on both metal and quartz substrates are in the range 20-45 nm. Nanostructured films with grain size under 20 nm are obtained by sol gel method.

## Polycrystalline Materials in the $V_2O_5$ - $MoO_3$ - $ZrO_2$ System

Maya Markova-Velichkova<sup>1</sup>, Reni Iordanova<sup>1</sup>, Yanko Dimitriev<sup>2</sup> and Dimitar Klissurski<sup>1</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail:* markova@svr.igic.bas.bg

<sup>2</sup>University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria.

A family of materials with general formulas  $AM_2O_7$  and  $AM_2O_8$  (A= Zr, Hf; M= V, Mo, W) has been shown to exhibit negative thermal expansion (NTE) over a wide temperature range [1]. Zero, or close to zero, thermal expansion is needed for various applications in optics, electronics, and other fields where exact positioning of parts is crucial [2]. At present several processes such as solid state reaction, sol-gel method and coprecipitation were employed for preparation of these materials [3]. The choice of synthesis method is very important for the design of structural features, properties and potential applications. In this study, the possibility for obtaining such materials by melt quenching technique was examined in the  $V_2O_5$ - $MoO_3$ - $ZrO_2$  system. The main task is to investigate tendency for amorphization and crystallization of series of compositions. The amorphous samples were obtained in the wide range of compositions up to 40 mol.%  $ZrO_2$ . The phase and structural transformations were monitored using x-ray diffraction and infrared spectroscopy. By heat treatment of glasses, fine polycrystalline  $ZrV_2O_7$  phase with narrow particle size distribution was obtained. The crystallization of these phases was also achieved from supercooled melts and solid state reactions. The obtained products are suitable for the preparation of composites with low thermal expansion.

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## Technologies for Biomass Conversion

Felicia Bucura, Violeta Niculescu, Elena David, Claudia Sisu and Marius Constantinescu

National R&D Institute for Cryogenics and Isotope Technologies, Rm Valcea  
Uzinei Street, No. 4, PO BOX 4, Zip Code 1000, Rm. Valcea, Romania

Biomass processing is a new technology within the area of renewable energies. Current energy supplies in the world are dominated by fossil fuels (some 80% of the total use of over 400EJ per year). Nevertheless, about 10-15% (or 45 + 10 EJ) of this demand is covered by biomass resources, making biomass by far the most important renewable energy source used to date. On average, in the industrialized countries biomass contributes some 9-13% to the total energy supplies, but in developing countries the proportion is as high as a fifth to one third. In quite a number of countries biomass covers even over 50 to 90% of the total energy demand. A large part of this biomass use is however non-commercial and used for cooking and space heating, generally by the poorer part of the population.

The (technical) potential contribution of bio-energy to the future world's energy supply could be very large. In theory, energy farming on current agricultural land could, with projected technological progress, contribute over 800 EJ, without jeopardizing the world's food supply. Organic wastes and residues could possibly supply another 40-170 EJ, with uncertain contributions from forest residues and potentially a very significant role for organic waste, especially when bio-materials are used on a larger scale. In total, the upper limit of bio-energy potential could be over 1000 EJ (per year). Classic application of biomass combustion is heat production for domestic applications. This is still a major market for biomass for domestic heating in countries like Austria, France, Germany and Sweden. Use of wood in open fireplaces and small furnaces in houses is generally poorly documented, but estimated contributions to meet heat demand are considerable in countries mentioned. A key issue for bio-energy is that its use should be modernized to fit into a sustainable development path. Especially promising are the production of electricity via advanced conversion concepts (i.e. gasification and state-of-the-art combustion and co-firing) and modern biomass derived fuels like methanol, hydrogen and ethanol from ligno-cellulosic biomass, which can reach competitive cost levels within 1-2 decades (partly depending on price developments with petroleum).

**Phase Formation in the System  $\text{Bi}_2\text{O}_3\text{-TiO}_2\text{-MoO}_3$** 

Milena Krapchanska<sup>1</sup>, Yanko Dimitriev<sup>1</sup> and Reni Iordanova<sup>2</sup>

<sup>1</sup>University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria.

*E-mail:* milena\_zk@abv.bg

<sup>2</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is ferroelectric phase with potential applications in capacitors, sensors, piezoelectric and electrooptic devices. The interest to this material strongly increased in order to obtain Ferroelectric Random Access Memories (FeRAM).

In the previous study have been investigated the phase formation in the system  $\text{Bi}_2\text{O}_3\text{-TiO}_2$  and the influence of additives  $\text{V}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$  (III Balkan Conference on Glass and Ceramics 2005). In this work was studied the system  $\text{Bi}_2\text{O}_3\text{-TiO}_2\text{-MoO}_3$ . The purpose is to elucidate the phase formation in super cooled melts.

With increasing of the  $\text{MoO}_3$  content (20 -30 mol %) the melting temperature decreases. The application of high cooling rate (roller quenching technique ( $10^4\text{-}10^5$  K/s)) leads to formation of predominantly amorphous samples. At slow cooling ( $10^2\text{-}10^3$  K/s) crystalline  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and  $\text{Bi}_2\text{MoO}_6$  have been identified by X-ray diffraction. Polycrystalline materials with controlled particle size have been obtained at the secondary heat treatment in the temperature range from 500 to 800 °C.

## HRTEM Study of Perovskite Lanthanum Lithium Titanate

I. Carazeanu Popovici<sup>1</sup>, E. Chirila<sup>1</sup>, V. Ciupina<sup>2</sup>, V. Popescu<sup>1</sup> and G. Prodan<sup>2</sup>

<sup>1</sup>Ovidius University, Chemistry Department, 124 Mamaia, Constantza, Romania.

*Email:* icarazeanu@univ-ovidius.ro

<sup>2</sup>Ovidius University, Electron Microscopy Laboratory, 124 Mamaia, Constantza, Romania.

Ionic conducting solid materials have received considerable attention in the last few years due to their potential utility in several solid state devices: electrochemical sensors, secondary (rechargeable) batteries, electrochromic displays etc.

The studies of solid electrolytes with lithium ionic conductivity have been of much interest because of potential applications in battery systems. Oxides like  $\text{La}_{1-x}\text{Li}_x\text{TiO}_3$  present a perovskite – type structure ( $\text{ABO}_3$ ) with cation deficiency at the A-sites. It has been shown that this deficiency is favorable for high ionic mobility of monovalent cations through the bottleneck formed by four adjacent  $\text{BO}_6$  octahedra. Since the A- and B- sites in this structure can tolerate different ions with different valence states in order to enhance the ionic conductivity. Moreover and since these compounds present some vacancies in their structure, intercalation of lithium ions can be considered.

In this paper lanthanum lithium titanate compounds belonging to the solid solution  $\text{La-La}_{1-x}\text{Li}_x\text{TiO}_3$  ( $x = 0.33$ ) have been investigated. Single phase  $\text{La}_{1-x}\text{Li}_x\text{TiO}_3$  ( $x = 0.33$ ) with fine particles was prepared by sol-gel. The synthesized product was characterized by structural (XRD), spectroscopic (FTIR) and thermal analyses (DTA-TG). Electron microscopy (SEM and HRTEM) was used to evaluate the morphology of synthesized  $\text{La}_{1-x}\text{Li}_x\text{TiO}_3$  ( $x = 0.33$ ). It was found that bulk quantities of nano-sized particles of layered  $\text{La}_{1-x}\text{Li}_x\text{TiO}_3$  could be obtained at temperatures below  $800^\circ\text{C}$  by this solutions technique.

We obtained by modified sol – gel method a nano-crystals of  $\text{La}_{1-x}\text{Li}_x\text{TiO}_3$  with mean diameter of about 123 nm.

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## Surface Modification of Macroporous Glycidyl Methacrylate Based Copolymers for Selective Sorption of Heavy Metals

Lj. Malović<sup>1</sup>, A. Nastasović<sup>2</sup>, Z. Sandić<sup>3</sup>, J. Marković<sup>4</sup>, D. Đorđević<sup>2</sup> and Z. Vuković<sup>5</sup>

<sup>1</sup>Faculty of Forestry, Kneza Višeslava 1, 11030 Belgrade, Serbia.

*E-mail:* ljilja\_m@yahoo.com

<sup>2</sup>ICTM, Center for Chemistry, Studentski trg 12-16, 11001 Belgrade, Serbia.

<sup>3</sup>Faculty of Science, Chemistry Department, Mladena Stojanovića 2, 78000 Banja Luka, BIH.

<sup>4</sup>Vinča Institute of Nuclear Sciences, P.O. Box 522, Belgrade, Serbia.

<sup>5</sup>ICTM - Center for Catalysis and Chemical Engineering, Njegoševa 12, Belgrade, Serbia.

Chelating polymers have attracted attention as the selective sorbents for heavy metal ions removal and/or recovery from wastewater streams of hydro-metallurgical and other industries [1]. They consist of crosslinked copolymer (solid support) and functional group (ligand) with N, O, S and P atoms capable for coordinating of different metal ions. The removal of heavy metals with chelating polymers is simple process, reduced only to filtration as the regeneration step. Also, process neither produces waste materials, nor generates secondary pollutants. Macroporous copolymers based on glycidyl methacrylate, GMA, are very attractive, since the epoxy group can be easily transformed into iminodiacetate, thiol, azole, pyrazole groups, etc. Functionalization of those copolymers with amines yields specific sorbents with high capacity, fast kinetics and good selectivity for the heavy metal ions, as well as chemical and mechanical stability [2-5]. In this study, samples of crosslinked poly(GMA-co-EGDMA) with different porosity parameters (pore volume, surface area, and pore diameter) were synthesized by suspension copolymerisation of GMA and ethylene glycol dimethacrylate (EGDMA), in the presence of inert component (mixture of cyclohexanol and aliphatic alcohol). Porosity of poly(GMA-co-EGDMA) samples was adjusted by the variation of the type and content of aliphatic alcohol in the reaction mixture. After that, samples were modified by reaction of epoxy groups with ethylene diamine, diethylene triamine and triethylene tetramine. The influence of the porosity parameters, particle size and type of the ligand on the uptake behavior of macroporous amino-functionalized poly(GMA-co-EGDMA) towards heavy metals was studied.

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*Topic B.*

**Nanostructural Design of Composite Electrode  
Materials for Lithium-ion Batteries**



## Synthesis of Nanopowders for Li-ion Battery Anodes and Cathodes

Erik Maria Kelder, Ugo Lafont, Loic Simonin, Mario Valvo, Corrado Locati,  
Nooshin Tabrizi, Jan Marijnissen, Andreas Schmidt-Ott and Stephen Picken

Department of Chemical Technology, Faculty of Applied Sciences, Delft University of  
Technology, The Netherlands. *E-mail*: e.m.kelder@tudelft.nl

Nanomaterials become more and more important for use in Li-ion batteries as these can deliver increased gravimetric capacity and improved power performance. A brief overview is given of various methods for producing nanopowders for Li-ion batteries available in the group of NanoStructured Materials at the TUDelft – these are Laser-assisted Chemical Vapour Pyrolysis (LA-CVP), Spark Discharge Generation (SDG), Electrostatic Spray Pyrolysis (ESP) eventually in a reductive environment, and Advanced Sol-Gel.

LA-CVP is typically a pyrolytic method of making nanoparticles from gaseous reactants. The major steps in this process are: gas phase reaction, nucleation, collision, and sintering. Chopped infrared emission of a CO<sub>2</sub> laser provides the reaction energy. Silane and acetylene have been used as precursors. To suppress hard agglomeration and sintering, the residence time in the reaction hot zone is limited by confining the reaction zone.

SDG is based on discharge of a capacitor across the gap between two electrodes in an inert atmosphere of flowing gas. Through the high temperature of the spark, electrode material is rapidly evaporated, and condenses as to form a nanopowder. The spark lasts a few nanoseconds giving a temperature near 20000 K. Cooling proceeds within nanoseconds at a rate of 10<sup>10</sup> K/s.

ESP works as follows: when a high voltage is applied to a metallic nozzle through which a liquid is pumped at a low flow rate, the droplet shape at the outlet nozzle changes from a spherical to a conical one from the apex of which a jet emerge. This jet can break up into droplets with a narrow size distribution. When the liquid contains for instance dissolved salts or eventually sols, powders are formed during a drying process of the solvent. By oxidising/ reducing the salts desired powders are produced.

Advanced Sol-Gel methods using surfactants or porogene (urea) are used in order to synthesise oxidic nanopowders. Another important point of these syntheses is that texture of the desired materials can be tuned, i.e. high surface area, porosity and particles size distribution. These processes have been applied for synthesis of high surface area nano anatase TiO<sub>2</sub>, nano LiCoO<sub>2</sub> and nano high voltage spinel (LiMg<sub>0.05</sub>Ni<sub>0.45</sub>Mn<sub>1.5</sub>O<sub>4</sub>).

## Iron-Based Composite Oxide as Alternative Negative Electrode for Lithium-ion Batteries

Ivan Uzunov<sup>1</sup>, Snezhana Uzunova<sup>2</sup>, Daniela Kovacheva<sup>1</sup> and Anton Momchilov<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Acad.G.Bonchev Str., bl.11, IGIC-BAS. *E-mail:* [uzunov\\_iv@svr.igic.bas.bg](mailto:uzunov_iv@svr.igic.bas.bg)

<sup>2</sup>Institute of Electrochemistry and Energy Systems (former CLEPS), Bulgarian Academy of Sciences.

Iron oxides are attractive materials for Li-ion batteries due to their abundance, low cost and environmentally benign products. They have also shown promising initial capacity values (300 – 600 mAh.g<sup>-1</sup>) but exhibit significant capacity fading on continued cycling. To overcome this fact we synthesized composite iron oxides - silica by a sol-gel method. The effect of silica matrix on the phase composition and electrochemical properties of mixed iron oxides were studied.

The electrochemical behavior of the compounds was investigated galvanostatically within the 0,01-3,0 V range at a current density of 0,80 mA.cm<sup>-2</sup>.

The X-ray data of sample synthesized with 10% silica show the presence of two phases: LiFe<sub>5</sub>O<sub>8</sub> and LiFeO<sub>2</sub>. The mean particle size is about 100 - 200 nm determined by SEM method. XRD analysis of the material synthesized with 50% colloidal silica shows presence of a pyroxene phase, LiFe(SiO<sub>3</sub>)<sub>2</sub> and less than 5% Fe<sub>2</sub>O<sub>3</sub> (h). The mean particle size for LiFe(SiO<sub>3</sub>)<sub>2</sub> determined by XRD-line profile analysis is 16 – 20 nm.

The Li/Li-Fe-Si-O cell with 10% silica showed high initial reversible capacity of 1090 mAh.g<sup>-1</sup> and capacity at the 30<sup>th</sup> cycle 520 mAh.g<sup>-1</sup>. It was established that pyroxene phase is electrochemical inactive within the voltage range 0,01-3,0 V.

The results show that the new iron-based composite oxide material is suitable material for use as anode in lithium-ion batteries.

## Particle Size Effect Influencing the Electrochemical Efficiency of Lithiated Manganese Oxide

Hristina Vasilchina, Albena Aleksandrova, Neli Velinova, Branimir Banov,  
Atanaska Trifonova and Anton Momchilov

Institute of Electrochemistry and Energy Systems – IEES-BAS (former CLEPS)  
1113 Sofia, Bulgaria. *E-mail*: bbanov@cleps.bas.bg

The lithium cobaltate is the material used in commercial rechargeable lithium ion batteries [1-5]. It possesses good cyclability, high discharge potential and acceptable energy density. The synthesis of lithium cobaltate is easy and can be realized on a large industrial scale. On the other hand, the price of cobalt is very high and determines the end user price of the lithium battery. The cobalt and its oxides are very toxic. Thus the nearest future is devoted to positive electrode materials with high specific energy density – volumetric and gravimetric, high columbic efficiency - close to the theoretical one, long cycle life, non-toxic, environmentally friendly and with low cost [6-9]. There are two possibilities – new cathode materials or improvement of columbic efficiency of already well-known cathode materials. We have chosen the latter. Lithium manganese dioxide spinel is the material combining the above-sited requirements. But it possesses also some disadvantages as low starting capacity and low stability at elevated temperatures [7,8]. Optimising the synthesis way and elucidating the factors influencing the electrochemical stability we have succeeded to show how the manganese dioxide spinel can be transformed to very attractive and prospective cathode material for large scale application [9]. Improved columbic efficiency of all cathode materials based on manganese dioxide confirms the correctness of the direction for enhancing other active electrode materials. The role of particles size, specific surface area and pore size distribution for the improvement of electrochemical parameters are largely discussed [7,9]. Cathode materials based on lithiated manganese oxide and spinel with high columbic efficiency close to 90% at elevated temperatures of 55°C, discharge rates of 4C and cycle life up to 300 are presented.

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## **A New Method for the Preparation of Nanosized Olivine-Type Compounds $\text{LiMPO}_4$ ( $\text{M}^{2+} = \text{Mn, Fe, Co, Ni}$ ) for Cathode Materials in Li-ion Batteries**

Violeta Koleva, Ekaterina Zhecheva and Radostina Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: vkoleva@svr.igic.bas.bg

In harmony with the increasing social demand for cheaper, non-toxic, stable and safe rechargeable lithium battery with high capacity, the olivine-type compounds  $\text{LiMPO}_4$  ( $\text{M}^{2+} = \text{Mn, Fe, Co, Ni}$ ) are promising cathode materials. The main problem with the phospho-olivines is their poor rate capability, which is attributed to the low Li-ion diffusion and/or low electronic conductivity. In order to increase the rate capacity, recent efforts are focused on the development of methods, which have to provide a proper morphology of the  $\text{LiMPO}_4$  powders as nanosized particles with homogeneous particle size distribution. In this contribution, we have developed a new method based on the "soft chemistry" rules for the preparation of nanosized  $\text{LiMPO}_4$  ( $\text{M}^{2+} = \text{Mn, Fe, Co, Ni}$ ) powders. The method consists of freeze-drying of transparent aqueous solutions containing  $\text{Li}^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{M}^{2+}$  ( $\text{M}^{2+} = \text{Mn, Fe, Co, Ni}$ ) and  $\text{HCOO}^-$  ions ( $\text{M}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  salts are used). The amorphous formate-phosphate precursors thus obtained are heated at different temperatures in an argon atmosphere for Mn- and Fe- and in air for Co- and Ni-salts, respectively. The influence of the concentration and pH of the initial solutions, the temperature and the duration of the thermal treatment on the morphology of the final products has been studied. The prepared phosphates are characterized by X-ray powder diffraction, IR spectroscopy, BET measurements and SEM. It has been established that: (i) single phases having an ordered olivine structure (SG Pmnb) are produced at a low temperature (350°C); (ii) the powders have nanosized particles (below 100 nm) with BET surface areas of about 30 m<sup>2</sup>/g; (iii) no  $\text{M}^{3+}$  impurities have been detected due to the use of the formate precursors, thus providing a reduction medium during the synthesis; (iv) the method is also applicable for the preparation of mixed and doped phospho-olivines as well as of composite materials of the type  $\text{LiMPO}_4/\text{carbon}$ . The results obtained demonstrate that the new freeze-drying method is very effective and suitable for the preparation of nanosized olivine-type compounds  $\text{LiMPO}_4$  ( $\text{M}^{2+} = \text{Mn, Fe, Co, Ni}$ ) as cathode materials in lithium-ion batteries.



## Effect of the Precursor on the Ni,Mn Distribution in Layered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> Oxides at a Nano-Scale Region

Meglina Yoncheva, Radostina Stoyanova and Ekaterina Zhecheva

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia,  
Bulgaria. *E-mail*: meglena@svr.igic.bas.bg

The complex solid solutions of well-known layered lithium nickelates, LiNiO<sub>2</sub>, with monoclinic lithium manganates, Li[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub>, have been recently shown to be promising cathode materials in the 4V-range, characterized with a higher theoretical capacity (280 mAh/g) [1,2]. Of importance is that both cationic distribution and electrochemical performance of these materials displays a strong dependence on the synthesis procedure.

The aim of this contribution is to prepare LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>-based cathode materials with a controlled Ni/Mn distribution at a nano-scale region. Two synthesis procedure based on metal-inorganic and metal-organic precursor techniques were adopted for the preparation of layered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>. The oxides prepared were characterized by powder XRD analysis and IR spectroscopy. The amount of Ni ions in the lithium layers was estimated from structure refinement of the XRD diffraction patterns (Rietveld analysis). The electron paramagnetic resonance spectroscopy (EPR) was used as a local experimental tool to assess the Ni/Mn nano-scale cationic ordering.

For the synthesis of LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>, we have considered a synthetic procedure involving a solid-state reaction between Ni,Mn precursors and LiOH.H<sub>2</sub>O in the temperature range of 700 - 900 °C. The Ni,Mn precursors were prepared from co-precipitated hydroxides and carbonates, as well as from freeze-dried citrates. It has been found that thermal decomposition at 400 °C of Ni,Mn citrates yields Ni,Mn oxide with spinel structure, while Ni,Mn oxide with ilmenite-type structure was formed during thermal decomposition of Ni,Mn hydroxides and carbonates. Further solid state reaction with LiOH displays strong sensitivity on the type of the crystal structure of Ni,Mn-oxide precursors.

Although Ni<sup>2+</sup> and Mn<sup>4+</sup> are EPR active, an EPR response from Mn<sup>4+</sup> ions only has been detected. In the X-band, comparative analysis of the EPR line width of Mn<sup>4+</sup> ions permits to extract the composition of the first coordination sphere of Mn in layered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> obtained from hydroxides, carbonates and citrates precursors. It has been shown that “α,β”-type cationic arrangement with some extent of local disorder describes the Li<sup>+</sup>, Ni<sup>2+</sup> and Mn<sup>4+</sup> distribution in [Li<sub>δ</sub>Ni<sub>0.5-δ</sub>Mn<sub>0.5</sub>]O<sub>2</sub>-layers. The extent of local cationic disorder depends on both the precursor used and temperature of annealing.

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## Influence of the Synthesis Conditions Over the Formation of Solid Solution $\text{LiNiO}_2$ - $\alpha\text{LiAlO}_2$ in the Whole Concentration Range

E. Shinova<sup>1</sup>, E. Zhecheva<sup>1</sup>, R. Stoyanova<sup>1</sup>, G. Bromiley<sup>2</sup>, T. Boffa Ballaran<sup>2</sup>,  
R. Alcantara<sup>3</sup> and J.L. Tirado<sup>3</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. E-mail: elitza@svr.igic.bas.bg

<sup>2</sup>Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany.

<sup>3</sup>Laboratorio de Química Inorgánica, Facultad de Ciencias, Universidad de Córdoba, 14071 Córdoba, Spain.

$\text{LiNiO}_2$  oxides with layered crystal structure are of great interest as cathode materials for lithium-ion batteries because of their higher capacity (185÷210 Ah/kg at potential 4.1V and 4.2V, respectively) compared to that of  $\text{LiCoO}_2$  (140 mAh/g), and lower price.  $\text{LiNiO}_2$  oxides are not still used as commercial cathode materials because of the difficulty in the synthesis of the stoichiometric composition and the poor thermal stability of the delithiated oxide. In an attempt to improve the stability of layered structure of  $\text{LiNiO}_2$  and its capacity retention during cycling, replacement of  $\text{Ni}^{3+}$  by non-electrochemically active  $\text{Al}^{3+}$  was carried out.

The aim of this contribution is to prepare layered solid solutions  $\text{LiAl}_y\text{Ni}_{1-y}\text{O}_2$  in the concentration range  $0 \leq y \leq 1$ . Structural characterization of the oxides was performed using XRD, SEM analysis, IR spectroscopy, EPR spectroscopy and chemical analysis. Electrochemical experiments were carried out in Swagelok-type cell using a MacPile system in galvanostatic and potentiostatic mode.

Three methods of synthesis were adopted for the preparation of  $\text{LiAl}_y\text{Ni}_{1-y}\text{O}_2$ : two “soft” chemistry routes using citrate precursors or boehmite-type co-precipitated Al-Ni oxide-hydroxides, respectively, and a high-pressure synthesis in an oxygen-rich atmosphere.

When using citrate precursors, the aptitude of  $\text{LiNiO}_2$  to dissolve Al reaches up to 50% at atmospheric pressure,  $\text{LiAl}_{0.5}\text{Ni}_{0.5}\text{O}_2$  with  $0 \leq y \leq 0.5$  being formed. Contrary, from the Al-Ni boehmite-type precursors, only Al-rich phases were obtained:  $\text{LiAl}_y\text{Ni}_{1-y}\text{O}_2$  with  $0.50 < y \leq 1$ . Under high oxygen pressure, the single phases have an aluminum content  $0 \leq y < 0.50$  and  $0.90 \leq y \leq 1$ , respectively. All oxides were found to have a layered structure (space group R-3m), were  $\text{Ni}^{3+}$  substitutes for  $\text{Al}^{3+}$  in the metal layer. Rietveld refinement shows that the local trigonal distortion of the  $\text{MO}_6$ - and  $\text{LiO}_6$ -octahedra depends not only on the Al/Ni ratio, and also on the synthesis procedure. EPR spectroscopy at 9.23 GHz was used to monitor the cation distribution in the metal layers. SEM analysis was performed for determination the effect of the preparation route on particle size and morphology.

Electrochemical experiments have shown that replacement of  $\text{Ni}^{3+}$  with  $\text{Al}^{3+}$  in  $\text{LiNi}_{1-y}\text{Al}_y\text{O}_2$  results in a decreased lithium capacity at the expense of the improved cycling stability.

## Structural Characterization of Manganese-Based Composite Electrode Materials for Lithium-ion Batteries

Svetlana Ivanova, Radostina Stoyanova and Ekaterina Zhecheva

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: svetlana@svr.igic.bas.bg

Lithium-transition metal oxides represent the main class of electrode materials for lithium-ion batteries due to their ability to intercalate large amounts of lithium reversibly at potentials higher than 4V vs. Li. The drawback of electrode materials based on single phase oxides with layered or spinel-type structure still remains the poor performance at elevated temperatures. To improve the electrochemical performance, recent research interest is focused on composite electrode materials, especially in regard of the structural integration of the electro-active oxides into the electro-inactive oxides [1, 2].

In this contribution we provide data on synthesis and structural characterization of new composite oxide systems consisting of domains with  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  and  $\text{Li}_2\text{MnO}_3$  compositions. For the preparation of lithium-manganese oxides, we used the acetate precursor method. This method consists in freeze-drying of acetate salts of the corresponding metal ions, followed by thermal decomposition in air. Powder XRD analysis and IR spectroscopy were used for structural characterization of the samples obtained. The manganese and lithium content of the samples was determined by complexometrically and by atomic absorption analysis. The mean oxidation state of Mn was established by redox titration.

At 400 °C, the acetate precursor method allows synthesis of the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  spinel containing  $\text{Mn}^{4+}$  ions only. Due to the thermal instability of  $\text{Mn}^{4+}$  in air, the controlled thermal treatment of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  in the temperature range of 400 - 800 °C yields a composite oxide system with a general formula  $(1-a)\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4.a\text{Li}_2\text{MnO}_3$ . Electron paramagnetic resonance (EPR) of  $\text{Mn}^{4+}$  was used as an experimental tool for microdomain characterization in the composite oxides  $(1-a)\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4.a\text{Li}_2\text{MnO}_3$ . The information on the cationic distribution in  $(1-a)\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4.a\text{Li}_2\text{MnO}_3$  was extracted by comparative analysis of the EPR line width with that of the end compositions - the spinel  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  and the monoclinic  $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_3$ . Whereas the EPR signal for  $\text{Li}_2\text{MnO}_3$  corresponds to exchange coupled  $\text{Mn}^{4+}$  ions, the collective  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  spin system contributes to the EPR response of  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  spinels. As a result, the EPR line width increases from 21 to 220 mT for  $\text{Li}_2\text{MnO}_3$  and  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ , respectively. Based on the different EPR line width, the EPR method allows monitoring the evolution of the domain structure and the domain composition as a function of annealing temperature and cooling rate.

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## **Vanadium Bronzes Particle Size Dependence on the Current Rate Ability and Electrochemical Capacity**

Albena Aleksandrova, Branimir Banov and Anton Momchilov

Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Science, 1113 Sofia, Bulgaria. *E-mail*: aamomch@cleps.bas.bg

Vanadium bronzes,  $\text{LiV}_3\text{O}_8$ ,  $\text{KV}_5\text{O}_{13}$  and  $\text{K}_2\text{V}_8\text{O}_{21}$ , are attractive materials for rechargeable lithium batteries. The electrochemical behaviour of bronzes depends from the synthesis method due to the particle size of the obtained material. Vanadium bronzes were obtained via two preparing methods, Low External Temperature Method (LETM) and Solid State Reaction (SSR). LETM method consists of convective drying of the starting compounds solution in liquid media. Obtained precursor were heated in fluidized bed with airflow at  $300^\circ\text{C}$ .

The materials synthesized via SSR were additionally treated in autoclave at different temperatures to obtain different size particles.

The obtained materials were investigated by XRD, SEM and B.E.T. to determine their phases and average particle size of the materials. The electrochemical behaviour of the materials with different average particle size was investigated in order to determine the current load for practical use. The average particle size on the capacity obtained as well as the cycleability of the material was studied. It is shown the strong influence of the average particle size on the electrochemical behaviour of vanadium bronzes.

## Influence of the Synthesis Methods on the Particle Size of LiVMoO<sub>6</sub> Phase

Margarita Milanova<sup>1</sup>, Reni Iordanova<sup>1</sup>, Yanko Dimitriev<sup>2</sup> and Sasho Vassilev<sup>3</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: margi@svr.igic.bas.bg

<sup>2</sup>University of Chemistry Technology and Metallurgy, Sofia 1756, Bulgaria.

<sup>3</sup>Institute of Electrochemistry and Energy Systems, 1113 Sofia, Bulgaria.

The search for the newer materials, in terms of cost and environmentally friendly nature, has opened a new era in solid state materials research. As a part of this venture a new 4V-class lithiated transitional metal oxide LiVMoO<sub>6</sub> has recently attracted special attention. Five different variations of conventional solid state reaction [1, 2] and wet chemistry technique (sol-gel, soft-combustion synthesis and rheological phase reaction) [2-4] were reported in the literature for its preparation. Our experience in the synthesis of vanadates and molybdates phases provokes the interest to extend the experimental techniques for LiVMoO<sub>6</sub> preparation. In this work we have attempted to synthesize this compound by: melt quenching, crystallization of a glass, soft-combustion and conventional solid state synthesis. Comparison of the applied techniques shows that there is a difference of the particle size and the morphology of the obtained product. The smallest grains (32 nm) of LiVMoO<sub>6</sub> powder were achieved by crystallization of a glass. Depending on the preparative methods there is a deviation of the product colour from light yellow to dark due to different stoichiometry. The shorter time for the LiVMoO<sub>6</sub> synthesis was attained by melt quenching technique.

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## Tin-Based Amorphous and Composite Materials

Ekaterina Popova<sup>1</sup> and Yanko Dimitriev<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: ekpopova@svr.igic.bas.bg

<sup>2</sup>Department of Silicate Technology, University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria.

The paper reviews the studies of SnO-based oxide glasses and presents our experience in developing such amorphous materials. The obstacles in producing such materials are oxidation or disproportionation of SnO at high temperatures. Different techniques were applied to established reproducible methods for synthesis of Sn-containing glasses. Tin oxide glasses were obtained in the binary systems with classical glass-former oxides: SnO-SiO<sub>2</sub>, SnO-GeO<sub>2</sub>, SnO-B<sub>2</sub>O<sub>3</sub>, SnO-P<sub>2</sub>O<sub>5</sub>, SnO-BPO<sub>4</sub> and in oxyhalide systems SnX<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>, (X=F, Cl). Available data concerning composition depending properties and the influence of melting conditions and the role of modifiers have been summarized. SnO essentially improves some technological characteristics of glasses, but many unsolved problems regarding the mechanism of its influence still remain. Several structural models for the amorphous network based on the spectral and diffractive data were proposed. Depending on the composition, SnO tends to change its behavior from network-modifier to network-former. But the structural role and chemistry of tin in inorganic glasses is still not clearly understood. In recent years increasing attention has been devoted to tin composite oxide glasses (TCO glasses), which are most promising candidates as anode materials in lithium secondary batteries for portable electronic devices. They exhibit high specific capacity twice that of carbon materials used as anodes for commercial batteries. On the other hand, the SnO-containing glass materials are desirable from environmental viewpoint as Pb-free low melting glasses, sensing elements, non-linear optical materials and coatings. Our studies were focused on the systems of SnO-P<sub>2</sub>O<sub>5</sub>, SnCl<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>, SnCl<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-MeCl<sub>2</sub> (Me<sub>n</sub>O<sub>m</sub>). The influence on the quality of glasses of different factors, such as nature of raw materials, the batch preparation and the melting conditions, has been studied. Low-melting stable glasses have been obtained at ambient atmosphere. The glass-forming ability of SnO was proved by increasing its content above 50 mol% (nominal composition).

*Topic C.*

**Materials for Hydrogen Storage  
at a Nano-Scale Level**





## Hydrogen Storage in Light Weight Metal Hydrides and Reactive Hydride Composites

M. Dornheim<sup>1</sup>, G. Barkhordarian<sup>1</sup>, U. Bösenberg<sup>1</sup>, N. Eigen<sup>1</sup>, S. Doppiu<sup>2</sup>, A. Borgschulte<sup>1</sup>, O. Metz<sup>1</sup>, X. Qi<sup>1</sup>, C. Keller<sup>1</sup>, O. Gutfleisch<sup>2</sup>, T. Klassen<sup>1,3</sup> and R. Bormann<sup>1,4</sup>

<sup>1</sup>Institute for Materials Research, GKSS-Research Centre Geesthacht GmbH, 21502 Geesthacht, Germany. *E-mail:* martin.dornheim@gkss.de

<sup>2</sup>Leibniz Institute for Solid State and Materials Research, 01069 Dresden, Germany.

<sup>3</sup>Institute of Material Science, Helmut Schmidt University, 22043 Hamburg, Germany.

<sup>4</sup>Dept. Materials Science and Technology, Hamburg University of Technology, 21073 Hamburg, Germany.

Hydrogen storage is a key issue for a future hydrogen based economy. Appropriate storage facilities, both for stationary and for mobile applications, are complicated, because of the very low boiling point of hydrogen (20.4 K at 1 atm) and its low density in the gaseous state (90 g/m<sup>3</sup>). Furthermore, the storage of hydrogen in liquid or gaseous form imposes safety problems, in particular for mobile applications, e.g. the future zero-emission vehicle. Metal hydrides are a safe alternative for H-storage and, in addition, have a high volumetric energy density that is about 60% higher than that of liquid hydrogen.

Compared to conventional room temperature hydrides lightweight metal hydrides have much higher gravimetric hydrogen storage densities. However, so far light metal hydrides have not been considered competitive because of thermodynamic or kinetic limitations. Lightweight hydrides exhibited rather sluggish sorption kinetics. Filling a tank could take several hours. Moreover, the hydrogen desorption temperature is rather high for most lightweight metal and complex hydrides.

A breakthrough in hydrogen storage technology was achieved by preparing nanocrystalline hydrides using high-energy ball milling as well as adding suitable catalysts/dopants. This enabled the preparation of novel lightweight materials for hydrogen storage with much higher gravimetric hydrogen storage densities. Some of these new materials show very fast ab- and desorption kinetics within few minutes. However there are still a lot of hydrides like the borohydrides with very high gravimetric hydrogen storage densities, which cannot be reversibly hydrogenated under moderate conditions. This demonstrates the demand for novel approaches to enhance the kinetics of lightweight hydrides.

One very exciting, successful and promising novel approach is the concept of the Reactive Hydride Composites (RHC). Such systems show reduced total reaction enthalpies as well as significantly improved ab- and desorption kinetics compared to the pure hydrides. Furthermore, in RHC reversibility is demonstrated for hydrides, which have been considered as irreversible using moderate hydrogen pressures and temperatures.

## Hydrogen Storage in Magnesium Clusters

Rudy Wagemans, Joop H. van Lenthe, Petra E. de Jongh, A. Jos van Dillen, Krijn P. de Jong

Chemistry and Catalysis & Theoretical Chemistry, Debye Institute, Utrecht University.

Magnesium hydride is cheap and contains 7.7 wt% hydrogen, making it an attractive hydrogen storage material. The problem of the slow kinetics for reversible (de)hydriding has mostly been solved during the last decade by introducing small amounts of transition metal elements and reducing the crystal grain size to 20-50 nm by ball milling. Unfortunately, despite the improvement in the kinetics, thermodynamics still dictate that bulk  $\beta$ -MgH<sub>2</sub> only decomposes above ca. 300 °C (at 1 bar H<sub>2</sub> pressure), which is a major impediment for practical application. It is well known that fundamental properties of materials can change dramatically when material dimensions shift into the nanometer regime. We theoretically investigated the influence of the magnesium particle/crystal grain size much below the 20-50 nm range normally achieved by ball-milling. Density functional theory (DFT) calculations were performed on nanometer-sized Mg and MgH<sub>2</sub> clusters. Figure 1 shows desorption energies as a function of the cluster size and the energies for stepwise H<sub>2</sub>-desorption from selected clusters.

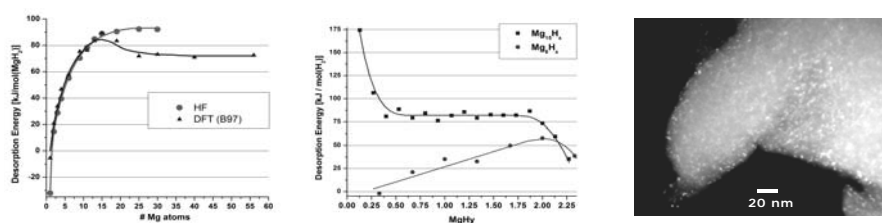


Figure 1. Left: Calculated desorption energies for MgH<sub>2</sub> clusters with both the HF and DFT method (B97 functional). Right: Synthesized Magnesium-Carbon nanocomposites.

Our calculations clearly show (using zero-point energy correction, different functionals and comparing with Hartree-Fock calculations) that the desorption enthalpy of MgH<sub>2</sub>, and hence the dehydriding temperature, can be significantly reduced for particles sizes of the order of 1-2 nm. The projected shift towards more favorable operation temperatures is crucial for the application of Mg as a reversible hydrogen storage material. Intriguing results are obtained for the stepwise desorption of clusters with different sizes. It is experimentally very demanding to obtain such small particles, and/or to stabilize crystal grains of such a small size. We now focus on novel experimental routes to prepare supported magnesium clusters. Early results show that Mg-C nanocomposites with Mg clusters of 3 nm and smaller have been synthesized successfully.

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## Reactive Mechanical Grinding of Mg<sub>2</sub>Ni and 90wt% Mg<sub>2</sub>Ni - 10 wt% Graphite (Co)

Jean-Louis Bobet<sup>1</sup>, Eli Grigorova<sup>2</sup>, Maria Khrussanova<sup>2</sup> and Pavel Peshev<sup>2</sup>

<sup>1</sup>Institut de la Chimie de la Matière Condensée de Bordeaux, Université Bordeaux I  
87, Avenue du Dr. A. Schweitzer, Pessac, Cedex France.

<sup>2</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia,  
Bulgaria. *E-mail*: egeorg@svr.igic.bas.bg

Ball milling in inert and reactive media is a suitable method for preparation of hydrogen storage materials. Reactive mechanical grinding (RMG) has been used to improve the hydrogen storage properties of Mg- based materials, because ball milling under hydrogen facilitates the composite activation and leads to formation of nanocrystalline products.

RMG of Mg<sub>2</sub>Ni was also performed by other authors [1-4]. Under different conditions of RMG they have received a mixture of Mg<sub>2</sub>NiH<sub>0.3</sub> and Mg<sub>2</sub>NiH<sub>4</sub> phases or Mg<sub>2</sub>NiH<sub>0.3</sub> only.

The aim of this work is to investigate the influence of different additives (Co and graphite) as well as the conditions of ball milling on the transformation of Mg<sub>2</sub>Ni to Mg<sub>2</sub>NiH<sub>4</sub> upon RMG. Depending on the additive type RMG under 1.1 MPa H<sub>2</sub> of pure Mg<sub>2</sub>Ni and mixtures of 90wt.% Mg<sub>2</sub>Ni- 10wt.% Co(graphite) leads to formation of Mg<sub>2</sub>NiH<sub>4</sub> or Mg<sub>2</sub>NiH<sub>0.3</sub>. Mg<sub>2</sub>NiH<sub>4</sub> has been detected by X- ray diffraction analyses in pure Mg<sub>2</sub>Ni and 90wt.% Mg<sub>2</sub>Ni- 10wt.% Co after RMG for 1h. When the additive is graphite only Mg<sub>2</sub>NiH<sub>0.3</sub> is found even after 10h RMG.

The hydrogen sorption properties of RMG composites with additives of graphite or Co have also been investigated. Graphite containing composites have better hydrogen absorption properties. All investigated composites desorb hydrogen at 513K or at 523K which are relatively low temperatures for desorption from Mg-containing materials.

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## Hydrogen Absorption by the Nanocomposite 85%Mg - 15%Mg<sub>2</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub> Obtained by Ball Milling

Maria Khrussanova, Tsveta Mandzhukova, Eli Grigorova, Mitko Khristov and Pavel Peshev

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: tsvetam@svr.igic.bas.bg

The introduction of additives to magnesium composites obtained by ball milling is an efficient method for improving their hydriding kinetics, the hydrogen absorption capacity remaining sufficiently high.

The present study deals with the hydriding kinetics and hydrogen absorption capacity of a magnesium composite with the composition 85%Mg-15%Mg<sub>2</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub> obtained by mechanical alloying in a planetary mill under inert atmosphere. The hydrogen absorption was measured at 373-573 K and P = 1 MPa, while desorption was investigated at 573 K and P = 0.15 MPa. The possibility of prolonged cycling of the composite without drastic decrease in its absorption capacity was also studied. The experimental data obtained illustrate the catalytic effect of the intermetallic additive, which consists in (a) significant improvement of the hydriding kinetics of magnesium, (b) a high absorption capacity of the composite over the range 373 – 573 K and (c) preservation of its high value (5.2 wt %) after 70 absorption-desorption cycles. Comparison of the hydriding of the intermetallics Mg<sub>2</sub>Ni and Mg<sub>2</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub> reveals improved hydriding kinetics of the intermetallic Mg<sub>2</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub> due to the presence of cobalt in it.

On the basis of the experiments performed, the behaviour of the composite 85%Mg-15%Mg<sub>2</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub> during hydriding was assumed to be due to nickel and cobalt clusters on the surface established by magnetic studies and facilitating the dissociative chemisorption of hydrogen as well as to the mechanical activation process.

These results could also explain the hydriding behaviour of the magnesium nanocomposites containing the intermetallics Mg<sub>2</sub>Ni<sub>1-x</sub>Co<sub>x</sub> obtained in a previous paper [1].

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## Effects of Nickel Foam Dimensions on Catalytic Activity of Supported Co-Mn-B Nanocomposites for Hydrogen Generation from Stabilized Borohydride Solutions

Mario Mitov<sup>1</sup>, Rashko Rashkov<sup>2</sup>, Nikolay Atanassov<sup>2</sup> and Andreas Zielonka<sup>3</sup>

<sup>1</sup>Department of Chemistry, South-West University “Neofit Rilsky”, 66 Ivan Mihailov Str., 2700 Blagoevgrad, Bulgaria. *E-mail*: mitovmario@mail.bg

<sup>2</sup>Institute of Physical Chemistry – BAS, 11 Acad. G. Bonchev Blvd., 1113 Sofia, Bulgaria.

<sup>3</sup>Research Institute for Noble Metals and Chemistry of Metals, Schwaebisch Gmuend, Germany.

The successful application of hydrogen as an energy source for the future depends largely on the conception of a safe and convenient method for the hydrogen storage and production. Sodium borohydride (NaBH<sub>4</sub>) is one of the most attractive hydrogen storage systems in view of its various advantages. It has a high hydrogen content of 10.8 wt.% and can preserve hydrogen stably in alkaline solution. On demand, a large amount of H<sub>2</sub> can be produced by hydrolysis of a base-stabilized NaBH<sub>4</sub> solution using suitable catalysts. Currently nanosized Ru and Pt particles are mainly used as catalysts for hydrolysis of NaBH<sub>4</sub> in alkaline solution [1,2]. Since the prize of noble metal catalysts is so high, the development of alternative low-cost catalysts for hydrogen generation from alkaline borohydride solution is of a big importance.

The object of this work was to produce by electrodeposition nanocomposite Co-Mn-B multilayers on Ni-foam and investigate their performance as catalysts for hydrolysis of NaBH<sub>4</sub> in alkaline solution. Deposition was done on two types of Ni-foam (RECEMAT Int.) with different pore size, specific surface area and thickness. Higher deposit loading as well as bigger real surface area was obtained with foam samples possessing bigger pore size. When contacted with a base-stabilized NaBH<sub>4</sub> solution, the catalyst deposited on bigger pore foam promoted hydrogen generation with higher rates than the other one, but the same activation energy value was obtained for both catalyst types. Based on the experimental results, it may conclude that the geometric factor plays predominant role for the catalytic activity of studied catalysts for the borohydride hydrolysis reaction. Relatively low activation energy value presumes some diffusion limitations of reaction on these catalysts, which should be taken into account in further investigations, aiming an improvement of their activity and increase of hydrogen generation rate.

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## Hydrogen Sorption in Amorphous and Nanocrystalline Mg<sub>2</sub>Ni Alloys

Nikola Drenchev<sup>1</sup>, Stoyan Bliznakov<sup>2</sup> and Tony Spassov<sup>1</sup>

<sup>1</sup>University of Sofia, Department of Chemistry.

<sup>2</sup>Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia, Bulgaria. *E-mail*: ndrenchev@chem.uni-sofia.bg

Amorphous and nanostructured Mg<sub>2</sub>Ni-based alloys are synthesized by mechanical alloying under protective argon atmosphere. Scanning Electron Microscopy and X-ray diffraction are used for morphological and microstructural characterization of the as-milled and hydrided materials. The thermal properties of the as-milled materials are studied by Differential Scanning Calorimetry.

Hydriding/dehydriding properties of the alloys synthesized are investigated from a hydrogen gas phase by a volumetric Sievert's type apparatus, thermogravimetrically and electrochemically by galvanostatic charge/discharge cycling.

The hydrogen storage characteristics and the corrosion behavior of the materials studied as well as the influence of the microstructure on the hydriding properties are determined.

## Hydrogen in Amorphous and Nanocrystalline TiNi-Based Alloys

Boris Drenchev and Tony Spassov

University of Sofia, Department of Chemistry, 1 James Bourchier str., 1164 Sofia, Bulgaria.

*E-mail:* [bdrenchev@chem.uni-sofia.bg](mailto:bdrenchev@chem.uni-sofia.bg)

Amorphous and nanostructured TiNi and TiSnNi alloys are synthesized by mechanical alloying and by rapid quenching from the melt. The morphology and microstructure of the as-prepared and hydrided materials are characterized by electron microscopy and x-ray diffraction. Differential scanning calorimetry is used for studying the thermal stability and crystallization of the amorphous materials.

Hydrogen absorption/desorption properties of the alloys synthesized were investigated from a hydrogen gas phase by a volumetric Sievert's type apparatus and electrochemically by galvanostatic charge/discharge cycling as well as by means of thermogravimetric analysis.

The hydrogen storage characteristics of the materials studied as well as the influence of hydrogen on the phase transformations in the TiNi alloys during annealing are determined. The influence of Sn on the hydriding properties of  $Ti_{1-x}Sn_xNi$  is studied as well.





*Topic D.*

**Microstructural Effects in SOFC's**



## How Processing and Durability of Microstructure Determines SOFC Performance

Hans Peter Buchkremer, Detlev Stöver, Frank Tietz and Sven Uhlenbruck

Institute for Materials and Processes in Energy Systems,  
Research Centre Juelich, D-52425 Juelich, Germany  
*E-mail*: h.p.buchkremer@fz-juelich.de

Solid Oxide Fuel Cells (SOFC) are under development due to their potential to generate electrical power from fossil fuels with a possible efficiency of 70%. Therefore future SOFC power plants could make an important contribution to a reasonable and clean use of the limited resources of fossil fuel. To become commercially feasible, SOFC's have to overcome a few of the current technical limitations concerning power density, degradation, durability and dynamic behaviour. Especially power density and degradation of the SOFC's during operation is strongly dependent on the engineered microstructure and its long term stability. In the first part of this presentation key processing steps are described to establish an anode supported solid oxide fuel cell with thin electrolyte. The cell's microstructure results in an arrangement with sufficient mechanical strength and high power density under operating conditions. Due to the different functionality of the layers the typical microstructure dimensions can range from some nanometers to hundreds of micrometers. Examples and the underlying model assumption of layers with coarse as well as fine microstructures are given.

The second part of the contribution deals with changes in microstructure during long term operation. These modifications cause aging effects of the SOFC which result in deterioration of performance and mechanical integrity. The main degradation mechanisms are described with respect to microstructural changes, and attempts are discussed to improve the long term stability of different SOFC components.

## Bifunctional Catalysts and Electrodes for Oxygen Reduction and Evolution

K. Petrov<sup>1</sup>, V. Nikolova<sup>1</sup>, P. Iliev<sup>1</sup>, T. Vitanov<sup>1</sup>, R. Stoyanova<sup>2</sup>, E. Zhecheva<sup>2</sup>  
V. Rashkova<sup>3</sup>, S. Kitova<sup>3</sup>, I. Konstantinov<sup>3</sup>, I. Valov<sup>4</sup> and D. Stoychev<sup>4</sup>

<sup>1</sup>Institute for Electrochemistry and Energy Systems, Bulgarian Academy of Sciences,  
1113 Sofia, Bulgaria.

<sup>2</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,

<sup>3</sup>Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences

<sup>4</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences

Oxygen Reduction and Evolution are basic processes in many environmentally related energy fields: (i) Hydrogen/Oxygen and Methanol Fuel Cells; (ii) Rechargeable Metal – Air and Metal Hydride – Air (MH – Air) Batteries; (iii) Water Electrolysis and Chloralkali Cells; (iv) Unitized Rechargeables Fuel Cells (URFCs) – a promising dual mode energy storage system for uninterrupted power supplies, solar applications, satellites, etc.

Efforts to develop air/oxygen bifunctional electrode that will operate in both cathodic and anodic modes are met by major problems, like corrosion, irreversibility of oxygen reaction, catalytic activity and others.

This paper presents the efforts of several research groups in BAS to develop catalysts and electrode structures suitable for work in both anodic and cathodic mode.

Three methods for catalysts synthesis have been applied; (i) thermal decomposition of nitrates and carbonate precursors for preparation of  $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ ,  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$ ; (ii) vacuum co-evaporation of Co, Ni and  $\text{TeO}_2$ ; (iii) electrodeposition from saturated univalent alcohol containing  $\text{ZrCl}_4$  and  $\text{CoCl}_2$  for preparation of  $\text{Co}_3\text{O}_4 - \text{ZrO}_2$ .

The catalysts were characterized physically by XRD, XPS, FTIR, BET and SEM. Electrochemical tests included CVA, steady state galvanostatic  $i - E$  curves and charge-discharge cycle life on different types model gas diffusion electrodes.

The electrochemical activity at higher current density for OE reaction increases in order:  $\text{Co}_3\text{O}_4 - \text{ZrO}_2 < \text{CoO-TeO}_2 < \text{Cu}_{0.2}\text{Co}_{2.8}\text{O}_4$ , while in OR reaction the order is:  $\text{CoO-TeO}_2 < \text{Co}_3\text{O}_4 - \text{ZrO}_2 = \text{Cu}_{0.2}\text{Co}_{2.8}\text{O}_4$ .

Gas-diffusion electrodes, catalyzed with chemically synthesized catalyst were tested in a real (MH – Air) battery: 200 charge-discharge cycles with stable current-voltage characteristics were achieved.

## Investigation of Nanostructured Platinum Based Nafion Membrane Electrode Assemblies Using New Method and Cell

Ivan Radev, Evelina Slavcheva and Evgeni Budevski

Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, 1113  
Sofia, Bulgaria. *E-mail*: ivan.radev@gmail.com

Among the different fuel cell technologies, due to their low operating temperature (60-150°C), fast start-up and complete absence of polluting emissions, polymer electrolyte membrane fuel cells (PEMFCs) are promising candidates for application of portable power source, electric vehicle, and transportation applications [1-3]. Although the fuel cell market is rapidly increasing, the assembly of factors such as cost, efficiency, running time, etc. is still insufficient and a further optimization is obviously required. The conventional optimization technology is generally limited to the variation and standardization of test procedures of ready available fuel cells using the whole needed cumbersome running infrastructure. Moreover the complicated running conditions are the main hindrance for a deeper understanding and optimization of the fuel cells.

The principle of the new test cell is based on the fact that electrode reactions can be run both in the forward and backward directions, using and recovering the reagents unified in one gas compartment with a near to 100 % faradic efficiency [4]. The consequence of the used principle is the strict self-regulating mechanism of the working conditions, thus avoiding the complicated, hazardous and expensive running periphery. Due to the principle of the new electrochemical system and the similarity of preparation procedures used in the electrodes for PEMFC and PEM water electrolyzer there are possibilities for investigation of each electrode both in the fuel cell and electrolyzer modes.

In the electrodes under study nanocrystalline Pt electro-catalyst sized 3-5 nm is used. This size of the Pt clusters is optimal for the architecture of the reactive zone of the fuel cell and electrolyzer. The influence of the total and partial pressures of the reactants on the electrode performance was investigated. Extending the working conditions to non standard ranges valuable kinetic information for evaluation and assessment purpose is obtained.

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## Structure and Electric Conductivity of (La, Sr)(Ga, Mg)O<sub>3</sub> Solid Electrolyte

V. Fruth<sup>1</sup>, C. Andronescu<sup>1</sup>, C. Hornoiu<sup>1</sup>, S. Preda<sup>1</sup>, S. Stoleriu<sup>2</sup> and G. Voicu<sup>2</sup>

<sup>1</sup>Institute of Physical Chemistry, Spl. Independentei 202, Bucharest 060021, Romania.

*E-mail:* candronescu@icf.ro

<sup>2</sup>Politehnica University, Polizu 1, Bucharest, Romania.

Doped LaGaO<sub>3</sub> is an excellent oxide ion conductor with potential application in solid oxide fuel cells.

Present paper deals with investigation regarding the obtaining and characterization of doped LaGaO<sub>3</sub> powder and sinters bodies. The powders were obtained by solid state reaction, starting from corresponding oxides.

The characterization methods were used: scanning and transmission microscopy (SEM), X-rays diffraction and infrared spectroscopy (XRD) with Fourier transformation, impedance spectroscopy, density, porosity, DTA/TG e. t. c.

A correlation between composition-structure, preparation was established.

## Characterization of Electrodeposited Nanostructured CeO<sub>2</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> Films

Ivalina Avramova and Tsvetana Marinova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: iva@svr.igic.bas.bg

Solid oxide fuel cells (SOFC) are very attractive because of high efficiency of energy conversion and low emission of pollutants. Doped zirconia ceramics are typically used as electrolytes for SOFCs due to their mechanical integrity and stability in both the reducing and oxidizing atmospheres. In recent years, doped ceria solid solutions with high ionic conductivities have been considered as promising electrolytes for use in intermediate-temperature SOFCs (IT-SOFC) [1].

The main purpose of the present study is to analyze the nanostructured CeO<sub>2</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> mixed oxides films electrodeposited upon stainless steel substrate depending of different contents among Ce, Zr and Y, as a promising candidate for electrolyte in SOFCs application. X-ray photoelectron spectroscopy (XPS) results lead to the evaluation of the valence state of cerium, zirconium and yttrium, both for as-deposited and thermal treated at 450°C for 2h mixed oxide films. XPS data indicate the formation of solid solution and additional existence of Ce<sup>3+</sup> states near the surface of the films. The structure and phase composition of electrochemical deposited films after annealing were identified by X-ray diffraction (XRD) analysis. The results conformed the other obtained from XPS for the formation of solid solution. Crystallite size was calculated for these CeO<sub>2</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> films from XRD data and varies between 5.3 nm and 4.5 nm depending of different contents. The trivalent part of segregated Ce at the surface and decreasing of grain sizes in the thin films can be expected to increase the oxygen vacancy population, leading to a further increase in ionic transport.

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## Characterization of Nanosized Mixed Yttria and Zirconia Thin Films

Aleksandar Tsanev and Tsvetana Marinova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: tsanev@abv.bg

In the literature there are many investigations dealing with the preparation and characterization of thin films of Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ). Different methods for deposition of thin YSZ films have been used in the literature: conventional spray techniques, sol-gel methods, laser ablation, magnetron sputtering etc. It is important to choose a deposition method controlling the layer thickness, grain size and porosity as well as the element concentration and ensuring deposition at relatively low temperatures.

The aim of present work is to characterize films of mixed zirconia and yttria that were deposited electrochemically on stainless steel OC4004 from nonaqueous electrolytes based on ethyl alcohol, ZrCl<sub>4</sub> and YCl<sub>3</sub>·6H<sub>2</sub>O with different content.

The films are investigated by XRD. The analysis have showed that the grain size and microstructure are comparable with this obtained by other techniques. We have found that the microstructure and grain size varied with yttria contents. Both (the microstructure and the grain size) played an important role in the electrochemical performance of thin film SOFC's. Ionic conduction in the electrolyte is strongly dependent on crystal structure [1] and grain size [2]. It is known that the cubic phase of YSZ exhibits the highest ionic conductivity and nanosized YSZ grains have been reported to increase ionic conductivity [3].

The films compositions were determined by X-ray photoelectron spectroscopy (XPS). After annealing of the layers, mixed oxides were formed. The changes in the valence band below the Fermi level were studied on films with different Y/Zr ratios.

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## Microstructure of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ( $0 \leq x \leq 0.5$ ) Prepared by Metal-Citrate Precursor Method

Sonya Ivanova and Ekaterina Zhecheva

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: sonya@svr.igic.bas.bg

Perovskite-type oxides with general formula  $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ , where M is a transition metal ion, attract the research interest due to their application as materials for solid oxide fuel cells, oxygen separation membranes, catalysts, sensors, electronic and magnetic materials [1]. The microstructure of the perovskite materials has been recognized as a factor affecting their performance [1,2].

In this contribution we report a low-temperature method for the preparation of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  with  $0 \leq x \leq 0.5$ . The synthesis method consists in the preparation by freeze-drying of homogeneous of La/Sr-Co-citrate precursors followed by thermal pyrolysis. Citric acid has a strong ability to complex La/Sr and Co thus leading to a homogeneous metal distribution in the solution. Freeze-drying keeps the micro-scale mixing of the constituents from the solution into the solid precursors. For the sake of comparison,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  oxides were also prepared by solid state reaction between  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$  and  $\text{CoCO}_3$  in the temperature range of 700-1000 °C.

The metal-citrate precursor method yields well-crystallized single phase  $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$  at temperature higher than 700 °C whereas with increasing Sr content this temperature moves up 1000 °C for  $x=0.5$ . Structural characterization of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  was carried out by XRD analysis and IR spectroscopy. The oxygen content was determined by redox titration. The effect of the precursor used on the particle size and the morphology of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  was examined by SEM analysis.

Electron paramagnetic resonance spectroscopy and magnetic susceptibility measurements were used for the microstructural characterization of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ . Below 400 K, stoichiometric  $\text{LaCoO}_3$  is EPR silent. However, depending on the precursor used and the preparation temperature, low-intensity EPR signals appear. These signals were assigned to crystal structure defects and to impurity  $\text{Co}_3\text{O}_4$ , the latter being not detected by XRD. When La is replaced by Sr, a nearly symmetrical signal dominates in the EPR spectrum of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ . The signal can be interpreted on the basis of exchange coupled  $\text{Co}^{3+}$ - $\text{Co}^{4+}$  spin system. With decreasing the registration temperature, the EPR spectra of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  show a transition to a long-range ferromagnetic order. Synthesis conditions affect the parameters of the main EPR signal from  $\text{Co}^{3+}$ - $\text{Co}^{4+}$  in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ .

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## Structural and Electronic Properties of Electrochemically Deposited CeO<sub>2</sub>-ZrO<sub>2</sub> Thin Films

Genoveva Atanasova<sup>1</sup>, Dimitar Stoychev<sup>2</sup> and Plamen Stefanov<sup>1</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail:* genoveva@svr.igic.bas.bg

<sup>2</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

Cerium-zirconium mixed oxide has been the subject of extensive study in recent years mainly because of its high oxygen storage efficiency in the latest generation of the three-way catalysts (TWCs) used for purifying automobile exhaust gases, and other applications such as its use as ionic conductor (e.g., in fuel cells) or as active support in catalysts for reforming or water gas shift reactions.

In the present work, CeO<sub>2</sub>-ZrO<sub>2</sub> thin films were deposited on stainless steel by cathodic deposition. The electrodeposition offers the advantages of low processing temperature, normal handling pressure, high purity of deposition and controlled thickness of the film. XRD, SEM and XPS methods were used to investigate the structure, surface morphology, composition and chemical state of Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> thin films (0.1 < x < 0.9), after deposition and after thermal treatment at 450°C. It was found that the composition and structure, which are strongly related to oxygen storage capacity, depended on the parameters of deposition. X-ray diffraction analysis indicated that the electrochemical deposition induces the formation of solid solution with a contraction of the cell parameter for cubic ceria following the introduction of Zr into the lattice. SEM study showed that with increasing ZrO<sub>2</sub> content, the crystallite size of the mixed oxide decreased. The specific conditions of cathodic deposition may cause specific distribution and coordination of the Ce and Zr ions in the deposited thin films. To study this effect we used the concept of Auger parameter ( $\alpha$ ) since in mixed oxides the Auger transitions involving only core level electrons can be used to interpret changes of  $\alpha$  with composition in terms of changes in ground-state electronic structure, e.g. electron transfer and hybridization between different valence orbitals. This information can make an important contribution to the understanding of mixed-oxide formation at the electronic structure level.

## Screen Printed Perovskite Films for SOFC: Investigation of the Microstructure and Properties

Nadezhda Brashkova, Liliyana Pavlova and Vladimir Kozhukharov

University of Chemical Technology and Metallurgy, 8 Kliment Okhridski blvd., Sofia 1756, Bulgaria. *E-mail:* brashkova@uctm.edu

Materials with perovskite structure can find many applications for instance as active layers in variety of solid-state ionic devices, such as solid oxide fuel cells for energy conversion, chemical sensors for monitoring and control of combustion, and membranes for oxygen separation. [1] Perovskite films can be dense or porous, thin or thick and deposited on both dense and porous substrates in dependence on the specific application. Perovskite-type  $\text{La}_{1-x}\text{Sr}_x\text{Mn}(\text{Co}, \text{Fe})\text{O}_3$  [2] and perovskite-related  $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$  [3] materials as mixed conductors have attracted much attention due to their high ambipolar conductivity and excellent catalytic activity for oxygen reduction and evolution.

The aim of the present work is to investigate the influence of applied screen-printing method of synthesis and deposition on microstructure, some physical-mechanical and electrical properties of the obtained by screen printing perovskite films.

It was synthesized perovskite films with nominal composition  $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ ,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  and  $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$  (where  $x = 0,2; 0,4; 0,6; 0,8$ ) at temperatures from 900 to 1250 °C. [3.] The films produced were precisely analyzed by microelement analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and BET-adsorption. The results show well-defined perovskite phase with increasing of sintering temperature. A homogeneous microstructure and uniform grain size and pores distribution are observed. The films are characterized with thickness from 10 to 20  $\mu\text{m}$  and with specific electrical mixed electronic and ionic conductivity and catalytic properties. Screen-printing methods of deposition of perovskite films on ceramic substrates are appropriate for application as cathodes in Solid Oxide Fuel Cells.

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## Chemistry and Structure Investigation of $\text{La}(\text{Fe}_x\text{Co}_{1-x})\text{O}_3$ ( $x=0.6$ ) Synthesized by Low-Temperature Method

I. Carazeanu Popovici<sup>1</sup>, E. Chirila<sup>1</sup>, V. Ciupina<sup>2</sup>, V. Popescu<sup>1</sup> and G. Prodan<sup>2</sup>

<sup>1</sup>Ovidius University, Chemistry Department, 124 Mamaia Blvd. 900527 Constantza, Romania.

*Email:* icarazeanu@univ-ovidius.ro

<sup>2</sup>Ovidius University, Electron Microscopy Laboratory, 124 Mamaia Blvd. 900527 Constantza, Romania.

Considerable interest has been shown in perovskite – type oxides,  $\text{LnMO}_3$  with lanthanide elements (Ln) and transition metal (M), because these materials can be used in solid-oxide fuel (SOFCs) cells and catalysts and sensor materials for oxygen, humidity, alcohol and carbon monoxide. These perovskite – type oxides are conventionally prepared by solid-state reactions at high temperatures of the corresponding oxides. Several methods for low-temperature synthesis of perovskite – type oxide have been reported [1- 3].

In this paper nanometer-sized perovskite – type oxides  $\text{La}(\text{Fe}_x\text{Co}_{1-x})\text{O}_3$  particles were synthesized by the modified sol-gel method, from  $\text{La}(\text{NO}_3)_3$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  an ideal cation stoichiometry for  $\text{La}(\text{Fe}_x\text{Co}_{1-x})\text{O}_3$  perovskite. Ethylenediaminetetraacetic acid (EDTA) was used like chelating agent.

XRD and electron diffraction analysis was used to evaluate the purity and the phase composition of  $\text{La}(\text{Fe}_x\text{Co}_{1-x})\text{O}_3$  obtained after heating in the range of 600-800°C. Powder X-ray diffraction method using a Shimadzu XRD 6000 diffractometer with  $\text{CuK}_\alpha$  radiation carried out the phase analysis of the fired specimens.

For the electron microscopy the equipment was a Philips CM 120 ST operating at 100 kV and magnification maxim 1200000x. The resolution obtained in our cases was about 2Å. SAED images help us to identify the phase. Also the nano - crystals size distribution was study.

The formation of  $\text{La}(\text{Fe}_x\text{Co}_{1-x})\text{O}_3$  is complete at 600°C. The XRD analysis show the great intensity of specific interference of  $\text{La}(\text{Fe}_x\text{Co}_{1-x})\text{O}_3$  obtained by sol-gel method which proves the superiority of this method; the organic phase (component of the reaction mixture) has a double role: carrying agent of  $\text{La}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  ions and heat generation. These factors contribute to the early formation of  $\text{La}(\text{Fe}_x\text{Co}_{1-x})\text{O}_3$ . The HRTEM photographs reveal nanoparticles in the size range of 2 – 30 nm with mean diameter found at 10 nm.

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*Topic E*

**Size Effects in Supported Metal Catalysts**



## The Importance of Nuclearity in the Design and Properties of Catalysis-Related Nanomaterials

Michel Che

Université Pierre et Marie Curie&Institut Universitaire de France, Paris, France.

*E-mail:* che@ccr.jussieu.fr

Nearly half a century ago, Richard Feynman gave the first talk on nanotechnology, entitled *There's Plenty of Room at the Bottom* [1], in which he stated: “*What I want to talk about is the problem of manipulating and controlling things on a small scale*“. At the end of his talk, he considered the possibility of direct manipulation of individual atoms as a powerful form of synthetic chemistry to construct larger molecules, which has been coined as the “bottom up“ approach, in opposition to the “top down“ approach consisting in the always more demanding miniaturization of devices.

Following the first approach, molecular chemists have perfected the art of producing molecules of ever increasing complexity using sophisticated multistep or even better one-pot syntheses, starting from molecular bricks and employing self-assembling rules and/or biomimetic processes. At the other extreme, following the “top down“ approach, engineers of microelectronics have succeeded in fabricating the remarkable integrated circuits that control the world’s most powerful miniaturized computers. In between, there is a no man’s land, an uncharted world, coined “nanoworld“, in the size domain going from say a few nm to several 100 nm, which can not be easily reached by either molecular wires-related “covalent“ chemists or three-dimensional matter “microlithograph“ experts.

There are many examples where materials see a drastic change in their physical properties, from discrete to collective, for a certain critical size. This critical size concept has been expanded and may strongly differ depending on the property which is being studied. The latter may be physical, *e.g.*, the colour and its associated quantum size effect [2], but also chemical, *e.g.*, the catalytic hydrogenolysis of saturated hydrocarbons, and the associated ensemble of atoms required at the catalyst surface to promote this reaction [3], or simply geometrical (as size-dependent property), *e.g.*, pores taken as molecular nanoreactors and as a way to control the molecular traffic in mesoporous materials, such as MCM-41 [4].

This lecture will focus mainly on catalysts preparation and show that this field of research happens to be located at the crossroads of the bottom up and top down approaches.

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## Temperature Dependent Structural Variation in Alumina Supported Rh Nanoparticles: in what way is it reactively deterministic?

Mark A. Newton<sup>1</sup>, Andrew J. Dent<sup>2</sup>, Steven G. Fiddy<sup>3</sup>, Bhrat Jyoti<sup>4</sup> and John Evans<sup>2,4</sup>

<sup>1</sup>The European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP220, 38043 Grenoble, France. *E-mail:* newton@esrf.fr

<sup>2</sup>Diamond Light Source, Chilton, Oxford, United Kingdom.

<sup>3</sup>Synchrotron Radiation Source, Daresbury, Warrington, United Kingdom.

<sup>4</sup>School of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, United Kingdom.

Dispersive Extended X-ray absorption fine structure (EDE) measurements made on reduced 5wt% Rh/Al<sub>2</sub>O<sub>3</sub> catalysts indicates that above between 473K and 573K the structure of the supported nanoparticles appears to change considerably; the atomicity of the Rh particle appears to decrease from ca. 30-50 atoms (T < 450K) to ca 10-15 (T = 573K). This change in structure of the supported nanoparticles can be directly correlated to the quantitative kinetics of reduction oxidised Rh particles,<sup>1</sup> and the net selectivity toward N<sub>2</sub> formation derived from the interaction of reduced Rh particles with NO) over a 60 second period. The implications of these, and other, observations made using synchronous, energy dispersive EXAFS and /DRIFTS spectroscopies,<sup>2</sup> will be discussed.

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## Charging/Discharging of Metallic Nanoparticles as Revealed by XPS

Sefik Suzer

Bilkent University, Chemistry Department and the Laboratory for Advanced Functional Materials, 06800 Ankara, Turkey. *E-mail*: suzer@fen.bilkent.edu.tr

By recording the XPS spectra while applying external voltage stress to the sample rod we can control the extent of charging developed on gold nanoparticles deposited on a copper substrate, both in a steady-state and also in a time-resolved fashion. The charging manifests itself as a shift in the measured binding energy of the corresponding XPS peak. Whereas, the bare gold nanoparticles exhibit no measurable binding energy shift in the Au4f peaks, both the Au4f and the Si2p peaks exhibit significant and highly correlated (in time and magnitude) shifts in the case of gold(core)/silica(shell) nanoparticles. Using the shift in the Au4f peaks, the capacitance of the 15 nm gold(core)/6 nm silica(shell) nanoparticle/nanocapacitor is estimated as 60 aF. It is further estimated that, in the fully charged situation, only 1 out of 1000 silicon dioxide units in the shell carries a positive charge during our XPS analysis. Our simple method of controlling the charging, by application of external voltage stress during XPS analysis, enables us to *detect*, *locate*, and *quantify* the charges developed on surface structures in a totally non-contact fashion.

## **X-ray Induced Reduction of Au and Pt Ions on Silicon Substrates and Production of Nanoclusters**

Eda Ozkaraoglu, Ilknur Tunc and Sefik Suzer

Bilkent University, Chemistry Department and the Laboratory for Advanced Functional Materials, 06800 Ankara, Turkey. *E-mail*: suzer@fen.bilkent.edu.tr

Prolonged exposure to x-rays of  $\text{HAuCl}_4$ ,  $\text{PtCl}_4$  and their mixtures, deposited from an aqueous solution on to a silicon substrate, causes chemical reduction of the metal ions to their metallic states. The corresponding oxidation reaction is conversion of chloride ions to chlorine. The resultant metal atoms aggregate to form metallic/bimetallic nanoclusters as evidenced from their XPS chemical shifts. Hence, x-rays are usable for in-situ nanoparticle production or for direct-writing applications on silicon substrates.

## Size-Dependent Effects in Supported Metal Catalysts for Liquid-Phase Hydrogenation Reactions

Joaquim Luís Faria<sup>1</sup>, Bruno F. Machado<sup>1</sup> and Helder T. Gomes<sup>1,2</sup>

<sup>1</sup>Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Portugal. *E-mail*: jlfaria@fe.up.pt

<sup>2</sup>Departamento de Tecnologia Química, Escola Superior de Tecnologia e de Gestão do Instituto Politécnico de Bragança, Portugal.

Environmental awareness is pushing the development of more efficient and more selective heterogeneous catalysts for the production of fine chemicals and pharmaceuticals. The goal is to reduce the number of by-products and the consumption of hazardous solvents, making the processes efficient at molecular level. Heterogeneous catalysts can be tailored to specific needs, are easier to handle and lead to less amounts of waste chemicals in a given process. As preparation method, photochemical deposition of noble metals in different supports is gaining importance due to its simplicity and advantages. Its main advantage is the ability of spreading very effectively the metal throughout the support, leading to very high dispersions, resulting in higher molecular control, with a positive effect on both activity and selectivity. Hydrogenation of the carbonyl function in  $\alpha,\beta$ -unsaturated olefins still attracts too much attention due to the importance of the unsaturated alcohol as intermediate in many synthetic routes [1]. The concepts of chemoselectivity and diastereoselectivity are extremely important issues in steroid hydrogenation.

Noble metal catalysts (Pt and Ir) supported on titania, with different loads (1 and 5%wt) were prepared by liquid phase photodeposition of the appropriate precursors. Calcination (under N<sub>2</sub>) and reduction (H<sub>2</sub>) at various temperatures provided materials with variable particle sizes at the nanometer scale. In order to explore the possibility of a metal-support interaction two types of titania were used: Degussa P25 (crystal mean diameter of 30 nm) and a sample of TiO<sub>2</sub> prepared by a modified acid-catalyzed sol-gel method from alkoxide precursors (crystal mean diameter of 8 nm). These parameters will be discussed in terms of the performance of the catalytic materials in the hydrogenation of cinnamaldehyde. As a representative example, under laboratory conditions the catalyst Pt/TiO<sub>2</sub> (5%) (N<sub>2</sub> calcination at 773 K followed by H<sub>2</sub> reduction at the same temperature) revealed a maximum selectivity to the unsaturated cinnamyl alcohol of 64% at 79% conversion, against 26% maximum selectivity at 29% conversion under similar conditions for the untreated catalyst. Preliminary tests in steroid selective hydrogenation were also extremely promising.

In addition to the above reported, similar results were found for Ir supported catalysts, leading to the conclusion that by very simple photodeposition method catalysts can be prepared, which are very selective for carbonyl hydrogenation.

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## Synthesis of Ni-Nanocomposites as New Precursors for Supported Metal Catalysts

Dessislava Kostadinova<sup>1,2</sup>, Corine Gérardin<sup>1</sup>, Nicolas Sanson<sup>1</sup>, Didier Tichit<sup>1</sup>  
and Iovka Dragieva<sup>2</sup>

<sup>1</sup>Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique  
UMR 5618 CNRS ENSCM, 8 rue Ecole Normale, 34296 Montpellier cedex 5, France.

<sup>2</sup>Institut for Electrochemistry and Energy Systems, Bulgarian Academy of Sciences,  
10 Acad.G.Bonchev Str.1113 Sofia, Bulgaria. *E-mail*: [dessie\\_kostadinova@yahoo.fr](mailto:dessie_kostadinova@yahoo.fr)

It is known that the catalytic activity of supported metal catalysts is related to the dispersion degree of the metal on the support. The aim of the present work is the preparation of supported metal catalysts with tuneable properties, ie. control of the size and number of metal Ni particles, starting from new nanocomposite precursors. The support is Mg(Al)O mixed oxide, which is obtained by calcination of a Mg/Al layered double hydroxide precursor.

The first step is the preparation of the host layered structure, in which specific metal precursors will be intercalated by anion exchange route in a second step. The host LDH structure (Mg/Al=2 pH=10) was prepared with different charge compensating anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, terephthalate) in the interlayered space.

The second step consists in preparing Ni-colloids, whose charge and size are finely controlled so that they present the right characteristics to be intercalated in the LDH interlayer space. The Ni colloids were prepared by controlled Ni<sup>2+</sup> hydroxylation in the presence of complexing agents (citrate ions).

The next step of the present work is the intercalation of the negatively-charged Ni colloids in the LDH structure, leading to Ni-nanocomposites with the best dispersion and size and number control of the Ni entities in the host structures. The Ni-nanocomposites have then been reduced by H<sub>2</sub> at high temperature for obtaining the active Ni<sup>0</sup> ensembles. Characterization of the materials has been made by the following methods: XRD, TEM, BET and chemical analysis. The results of this work show a good control of the number and size of Ni<sup>0</sup> nanoparticles.

In the future, the catalytic behaviour of the present supported metal catalysts will be investigated in selective hydrogenation reactions.

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## Manganese Oxide Doped Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts for n-hexane Oxidation. Effect of Pt Crystallite Size

Boško Grbic<sup>1</sup>, Nenad Radic<sup>1</sup>, Plamen Stefanov<sup>2</sup>, Dimitar Stoychev<sup>3</sup> and Tsvetana Marinova<sup>2</sup>

<sup>1</sup>ICTM, Department of Catalysis and Chemical Engineering, 11000 Belgrade, Serbia and Montenegro. *E-mail*: bgrbic@nanosys.ihtm.bg.ac.yu

<sup>2</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria.

<sup>3</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria.

Precious metal based catalysts for VOCs removal are frequently doped with base metal in order to decrease noble metal content or to improve the catalytic activity. Among the transition metal oxides, Mn oxides are the most studied due to their low volatility and high activity. Our previous investigation of the doping effect of low loadings of MnO<sub>x</sub> on the catalytic activity of highly dispersed Pt on Al<sub>2</sub>O<sub>3</sub> (mean Pt crystallite size of 1 nm) have shown that the Pt-Mn catalysts exhibit a better light-off characteristic than does the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for n-hexane oxidation [1]. Improved performances of Mn doped Pt catalysts for n-hexane oxidation is ascribed to the synergetic effect between Mn and Pt, i.e. existence of Pt oxide-like species. These kinds of Pt-Mn active centres change the properties of adsorbed oxygen.

Within this work, we have created large Pt crystallite size with mean Pt diameter of 15 nm, under controlled thermal treatment. The manganese is deposited by the same procedure as in the case of catalyst with small Pt crystallite size [1]. The catalysts samples were characterized by Scanning electron microscopy (SEM), X-ray photoelectron spectrum (XPS) and selective CO chemisorption. The catalysts were tested in the oxidation of n-hexane in air.

Comparison between large and small Pt crystallites (1 and 15 nm) doped with manganese have been made and discussed.

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## Complete Benzene Oxidation on Co and Co-Pt Catalysts: Effect of the Particle Size and Support

Silvia Todorova<sup>1</sup>, Georgi Kadinov<sup>1</sup>, Krasimir Tenchev<sup>1</sup>,  
Yuri Kalvachev<sup>2</sup> and Vladislav Kostov-Kytin<sup>2</sup>

<sup>1</sup>Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 11, 1113 Sofia, Bulgaria. *E-mail*: todorova@ic.bas.bg

<sup>2</sup>Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Sciences Acad. G. Bonchev St., Block 107, 1113 Sofia, Bulgaria.

Cobalt oxide is reported to be quite promising among the metal oxides used for preparation of supported catalysts for the removal of VOC. Platinum has widely been used in complete hydrocarbon oxidation, especially for aromatic hydrocarbons due to its high activity and stability. Even though cheaper, cobalt taken alone is not so active in reactions of complete VOC oxidation and the addition of Pt may enhance the catalytic activity by increasing the reducibility of Co oxide. The active phase dispersion in supported catalysts is known to control catalytic activity.

The aim of the present work is the preparation of supported cobalt and Co-Pt samples with different particle size and to establish the influence of the cobalt oxide dispersion and the type of support on and catalytic activity in the reaction of complete benzene oxidation. SiO<sub>2</sub> and synthetic kenyaite (layered silicates, named Ken) were used as supports. Co was introduced by ammonia method (samples named AM) or impregnation (samples denoted as I) in order to obtain about 7 wt% Co. Pt was deposited by impregnation in order to obtain 0.15 wt% Pt. The catalysts were characterized by elemental analysis, XRD, XPS and TPR.

XRD patterns and TPR profiles show that the ammonia method of preparation leads to the formation of finely dispersed Co<sub>3</sub>O<sub>4</sub> (particle size about 4-5 nm) on both supports. The difficult for reduction cobalt silicate supported phases, besides Co<sub>3</sub>O<sub>4</sub>, are formed mostly on the SiO<sub>2</sub>. The Co<sub>3</sub>O<sub>4</sub> particle size of the impregnated samples is about 20 nm. Co/SiO<sub>2</sub>-AM exhibits the lowest catalytic activity, which can be related to the fact that on SiO<sub>2</sub> cobalt is mostly in the form of difficult for reduction cobalt silicates. It is well known that the transient metal oxides operate in total oxidation of hydrocarbons by a redox type mechanism, according to which the metal oxides are regenerated by the oxygen-containing gaseous phase. When kenyaite is used as support, the sample Co/Ken-AM is more active than Co/Ken-I. The better performance of the former sample is due to finely dispersed and easily reducible Co<sub>3</sub>O<sub>4</sub>.

Addition of Pt improves the combustion activity and the promoting effect is more evident for the impregnated sample. This result can be explained by synergy effect of cobalt oxide species and Pt. The less promoting effect of Pt on the catalytic activity of Co+Pt/Ken-AM can be attributed to a strong interaction between Co oxide phase and Pt during the preparation of the catalyst.

## Effects of Morphology and Cesium Promotion over Silver Nanoparticles Catalysts in the Styrene Epoxidation

R.J. Chimentão<sup>1</sup>, F. Medina<sup>1</sup>, J.L.G. Fierro<sup>2</sup>, J.E. Sueiras<sup>1</sup>, Y. Cesteros<sup>1</sup> and P. Salagre<sup>1</sup>

<sup>1</sup>Departament d'Enginyeria Química, Universitat Rovira i Virgili, 43007 Tarragona, Spain.

*E-mail:* [rchiment@urv.net](mailto:rchiment@urv.net)

<sup>2</sup>Instituto de Catalisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain.

Direct gas phase partial oxidation of olefins by molecular oxygen to epoxides is long considered one of the most important reactions in commercial catalysis [1]. Silver is considered almost the unique effective catalyst for the heterogeneous epoxidation [2]. The synthesis of controlled shapes of silver nanoparticles can open a new avenue in the study of selective oxidation reactions.

Silver nanowires catalysts were synthesized via polyol process [3]. The nanowires had a mean diameter of 150 nm. The support employed was  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. For comparison silver catalysts were also prepared by wetness impregnation. Irregularly shaped silver particles were observed in the sample prepared by impregnation. Epoxidation of styrene by molecular oxygen was studied over the silver catalysts. Styrene oxide (SO) and phenylacetaldehyde (Phe) were the main products. The effect of the reaction temperature, Cs promotion and O<sub>2</sub>:C<sub>8</sub>H<sub>8</sub> molar ratio on the catalytic epoxidation was also investigated. Low reaction temperatures or high O<sub>2</sub>:C<sub>8</sub>H<sub>8</sub> ratios improved the selectivity to SO. Silver nanowires catalysts showed superior catalytic activity compared to those prepared by impregnation method. The catalytic activity showed a maximum performance for silver nanowires promoted with 0.25 wt% of Cs. Temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) were employed to detect the presence of different species of oxygen on the catalyst. The samples were also characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

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## Size-Dependent Effects in Series of Supported Catalytic Samples Fe and Fe-Me (Me=Pt or Pd)

Zara Cherkezova-Zheleva, Maya Shopska, Gias Gouliev, Ivan Mitov,  
Georgi Kadinov and Lachezar Petrov

Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.  
*E-mail: zzhel@ic.bas.bg*

A series of catalytic samples Fe and Fe-Me (Me=Pt or Pd) supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> (anatase) or diatomite were prepared by the incipient wetness impregnation method. The metal loading was 8 wt.% Fe and 0.7 wt.% noble metal. The preparation conditions of all studied samples were identical. The obtained samples were studied at different steps of their preparation and catalytic tests. A set of physicochemical methods – XRD, Moessbauer spectroscopy, XPS, SEM, TEM, BET method was used for the sample characterization. The catalytic activity of the samples was tested in the reaction of complete oxidation of C<sub>6</sub>H<sub>6</sub>.

The study data showed that the preparation procedure resulted in the formation of octahedrally coordinated high spin Fe<sup>3+</sup> ions in ultradisperse hematite-like particles supported on the carrier. The superparamagnetic behavior of all Fe oxide particles, as prepared as well as the core-shell ratio of the surface to the bulk iron ions ~ 1:1, showed that the particle size is about 3-4 nm. The noble metal particle size in bimetallic samples was about 1-2 nm.

Depending on the used support and the presence of noble metal in active phase, the superparamagnetic behavior of supported iron oxide phase was preserved or changed. In the latter case the iron oxide particle size partially increased up to 10-15 nm and a collective magnetic excitation effect was observed in the samples. There were no data on noble metal agglomeration during treatment and catalytic tests. Bulk samples of mechanical mixture with the same composition are included in the present study for comparison.

The size-dependent effect of physicochemical properties and catalytic behaviour of the investigated supported samples was observed in the course of this study.

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## Oxidation State of Gold on Titania after Various Pretreatments

Hristo Klimev<sup>1</sup>, Katja Fajerwerg<sup>2</sup>, Kristina Chakarova<sup>1</sup>, Laurent Delanoy<sup>2</sup>, Catherine Louis<sup>2</sup>  
and Konstantin Hadjiivanov<sup>1</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: kih@svr.igic.bas.bg

<sup>2</sup>Laboratoire de Réactivité de Surface, Université P. et M. Curie, Paris, France.

Metal gold nanoparticles are known to form easily under various thermal treatments (air, hydrogen, neutral gas), and an important issue is to know if gold oxidation state may however vary to some extent. For that, an FTIR study of CO adsorption at low temperature (100 K) was performed on a 4.0 wt % Au/TiO<sub>2</sub> sample prepared by deposition-precipitation.

The sample pellet was first activated under O<sub>2</sub> (13.3 kPa) at 673 K and subsequently evacuated at 673 K. CO adsorption led to carbonyls bands formed with the support and of one band at 2106 cm<sup>-1</sup> (assigned to Au<sup>0</sup>-CO species) with a shoulder at 2131 cm<sup>-1</sup> (for its assignment see below). The 2106 cm<sup>-1</sup> band decreased in intensity during evacuation at 100 K and is gradually shifted to 2125 cm<sup>-1</sup>. The shoulder was more resistant towards evacuation.

The sample was then heated under O<sub>2</sub> (4 kPa) at 373 K and evacuated at 373 K. Subsequent CO adsorption revealed an intense band at 2136 cm<sup>-1</sup> with a weak Au<sup>0</sup>-CO shoulder at 2106 cm<sup>-1</sup>. When the oxidation was carried out at 673 K (followed by evacuation at 573 K), only the band at 2136 cm<sup>-1</sup> was detected. The position and the stability of the 2136 cm<sup>-1</sup> band are intermediate between those of the bands typical of Au<sup>0</sup>-CO species and Au<sup>+</sup>-CO carbonyls formed on isolated Au<sup>+</sup> sites (2176 cm<sup>-1</sup>). Therefore, we assign it to Au<sup>δ+</sup>-CO species. We propose that the Au<sup>δ+</sup> sites are gold(I) cations located on the surface of the metal gold particles and transferring positive charge to the metal particle bulk.

Then the sample was oxidized by a NO (1,33 kPa) + O<sub>2</sub> (2.66 kPa) mixture at 673 K, and evacuated at 573 K. CO adsorption revealed an Au<sup>δ+</sup>-CO band at 2155 cm<sup>-1</sup>. The higher position of the band is attributed to a more effective oxidation of the surface of the gold particles. This probably leads, due to competition, to a less efficient transfer of the positive charge. A similar oxidation procedure with an 1 wt % Au/TiO<sub>2</sub> sample (characterized by smaller metal particles) has led to appearance of isolated Au<sup>+</sup> species (respective carbonyl band at 2176 cm<sup>-1</sup>). This difference demonstrates an easier oxidation of smaller metal gold particles.

## Effect of Ceria Addition on the Particle Size and Properties of Alumina-Supported Gold

Miguel A. Centeno<sup>1</sup>, Hristo Klimev<sup>2</sup>, Tz. Venkov<sup>2</sup>, Jose A. Odriozola<sup>1</sup> and Konstantin Hadjiivanov<sup>2</sup>

<sup>1</sup>Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, Avda Americo Vespuccio s/n, 41092 Sevilla, Spain.

<sup>2</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria. *E-mail*: kih@svr.igic.bas.bg

The interest in gold catalysts increased enormously during the last years. This was provoked by the discovery about the high activity of supported gold in low temperature CO oxidation. However, only small metal gold particles are active in this reaction. In the present work we report the promotion effect of ceria on the properties of Au/Al<sub>2</sub>O<sub>3</sub> catalysts.

Two samples, Au/Al<sub>2</sub>O<sub>3</sub> and Au/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, were prepared by deposition-precipitation and characterized by different techniques (XRD, TEM, FTIR spectroscopy of adsorbed CO and catalytic test). The Au/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample demonstrated a much higher catalytic activity in the CO oxidation reaction than did the Au/Al<sub>2</sub>O<sub>3</sub> sample. Combined XRD and TEM studies revealed that fresh samples contained no metallic gold. However, samples calcined at 773 K contained metal particles with an average size of 8.2 – 8.9 nm for the Au/Al<sub>2</sub>O<sub>3</sub> sample and 3.8 – 4.5 nm for Au/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample.

Only metal gold was detected by low-temperature CO adsorption on the calcined Au/Al<sub>2</sub>O<sub>3</sub> sample (carbonyl IR band at 2206 cm<sup>-1</sup>) while the calcined Au/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample, in addition to a negligible fraction of metal gold (carbonyl band at 2115 cm<sup>-1</sup>), contained positively charged gold sites (carbonyl band at 2143 cm<sup>-1</sup>). The latter are believed to be located on the metal particle surfaces. Thus, the results show that ceria addition to the alumina support leads to an enhancement of gold dispersion and keeps gold in a more oxidized state. Comparison with the catalytic results strongly supports the idea about the decisive role of oxidized gold sites in the CO oxidation reaction.

## Peculiarities in the W4f Photo-Emission Line Shape of NiW Catalysts Supported on Alumina

Georgi Tyuliev, Radostina Palcheva, Alla Spojakina, and Luchezar Petrov

Institute of Catalysis, Bulgarian Academy of Sciences, G.Bonchev Str., bl.11, 1113, Sofia,  
Bulgaria. *E-mail*: tyuliev@yahoo.com

XPS measurements of NiW /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have shown that the W4f<sub>7/2</sub> and W4f<sub>5/2</sub> peaks are considerably broader as compared to those of bulk WO<sub>3</sub> samples. In order to find an explanation of this, a more detailed study of the W4f line was performed after different sample treatments, i.e. sulfidation, re-oxidation by exposing to ambient air, ozone treatment and prolonged irradiation with X-rays in vacuum. The experiments led us to the assumption for the following reasons for W4f line broadening: (i) – for particles of size comparable with the mean free path of the photoelectrons (~ 3 - 5 nm), the signal coming from the bulk is comparable in intensity with that coming from the Ni-W-O /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> interface and most probably, the two structures have different binding energies. Due to limited resolution of our instrument, the two lines are not resolved and as a result the peaks appear broadened; (ii) – the partial reduction of W due to the X-ray irradiation could produce similar changes in the peak width, small oxide particles supported on a rigid material are more sensitive to the irradiation as compared to the bulk oxide; (iii) – particles of different size have different binding energy because of different charge and/or relaxation energy, as a result, assuming that on the surface of alumina there exist particles different in size, the resulting effect is again broadening of the peaks. All these possibilities were checked by different experiments. The extensive irradiation of WO<sub>3</sub> powder samples induces some partial reduction of W, resulting in some asymmetry at the low binding energy side, a feature not observed for the supported Ni-W-O particles. After sulfidation of the samples with H<sub>2</sub>S at 400°C for 1 h, the W4f peaks become narrower and the difference between their widths for WO<sub>3</sub> and catalysts under study becomes smaller. This observation can be explained with better screening of the W4f core hole by WS<sub>2</sub> matrix as compared to that of Ni-W-O oxide. In addition, the complex photo emission spectra after sulfidation can be reproduced with two components, one representing WS<sub>2</sub> bulk standard and the other component from a catalysts in calcined form. This means, that the H<sub>2</sub>S treatment does not change significantly the interface to bulk ratio of supported oxide particles. All this led us to the conclusion, that the randomly distributed oxide particles of different size is the reason for the W4f line broadening.

## Synthesis of Supported Nickel Particles with Pre-determined Size by Successive Grafting, Reduction and Passivation

Mihail Mihaylov, Elena Ivanova and Konstantin Hadjiivanov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: eivanova@svr.igic.bas.bg

Development of preparative methods ensuring effective control on the size of supported metal particles is very important for studying structure sensitive catalytic reactions. In this work we report the results of a new method, namely successive grafting and reduction (SGR), applied to the preparation of supported nickel catalysts. Nickel content in the samples was established by AAA and of metal particle sizes were determined by XRD, FMR and TEM.

FTIR study of adsorbed CO on Ni/TiO<sub>2</sub> showed that grafting of Ni<sup>2+</sup> ions on titania resulted in blocking of the specific sites on the support where the grafting proceeded. However, subsequent reduction led to formation of nickel particles and simultaneous liberation of blocked sites. This allowed performance of a subsequent grafting-reduction cycle which led to an increase in nickel content and metal particle size. However, in this case the reduction transformed the catalyst into a SMSI state, which hindered the studies of structure sensitive catalytic reactions.

For that reason, we studied the possibility to apply SGR to the synthesis of Ni/SiO<sub>2</sub> catalysts since SiO<sub>2</sub> is a non-reducible support. As the re-oxidation of metal nickel between the grafting-reduction cycles led to partial re-blocking of the initial active sites, we restricted this process by passivation (successive grafting, reduction and passivation, SGRP). The results showed that Ni/SiO<sub>2</sub> catalysts containing uniform nanosized nickel particles were obtained in all cases. Increase of the number of SGRP cycles (from 1 to 5 cycles) resulted in an increase in nickel concentration and nickel particle sizes (in the range of 4 – 6 nm).

The catalytic test on decomposition of methanol to CO and H<sub>2</sub> (taking place below 500 K) showed that the catalyst activity passed through a maximum with the nickel particle size increase whereas the activity per unit mass and TOF decreased. On the contrary, the catalysts manifested the same TOF in the methanation reaction (proceeding above 500 K). This showed the methanol decomposition to be a structure-sensitive reaction. Hence, the catalysts prepared by SGRP may be used in studies of structure-sensitive catalytic reactions.

## The Effect of the Precursor on the State of Iron Particles in Nanodiamond Supports

Momtchil Dimitrov<sup>1</sup>, Daniela Paneva<sup>2</sup>, Ljubomira Ivanova<sup>1</sup>, Tanya Tsoncheva<sup>1</sup>, Ivan Mitov<sup>2</sup>  
and Christo Minchev<sup>1</sup>

<sup>1</sup>Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: md2@abv.bg

<sup>2</sup>Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

Nanodiamonds have opened new prospects as a result of their unusual properties caused by the presence of very small ultradispersed diamond particles (2-10 nm) in them. The main advantage of these materials as supports are their intrinsic defect structure comprising large number of functional groups and their high specific surface area [1].

In the present work we study the state of supported iron particles on various nanodiamond materials. The aim is to gain information about the influence of the iron precursor and the nanodiamond support used on the overall state of iron. Furthermore, special attention is paid to its phase transformations occurring under various pretreatment media (argon and hydrogen) as well as under reductive catalytic medium.

Nanosized iron particles in nanodiamond materials containing different amounts of ultradispersed diamond were prepared using two types of iron precursors – organic (iron acetyl acetonate) and aqueous (iron nitrate). The various nanodiamond supports (250-550 m<sup>2</sup>/g) were obtained through different synthesis conditions and/or postsynthetic purification treatments [2]. The iron content in the samples is 6 % wt. All samples were characterized by N<sub>2</sub> physisorption, X-ray diffraction, Temperature programmed reduction and Moessbauer spectroscopy as described in [3]. The catalytic behaviour of the obtained composite materials in methanol decomposition to H<sub>2</sub>, CO and methane has been also studied [3].

The combined physicochemical and catalytic results show that the state of the supported iron oxide nanoparticles and their phase transformations are determined by several factors, including the nature of the iron precursor used and the amount of the ultradispersed diamond within the support. The catalytic behavior of the samples is affected by the initial state of iron oxide nanoparticles and their further phase transformations to magnetite and/or metallic iron under the various pretreatment and reductive catalytic media.

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*Topic F*

**Catalysts Activation & Deactivation Caused by  
Redispersion or Sintering**





## Regeneration of Supported Monometallic and Bimetallic Catalysts by Redispersion

James A. Anderson

Surface Chemistry and Catalysis Group, Department of Chemistry, University of Aberdeen, Aberdeen, AB24 3UE, Scotland, UK. *E-mail*: j.anderson@abdn.ac.uk

The concept of size-dependent material properties has become recognised as being increasingly important in many applications. High dispersion of a supported metal over an inorganic oxide support is a key feature in many applications in catalysis<sup>1</sup> and obtaining and maintaining the nano-dimensional metal particles are important in terms of maximising exposure of the metallic phase, presenting highly active, low coordinate metal atoms and maximising the metal support interface. The latter plays an important role in stabilising the metal particles against sintering however long term application at elevated temperatures inevitably leads to particle growth and loss of metal surface area. The lecture presented will look at processes leading to reversal of sintering (i.e redispersion) and its effects and will focus on the mechanism by which supported metals may be redispersed by oxychlorination. Examples will be drawn from areas such as reforming, where redispersion of metals forms an integral part of catalyst regeneration (along with coke burn-off). The nature of the redispersed phase in both oxychlorinated and reduced forms will be presented for both monometallic and bimetallic systems and the affect that redispersion has on the distribution of components will be highlighted for systems containing more than one metal. Further examples will include potential application in systems such as the three-way catalysts and here the role played by additional components within the support oxide (in this case the ceria-zirconia oxygen storage material) will feature in terms of providing alternative location for the redispersed metal components during oxychlorination

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## Intermediates in the Reaction of Methane with NO<sub>x</sub> Species Adsorbed on Pd-promoted Tungstated Zirconia

Ilknur Cayirtepe and Margarita Kantcheva

Laboratory for Advanced Functional Materials, Department of Chemistry, Bilkent University, 06800 Bilkent, Ankara, Turkey. *E-mail*: margi@fen.bilkent.edu.tr

The interaction of methane at various temperatures with NO<sub>x</sub> species formed by room temperature adsorption of NO/O<sub>2</sub> mixture on tungstated zirconia and palladium(II)-promoted tungstated zirconia is investigated using in situ FT-IR spectroscopy. Tetragonal tungstated zirconia (18.6 wt% WO<sub>3</sub>, denoted as WZ) containing mesoporous phase was prepared by coprecipitation of aqueous solutions of ZrO<sub>2</sub>Cl<sub>2</sub>·8H<sub>2</sub>O and ammonium metatungstate using polyvinyl alcohol as a template [1]. Palladium(II) ions (0.1 wt%) were deposited on the WZ support by impregnation with Pd(II) nitrate solution (sample notation Pd/WZ). The average crystallite size for both samples is 4.9 nm. Dispersed Pd(II) species are present in two different environments: (i) Pd<sup>2+</sup> ions, which have only Zr<sup>4+</sup> ions in their second coordination sphere and (ii) Pd<sup>2+</sup> ions, which are linked to both zirconium and tungsten ions via oxygen bridges.

In order to evaluate the ability of the WZ and Pd/WZ samples containing preadsorbed NO<sub>x</sub> species for methane activation and to propose reaction mechanism, the following experiments were performed: (i) “Blank NO<sub>x</sub>” experiment involving thermal transformation of the NO<sub>x</sub> species formed at room temperature by NO/O<sub>2</sub> coadsorption; (ii) “Blank CH<sub>4</sub>” experiment consisting of interaction of the activated samples with methane at elevated temperatures; (iii) “CH<sub>4</sub>-NO<sub>x</sub>” experiment monitoring the interaction of methane at various temperatures with the catalysts containing preadsorbed NO<sub>x</sub> compounds; (iv) investigation of the routes of transformation of nitromethane adsorbed on the catalysts, and (v) interaction of adsorbed formaldehyde with NO-precovered Pd/WZ catalyst.

The experimental results show that the methane interacts in a different way with the NO<sub>x</sub>-precovered WZ and Pd/WZ catalysts, although both materials in absence of adsorbed NO<sub>x</sub> species are able to activate the hydrocarbon at the same temperature (250<sup>0</sup>C). In the case of the WZ sample the surface nitrates suppress the oxidation of the hydrocarbon whereas on the NO<sub>x</sub>-precovered Pd/WZ catalyst in situ formation of nitromethane is observed.

Mechanism for the reduction of NO over the Pd/WZ catalyst is proposed, which involves a step of thermal decomposition of the nitromethane to adsorbed NO and formates through the intermediacy of cis-methyl nitrite. The adsorbed NO is reduced by the HCOO<sup>-</sup> species to N<sub>2</sub>.

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## Comparative Studies between Hydrophobic Catalysts Used in Isotopes Exchange

Anisoara Preda, Felicia Vasut, Claudia Pearsica and Sebastian Brad

National R & D Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Valcea.

*E-mail:* anisoara@icsi.ro, claudia@icsi.ro

The process for hydrogen isotopes separation presents a great importance for nuclear technology. Thus, there is an important preoccupation to find more efficient catalysts with a long operating time. In this paper, we present comparative studies between the physical and structural properties of hydrophobic catalysts. For the study of the isotope exchange water-hydrogen there were prepared the Pt/C/PTFE and Pt/SDB catalysts. These catalysts were manufactured by impregnation. For all the types of catalysts prepared there were determined the metal contain (active catalytically compound). There were determined physical and texture properties such as specific surface, pore volume and its distribution after pore radius. The properties were determined by isotherm absorption to liquid nitrogen temperature 77,8 K and through penetration with Hg. The specific surface was calculated according to B.E.T. equation; micropore volume and its distribution after the range of radius were calculated using the approximation of cylindrical pore according to mathematical model Barret-Joyner-Haleda and nitrogen absorption data. One of the most important aspects for the utilization of hydrophobic catalyst in such processes is the stability radiation and impurities. Model catalysts are important because they offer a better prospect of controlling variables such as surface topography and composition than do normal technical catalysts. Using such a model catalysts it is better controlled the contamination of the surface structure.

## **NO Adsorption on Alumina Supported Oxides of Copper, Manganese and Copper-Manganese Prepared by *in situ* Precipitation in Pores**

Ivanka Spasova and Mariana Khristova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: [ispasova@svr.igic.bas.bg](mailto:ispasova@svr.igic.bas.bg)

NO<sub>x</sub> has been considered as a pollutant which contributes to acid rain, urban smog, and stratospheric ozone depletion. With growing concern about environmental pollution continuing efforts have been made to improve NO<sub>x</sub> abatement technology, especially concerning air with low nitrogen oxides impurities. The adsorption method may possess number of advantages for fine NO cleanup, where the most important are: the possibility to decrease NO concentration to very low values, the possibility for application at low temperatures, and no use of additional reduction agents.

Three series of samples are prepared via *in situ* precipitation of corresponding hydroxides of copper, manganese and copper-manganese on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The objective is to shorten the preparation time by working without an aging step, using a short and controlled residence time in order to maintain a constant supersaturation level in the reactor and constant particle properties. Aqueous solutions of metal nitrates with different concentrations in water are precipitated with aqueous solutions of NaOH, followed by a proper thermal treatment. This method allows the precipitate to be uniformly distributed in the pores of the support. The samples have been characterized by adsorption methods, magnetic methods, electronic paramagnetic resonance (EPR). Transient response technique at room temperature and temperature-programmed desorption (TPD) have been applied for investigation of the NO adsorption ability of the samples. The influence of the concentration of the initial solution on the NO adsorption has been investigated.

The investigation has shown that the metal content in all supported samples is almost close. Such prepared samples are highly disperse-manganese and mixed oxides are X-ray amorphous and poor crystalline copper oxide for copper samples appears. All samples have specific surface areas not substantially less from the support surface area or even equal. The results have shown that the studied alumina supported oxides by precipitation manifest adsorption capacity towards NO. The best adsorption ability towards NO show supported mixed copper-manganese oxides. The most appropriate initial metal concentration for all samples is shown to be 4 g/100ml. These samples possess the most suitable texture for adsorption and catalysis, where narrow pores combined with transport pores such as mesopores are necessary. The precipitation method using solutions with varying content enables different phase formation and choice of the optimal composition. At the same time the porous texture is optimal with respect the adsorption process.

## Complete Oxidation of Benzene Using Mixed Oxides Type Catalysts Cu-Cr Supported on $\text{Al}_2\text{O}_3 + \text{SiO}_2$

V. Georgescu, G. Dobrescu, F. Papa and V. T. Popa

Institute of Physical Chemistry “I. G. Murgulescu”, Romanian Academy, Romania.

E-mail: frusu@icf.ro, vgeorgescu@icf.ro

Total oxidation of basic organic compounds for the depollution of industrial environments is an acute problem. Using rare metals catalysts for oxidation through heterogeneous catalysis turned out to be success full. However, the higher prices of these catalysts stimulated the searching other alternatives, one of them being the mixed oxides type catalysts with spinel structure, deposited on support. In this work a mixed oxide type catalyst of Cu-Cr supported on  $\text{Al}_2\text{O}_3 + 20\% \text{SiO}_2$  from the complex precursor with tartaric acid  $[\text{CrCu}_4\text{Ta}_6].5\text{H}_2\text{O}$  was prepared [1]. After calcinations at  $650^\circ\text{C}$ , a catalyst with spinel structure and specific surface of  $175 \text{ m}^2/\text{g}$  was obtained. The catalyst was characterized by Infrared Spectroscopy (IR), X-Ray diffraction (XRD), UV-VIS Spectroscopy (UV-VIS), thermoprogrammed reduction (TPR) and thermoprogrammed desorption (TPD) studies; the thermogravimetric analysis (TGA) evidenced the spinel phase  $\text{CuCr}_2\text{O}_4$  that is the active phase of the catalyst [2,3]. The catalyst has been used in the oxidation reaction of benzene in a laboratory installation with continuum flux; the reaction products were chromatographic analysed. A good activity and stability of the catalysts has been evidenced by testing different benzene concentrations in the reaction mixture and different spatial velocities [4]. The chemical reactor was designed to simulate the industrial total oxidation reactors with pre-heating of the reaction mixture. The chemical reaction was initiated in the catalyst thin layer and it is continued in the gaseous-phase, in the inner part of the reactor. The contribution of the homogeneous process to the total conversion  $X$ , is more important as the reaction temperature increases. Taking into account the space where the heterogeneous catalytic initiated reaction can be continued in gaseous-phase (homogeneous), the spatial velocities: heterogeneous  $s_1$  and homogeneous  $s_2$ , respectively, and the contact times:  $\tau_1$  and  $\tau_2$  are related by the following equation:  $s_1/s_2 = \tau_2/\tau_1 = 20$ . The chemical reactor can be modeled as a two series-bounded tubular reactors system: the first reactor is working as a differential reactor (at  $X \leq 0.1$ ) or as a integral reactor (at  $X > 0.1$ ); the second one, the un-catalytically reactor, is a integral reactor. These contributions have been evidenced by kinetic analysis using some simplifying assumptions. Also, the preliminary analysis of the oxidation results is based on the selection of the experimental domains where the assumption of the higher importance of the heterogeneous reaction versus the global process is valid. **Differential analysis.** The experimental results for lower conversions ( $X \leq 0.1$ ) were used to compute the apparent kinetic constants. The Arrhenius curves lead to computing of the activation energies. **Integral analysis.** The apparent kinetic constants corresponding to the integral reactor were computed using an Excel-based computer code from the  $F(n,X) - \tau_1$  curves. The conversion integral function  $F(n,X)$  was computed using the trapezium-method with a step of  $\Delta V = 0.001$ .

The values of the activation energies of the total oxidation of benzene, within the kinetic temperature domain, (where a weak variation of activation energy on reaction rate is observed) are in agreement with our results obtained from work function data.

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## Alumina Supported Copper and Ceria Oxides as Catalysts for Reduction of NO with CO

Bozhidar Ivanov<sup>1</sup>, Mariana Khristova<sup>1</sup> and Tony Spasov<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: hristova@svr.igic.bas.bg

<sup>2</sup>Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria.

The problem with decreasing the harmful emissions of nitrogen oxides in industrial gases or in motor vehicles is an important contemporary task in relation to the environmental protection and people health. Recently, the investigations on this topic increase because of the growing concern about ecological standards.

Alumina supported copper and ceria oxides were prepared, characterized and tested in NO-CO reaction. The samples investigated were prepared by impregnation of Al<sub>2</sub>O<sub>3</sub> with aqueous solutions of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>. The active phase deposition was carried out simultaneously or subsequently (first copper and then ceria). For comparison samples only with supported copper and ceria were prepared.

The catalysts were characterized by chemical analysis, XRD, SEM and BET-analysis. Morphological differences between the catalysts deposited by the two techniques were detected. More homogeneous distribution of the active phase was found in the case of the simultaneously deposited catalyst. A noticeable difference of the surface area of both samples was also observed.

The catalytic investigations were carried out in a flow apparatus in the temperature region 20-300°C and studied by transient response technique. The reaction between NO and CO proceeded to N<sub>2</sub> and CO<sub>2</sub> (N<sub>2</sub>O was not detected). It was established that the most active in comparison to others was the sample prepared by simultaneous impregnation of the two metals - CC1/Al<sub>2</sub>O<sub>3</sub>, practically at 200°C it possesses 100% conversion. The results from the TPD investigations showed the existence of desorption peaks for NO, CO and for CO<sub>2</sub> except the sample with supported Ce where peaks for CO and CO<sub>2</sub> missing. It was suggested that the low temperature (below 100°C) mechanism of NO-CO reaction includes formation of (NO.CO)\* which was the rate limiting step. At temperatures above 100°C the interaction proceeded by a redox mechanism.

The present investigations have shown that alumina supported copper and ceria oxides are active in the conversion of NO at low temperature.

## The Influence of Pt Oxide Formation and Pt Dispersion on the NO<sub>x</sub> storage functions of Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/BaO/Al<sub>2</sub>O<sub>3</sub> Catalysts

Angelina Mihaylova, Anton Naydenov and Plamen Stefanov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,  
1113 Sofia, Bulgaria. *E-mail*: angelina@svr.igic.bas.bg

The most promising approach to the reduction of NO<sub>x</sub> under lean-burn conditions is based on the concept of NO<sub>x</sub> storage-reduction (NSR), where the engine is operated in a mixed lean/rich operation mode [1]. Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalysts are widely used to reduce NO<sub>x</sub> from combustion engines operating under lean conditions. For efficient storage and reduction of NO<sub>x</sub>, the dispersion and oxidation state of platinum is of major importance [2].

In this work, NO<sub>x</sub> sorption ability of Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalysts was measured in flow reactor experiments. The lowering of the performances of NO<sub>x</sub>SR catalysts with time due to the hydrothermal treatment in reaction conditions was studied with XPS. It is suggested that the activity decrease is due to formation of platinum oxide, which is less active than metallic platinum. The XPS measurements showed also some difference in the oxidation state of Pt between the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/BaO/Al<sub>2</sub>O<sub>3</sub>. The Pt4d photoelectron spectra evidenced that there is much more PtO<sub>2</sub> formed on Pt/BaO/Al<sub>2</sub>O<sub>3</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub>. Most likely the reason for the lower platinum oxide formation on platinum supported on Al<sub>2</sub>O<sub>3</sub> is that the alumina surface is acidic and accordingly is more electrophilic which reduces the electron density on Pt. In the case of the alkaline BaO/Al<sub>2</sub>O<sub>3</sub> support there is a higher electron density on Pt, which results in a larger electron transfer to oxygen, thus more platinum oxide is formed.

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## Change of Textural Properties of Catalysts Induced by Long-Term Desulphurization Process

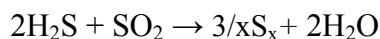
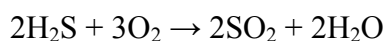
Goran Starčević<sup>1</sup> and Jugoslav Krstić<sup>2</sup>

<sup>1</sup>NIS-Oil Refinery, Spoljnosarčevačka bb, 26000 Pančevo, Serbia and Montenegro.

*E-mail:* ssova@sezampro.yu

<sup>2</sup>Institute of Chemistry Technology and Metallurgy, Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia and Montenegro.

The modified Claus process is widely used to recover elemental sulphur from the hydrogen sulphide present in gases from oil refineries, natural gas, coal gasification and other industries. This two-step process can be described as:



In the first step beside full oxidation of all hydrocarbons, one-third of the H<sub>2</sub>S is oxidised in low oxygen atmosphere producing H<sub>2</sub>S and SO<sub>2</sub> in the 2:1 ratio. In the second step most of residual H<sub>2</sub>S reacts with SO<sub>2</sub> in the gaseous phase and produces sulphur and water. Due to thermodynamic restrictions conversion is limited to 70% at this stage, and three to four catalytic stages are needed to obtain >95% conversion. In industrial conditions, remaining H<sub>2</sub>S is mixed with air and hot smoke and catalytically burned in burning chamber.

The most widely used Claus catalysts in sulphur recovery units are non-promoted spherical activated alumina together with alumina promoted with alkali metals. These catalysts allow H<sub>2</sub>S and SO<sub>2</sub> conversion to elemental sulphur and also the high efficiency conversion of more stable COS and CS<sub>2</sub>, present in low concentration. There are two main deactivation mechanisms of Claus catalysts. Filling up the pores by sulphur capillary condensation is one of mechanisms, while deposition of sulphur as sulphate salts is the second. Beside mentioned, deactivation can take place through changes in the textural properties of alumina obtained by heat treatments on temperatures above 550°C, especially in the burning chamber.

The aim of this paper was to define textural changes on catalyst during long-term exploitation in industrial facilities for desulphurization of waste gas in crude oil refining process. Four different commercially used catalysts were investigated before and after exploitation period by N<sub>2</sub> physisorption at -196°C, mercury intrusion porosimetry and SEM-EDS. The dramatic decrease of specific surface area, total pore volume has been established for all investigated catalysts as well as the change of shape of adsorption-desorption N<sub>2</sub> isotherm curves. These changes are specially emphasized with catalysts used in burning chamber. By correlation of sulphur content in investigated catalysts with change in their textural properties, the influence of particular deactivation mechanism has been defined.



## Synthesis and Characterization of Mo-Containing Micro/Mesoporous Materials

Nina G. Kostova<sup>1</sup>, Alla Spojakina<sup>1</sup>, Erika Godocikova<sup>2</sup> and Peter Balaz<sup>2</sup>

<sup>1</sup>Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

*E-mail:* nkostova@ic.bas.bg

<sup>2</sup>Institute of Geotechnics, Slovak Academy of Sciences, 0 43 53 Kosice, Slovakia.

The removal of sulfur and nitrogen atoms from oil fractions has become increasingly important as a result of the new legislation in many countries in 2010 that requires <20 ppm sulfur in gasoline and diesel. To reach these low levels of sulfur, much of the research over the past decade has aimed at improving the classic catalysts, which are based on molybdenum sulfide. There are many approaches to prepare better catalysts, such as changing the support, the active components and the preparation method. In the recent years, there has been interest in mesoporous materials like new supports for the HDS catalysts, due to the need to develop better catalysts, and availability of large number of new materials of high surface area and permit good dispersion of active components. Micro/mesoporous material was prepared via reaction of zeolite Beta seeds solution and mesoporous precursor solution under hydrothermal condition [1] and used as support in the present study.

The 12-molybdophosphoric heteropoly acid (HPMo) was used for preparation Mo-containing catalysts by two different methods: incipient impregnation of support with its aqueous solution and by the mechanochemical synthesis. The samples were treated by drying at 393 K and calcination at 623 K. The support and the catalysts were characterized by adsorption–desorption of nitrogen, XRD, TPR and IR spectroscopy. The alteration of catalytic activities due to support may arise as a result of important factors like variation in dispersion and morphology of active component and possible metal support interactions.

Physicochemical characterisation of the samples prepared show that both methods affect the phase composition and the particles size. The impregnation of the support with HPMo acid decreases the surface area and the Mo particles of the catalysts are high dispersed and consequently have a small particle size < 10 nm. Partial destruction of the components is observed after mechanochemical treatment. The aggregates are formed from the particles of different sizes. The samples were tested in the reaction of the thiophene hydrodesulfurization after their activation with H<sub>2</sub>S and mixture H<sub>2</sub>+H<sub>2</sub>S. The catalysts treated with H<sub>2</sub>S have the higher activity in comparison to that with H<sub>2</sub>+H<sub>2</sub>S. The activity of the mechanochemically synthesized samples is more stable than the activity of the impregnated samples.

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*Topic G*

**Novel High Surface Area Sorbents**



## The Importance of Developing Micropore Volume and Controlling Micropore Size Distribution to Improve Performance Applications of High Surface Activated Carbons

Angel Linares-Solano, Diego Cazorla-Amorós, Dolores Lozano-Castelló,  
María A. Lillo-Ródenas and Juan A. Macía-Agulló

Carbon Materials and Environment Research Group,  
(<http://www.ua.es/grupo/mcma/MCMA1/>), Inorganic Chemistry Department,  
University of Alicante, Spain. *E-mail*: [linares@ua.es](mailto:linares@ua.es)

Activated carbons, ACs, (powder, granular, fiber, monolith, etc.) are classical carbon materials that are deeply studied and used, since long time ago, due to their important properties and applications [1, 2]. Nevertheless, for classical applications (i.e. VOC removal [3]) as well as for emergent applications (i.e. gas, electricity and mechanical storages [4, 5]) a new generation of more powerful activated carbons is required.

This lecture will discuss the importance of controlling the different variables of the activation process for selecting the desired micropore volume (MPV) and the micropore size distribution (MPSD). In addition, the lecture will show the importance of doing a suitable characterization to improve the application performances of these high surface areas ACs.

After comparing different activation processes, we will conclude that activation by alkaline hydroxides [6, 7] permits a suitable control of the final properties of the ACs. Thus, it allows the preparation of ACs having high-developed surface area and MPV, concurrent with narrow MPSD (if required) which can hardly be prepared by other activation processes.

Improved performances of these well prepared ACs will be discussed using classical applications (VOC removal) as well as emergent ones (gas, energy and mechanical storage).

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## Heavy Metals Removal by Adsorption Using Diatomite

J. Pavlovic, S. Matic and Z. Kamberovic

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000  
Belgrade, Serbia and Montenegro. *E-mail*: smatic@tmf.bg.ac.yu

The need for safe and economical methods for heavy metals removal from contaminated waters has resulted in the implementation of alternative materials that may be used to reduce the metal content to the levels established by the legislative framework. The scope of this study was to choose an available adsorbent with porous structure and to evaluate the adsorption of copper, nickel, zinc, iron and manganese contained in groundwater. Diatomite has a large void volume and high surface area in addition to its highly porous structure, which is one of the main reasons for choosing it as a potential sorbent for heavy metals. It has also a unique combination of physical and chemical properties such as: low bulk density, low thermal conductivity, high melting point (about 1590 °C in pure state), whereas a very important parameter is its low cost.

In this paper characterization of diatomite obtained from the Kolubara region Serbia and Montenegro was done. The characterization of diatomite includes determination of type of diatomite using Scanning Electron Microscopy, determination of density using the pycnometer method, particle size distribution using the pipette method.

Treatment of adsorption was performed on contaminated groundwater with chemical composition similar to solution tailings natural leaching on location open pit "Veliki Krivelj" tailing pond, Bor's mining, Serbia and Montenegro.

The sample of diatomite (250g) was immersed in the wastewater (10L). That mixture put into laboratory glass (10L) was mixed with constant stirring rate at constant temperature. The samples were taken after different periods (30 min, 1h, 2h, 4h and 8h) and filtered. Chemical composition of filtrates was analyzed by Atomic Adsorption Spectroscopy (AAS). Obtained efficiency of heavy metals removal was very satisfied for nickel, iron, but a little bit lower for copper and manganese. On the other hand efficiency of zinc removal was low.

## The Porosity Evolution in Vitreous Carbon Obtained by Alkaline Resins Pyrogenation at Different Temperatures

Maria Paraschiv<sup>1</sup> and Valerica Slavescu<sup>2</sup>

<sup>1</sup>Ecole des Mines de Nantes, 44307, France.

<sup>2</sup>Metallurgical Research Institute, 060543, Bucharest, Romania.

*E-mail:* danslavescu@yahoo.co.uk

It is known that by pyrogenation at temperatures higher than 600 [°C] the synthetic resins (phenolic, phenol-formaldehyde or furan resins) generate vitreous carbon, a carbonaceous product with a characteristic structure, which involve the presence of crystallites with different sizes disperse in an amorphous matrix.

Such a material has a small density because of its large porosity. Prepared from pure resins, the vitreous carbon is a material with a high porosity, represented specially by closed pores.

The paper intent to show the influence of raw materials nature and their chemical composition regarding porosity of carbonaceous material generated by synthetic resins pyrogenation at 600, 800, 200 and 1450 [°C]. The experimental data show that the presence of a strong base, as KOH, in a large amount in resin composition, induce a specific evolution of porosity and structure of carbon matrix.

Three types of synthetic resins with modified chemical composition were studied: alkaline (pH=13), alcoholic solution (pH=3,5) and furan resin (pH=6,5).

The porosity and structural aspects of vitreous carbon matrix were investigated by mercury porosimetry (BET) and Scanning Electron Microscopy (SEM). The obtained structural information's allowed a rigorous analyze of material breaking during thermal treatment in order to establish the temperature influence on particles size and vitreous carbon behaviors.

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## Inorganic Compounds Effect on Adsorptive Properties of Carbonaceous Materials for Environmental Protection

Maria Paraschiv<sup>1</sup> and Valerica Slavescu<sup>2</sup>

<sup>1</sup>Ecole des Mines de Nantes, 44307, France.

<sup>2</sup>Metallurgical Research Institute, Bucharest, Romania. *E-mail*: danslavescu@yahoo.co.uk

The wastes from synthetic resins manufacturing represent a high problem because they are hazardous for environmental and for animals and human health. The destruction of such waste could be realized with their re-utilization. By pyrogenetic treatment the synthetic resins generate a carbonaceous material called vitreous carbon.

Vitreous carbon is a carbon product with a special structure, which takes it between graphitized carbon materials and those amorphous. There are three macroscopic structural types for vitreous carbon: solid (compact), reticulated (foam) and powder (sphere or polygonal particles) which are the same at microscopic level. This material has a small density because of its large porosity, represented by close and open pores.

Depending on precursors nature and technological parameters of pyrogenetic process, can be manufactured a vitreous carbon with open porosity. This specialty of vitreous carbons is useful in many applications (such as adsorption processes for waste water treatment). And when the raw material contains a high amount of inorganic compounds, the adsorptive properties could be significantly improved.

This paper presents the influence factors on adsorption capacity of the carbonaceous material generated by thermal treatment at 600 [°C] of different synthetic resins with modified composition. We state that all the usual adsorbents (chars) are obtained by thermal treatment at 600 [°C]. Also, depending on shape and particles size, the experimental data show that the adsorptive properties are different. A bi-phase liquid – solid system was studied, where the liquid phase was phenolic water with different initial phenol concentration. More like that, the experimental study allowed specifying some conclusions about the neutralization and turning to good of waste from preparing and proceeding synthetic resins manufactures.

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## Quantum Theoretical Study of Pyridine Adsorption on Fluorinated $\gamma$ -Alumina Surfaces. The Importance of the Size of Clusters Representing the Surface

Ljupčo Pejov<sup>1</sup>, Tomaž Skapin<sup>2</sup> and Vladimir M. Petruševski<sup>1</sup>

<sup>1</sup>Institute of Chemistry, Faculty of Science, Arhimedova 5, POBox 162, 1001 Skopje, Macedonia. *E-mail*: ljupcop@iunona.pmf.ukim.edu.mk

<sup>2</sup>Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia. *E-mail*: tomaz.skapin@ijs.si

Adsorption of pyridine on partially fluorinated  $\gamma$ -alumina surfaces was studied by quantum-chemical methods at Hartree-Fock (HF) and Density functional (DFT) levels of theory. The B3-LYP combination of exchange and correlation functionals was used in the hybrid HF-DFT approach employed, along with the 6-31++G(*d,p*) basis set for orbital expansion at both levels of theory. To simulate the solid partially fluorinated microcrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, a variety of electrically neutral finite atomic clusters were used (the geometries taken from the idealized spinel structure), representing the non-polar (100) and (110) planes exposed [1]. Besides the standard potential energy hypersurfaces (PESs) of the composite  $\gamma$ -Al<sub>2</sub>F<sub>x</sub>O<sub>y</sub>-pyridine clusters, also the counterpoise-corrected ones were explored at HF and DFT levels of theory. The counterpoise-corrected interaction energies between the exposed surfaces and the pyridine molecule were calculated, paying a special attention to the dependence of these quantities on the size of clusters representing the surface. Also, harmonic vibrational frequency shifts of pyridine  $\nu_8$  and  $\nu_{19}$  internal mode components upon adsorption on partially fluorinated clusters were calculated at both levels of theory and compared to the values corresponding to adsorption on non-fluorinated analogues. The cluster size dependencies were addressed in this case as well. Natural bond orbital (NBO) and Bader's atoms in molecules (AIM) analyses were employed to characterize the pyridine-surface interaction in the sense of its covalent or non-covalent character.

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## Porous Structure of Xylite Activated Carbon, the Key to High Performance Application

Georgeta Predeanu<sup>1</sup>, Silviu Lambescu<sup>1</sup>, Rohr Constantin<sup>1</sup>,  
Valerica Slăvescu<sup>1</sup> and Cornelia Panaitescu<sup>2</sup>

<sup>1</sup>Metallurgical Research Institute, 060543 Bucharest, Romania.

*E-mail:* gpredeanu@metal.icem.ro

<sup>2</sup>Faculty of Industrial Chemistry, University Politehnica Bucharest, Bucharest, Romania.

Based on the most important problems in the sorbents industry that are the rising of raw materials cost and increase of the activated carbon requirement, it becomes a necessity the utilization of novel materials similar to hardwood, available and valuable on long term.

The xylite-fossile wood - used for the activated carbon manufacturing in the Romanian prototype installation is determined as well by their physical-chemical and structural characteristics - the low content of mineral matter and the vegetal texture - which allow the obtaining of an adsorbent with a homogeneous porous structure that provides high performance application, comparable to the classical adsorbents. The porous structure depends to the greater extent on coal rank, grain size, carbonization and activation temperature and the reaction time during both processes. An important role is played by the porosity development as well as by the relationship between the particles microstructure and the type and dimensions of their microporosity versus the surface and adsorption capacities.

The use of xylite with an average ash content of 2.0-2.5% improved by mechanical preparation, grain size of 10-30 mm, pyrogenated in the rotary kiln at max. 500 °C and activated in a mixed steam and CO<sub>2</sub> flow at 950-1000 °C, allows the obtaining of an activated carbon with an increased adsorption capacity: iodine value over 700 mg/g, BET surface area over 600 m<sup>2</sup>/g, with a distribution of more than 80% of the pores with radii of 0-10Å, and an average radius of pores between 6.5-8.5%.

The paper provides important aspects regarding xylite activated carbon particular capacities in the process of primary wastewater purification by comparison with some sorts used usually for the removal of different inorganic and organic pollutants.

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## Clean Technologies for Energy Production From Coals

Violeta Niculescu, Elena David, Claudia Sisu, Marius Constantinescu and Felicia Bucura

National R&D Institute for Cryogenics and Isotope Technologies, Rm Valcea.

Uzinei Street, No. 4, PO BOX 4, Zip Code 1000, Rm. Valcea, ROMANIA.

*E-mail:* violeta@icsi.ro

Carbon dioxide is captured from exhaust gases by a selective separation using a cyclic adsorption process, wherein the adsorption step of the process is conducted by passing the gas mixture through an adsorption zone containing selective adsorbants such as carbon molecular sieve and zeolites. Physical adsorption system is operated in pressure swing adsorption (PSA) or temperature swing adsorption (TSA), wherein the gas is adsorbed and then the initial conditions are modified for to desorb the gas. The technical feasibility of the process is dictated by the adsorption step, whereas the desorption step controls its economic viability. Strong affinity of an adsorbent for captured CO<sub>2</sub> from exhaust gas is essential for an effective adsorption step and for this it is developed regenerable sorbents that have high selectivity, high regenerability and high adsorption capacity for CO<sub>2</sub>, properties critical for the success of the PSA/TSA process.

There will be used carbon molecular sieve made of ICSI, zeolites, laboratory plant that there is at ICSI, gas analyse devices (gas chromatograph, gas spectrometer, atomic adsorption spectrophotometer, etc.)

## **Experimental Study about Molecular Diffusion Coefficients of Gases on Carbon Molecular Sieves**

Claudia Sisu, V. Stanciu, Violeta Nicolescu, Felicia Bucura and Marius Constantinescu

National R&D Institute of Cryogenics and Isotopic Technologies – ICIT Rm. Valcea, Uzinei Street, no. 4, P.O. BOX 10, Rm. Valcea. *E-mail*: claudias@icsi.ro

The paper presents the results of recent experimental studies concerning the gases diffusion in samples of carbon molecular sieve (CMS) in the temperature range 25-150°C.

The effective diffusion coefficients were determined using a chromatographic method, proper description of the inter-granular diffusion.

The values of the effective diffusion coefficients were correlated with the porosity, pores-diameter and the influence of temperature.

## Synthesis and Characterization of Thiouracil Containing Carbon Sorbent

Paunka Vassileva, Penka Tsvetkova, Lako Lakov and Ognyan Peshev

Bulgarian Academy of Science, Institute of General and Inorganic Chemistry, Acad.  
G. Bonchev Str., Bl. 11, Sofia 1113. *E-mail*: adsor@igic.bas.bg

The problems of the environment protection are not new and still are considered worldwide as fundamental for mankind. Our efforts are directed towards the preparation of cheaper high quality activated carbons with desirable properties and their application to for purification of water. Activated carbon has been modified with various ligands in order to obtain a sorbent with a high selectivity towards metal ions.

The purpose of the present work is the modification of activated carbon with 2-hydroxy-2-mercaptopyrimidine (2-thiouracil) and the study of its sorption behavior towards the ions of some precious (Ag(I), Au(III), Pt(II) ) and heavy (Hg(II), Cu(II), Mn(II), Ni(II)) metals.

Synthesis of the sorbents is performed in three consecutive steps: (1) pyrolysis of the raw material in a stream of water vapour; (2) oxidation of activated carbon with HNO<sub>3</sub> (3) adsorption of thiouracil on the surface of activated carbon.

The characterization of the samples comprises determination of: surface area, pore volumes, the content of functional group with basic and acidic properties, IR spectra, sulfur content.

The sorption of metal ions is studied as a function of pH in the interval 1-7 and contact time (1-24 h). The static sorption capacities towards the metal ions are evaluated under optimum conditions at room temperature.

It is possible to achieve separate extraction of corresponding elements choosing appropriate pH value. The new sorbent containing thiouracil is appropriate for simultaneous preconcentration of the precious metals and mercury ions within a wide pH range. The modified activated carbon show a significantly higher capacity for Ag(I), Au(III), Pt(II) and Hg(II) as compared to the one.

## Silica-Containing Iron (III) Oxide Sorbents for Arsenic Removal

Penka Tsvetkova, Elena Russeva, Paunka Vassileva, Ivan Havezov, Lako Lakov,  
Ognyan Peshev and Emil Tsekulov

Bulgarian Academy of Science, Institute of General and Inorganic Chemistry,  
Acad. G. Bonchev Str., Bl. 11, Sofia 1113. *E-mail*: adsor@svr.igic.bas.bg

Two silica-based iron (III) oxide sorbents for arsenic removal with varying Fe:Si ratio are synthesized according to a classical sol-gel method involving tetraethyl orthosilicate (TEOS). The use of TEOS significantly simplifies the preparation procedure and reduces the time for synthesis. According to the sol-gel method TEOS was preliminarily hydrolyzed. The 30 % aqueous solution of iron (III) nitrate was added under constant stirring. The stirring was continued until the sol was completely homogenized. Then the mixture was gelatinized, dried at 100<sup>0</sup>C and finally heated at 200<sup>0</sup>C for 12 h. The resulting product was washed with distilled water (to remove the excess of iron nitrate) and until negative reaction for NO<sub>3</sub><sup>-</sup> (diphenylamine) and was repeatedly dried at 100<sup>0</sup>C.

The sorbents are characterized using X-ray fluorescence and X-ray diffraction analysis, Mössbauer and IR spectroscopy. Sorption of both arsenic (V) and arsenic(III) is studied as a function of pH in the interval pH=3-7 and time of contact from 30 to 90 min. Sorption of As(V) exceeds 70% for all studied pH values and time of contact, a maximum sorption (98-100%) being observed at pH 3-5. Sorption of As (III) varies from 60 to 100% with two maxima at pH 5 and 7. The reported adsorbents can be successfully applied to removal of both As (V) and As (V) from waters.

## **Effect of Supported Blood Plasma and its Subsequent Thermal Treatment on the Texture and the Chemical Nature of Activated Carbon Surface**

Radostin Nickolov<sup>1</sup>, Neli Stankova<sup>1</sup>, Lako Lakov<sup>1</sup> and Veselin Ivanov<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail*: radnick@svr.igic.bas.bg

<sup>2</sup>Department of Chemistry and Biochemistry, The Faculty of medicine, Tracian University, Stara Zagora, Bulgaria.

Recently, the great interest in activated carbons is determined by the possibility to modify their nano-porous textures and chemical surface natures.

Texture and chemical surface modifications of activated carbons can be performed by means of various techniques. Our preliminary experiments indicate, that blood plasma - water solutions can be used as agents for simultaneously modifications of the carbon porous textures and for the nitrogen enrichments of the carbon surfaces.

The effect of a such modification procedure on the nano-porous space and the chemical nature of the surface of activated carbons has been studied. The procedure includes: activated carbon impregnation with blood plasma/water solutions, lyophilization of supported products and subsequent thermal treatments of blood plasma /activated carbon materials in vacuum at different temperatures.

The pore texture parameters of both the initial and the modified carbon samples were calculated and compared in order to analyse the changes in the nano-porosity (i.e. in the micro- and mesopore sizes) occurred as a result of different treatments. Adsorption isotherms of the materials under study were determined using nitrogen as adsorptive at 77.4 K in a standard volumetric apparatus. It has been established that the blood plasma in activated carbon used and the subsequent thermal treatments do not lead to the considerable changes in the ranges of pore size. The degree of the nano-porosity formation depends on the initial activated carbon parameters – the higher the surface area of the larger pores, the larger changes in the initial activated carbon properties.

The surface composition of both the initial and the modified carbon samples was determined by XPS. The nitrogen content in the modified carbon samples is larger as compared to that in the initial carbon due probably to the destruction of blood products. The comparison of the relative concentrations of nitrogen in the bulk (determined by the Kjeldal method) with those at the surface shows that a considerably more amount of nitrogen is distributed at the surface in the case of samples treated at higher temperatures.





## **List of Participants**



## *List of Participants*

**Abrashev B.**

Institute of Electrochemistry and Energy Systems, BAS, 1113 Sofia, Bulgaria

**Aleksandrov L.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Aleksandrova A.**

Institute of Electrochemistry and Energy Systems, BAS, 1113 Sofia, Bulgaria

**Andonova St.**

Institute of Catalysis, BAS, 1113 Sofia, Bulgaria

**Andronesu Cr.**

Institute of Physical Chemistry "I. G. Murgulescu", RA, 060021 Bucharest, Romania

**Anderson J.**

University of Aberdeen Department of Chemistry, Aberdeen, AB24 3UE, Scotland, United Kingdom

**Atanasova G.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Avramova I.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Bachvarova-Nedelcheva A.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Banov B.**

Institute of Electrochemistry and Energy Systems, BAS, 1113 Sofia, Bulgaria

**Blaskov Vl.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Brashkova N.**

University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

**Buchkremer H. P.**

Institute for Materials and Processes in Energy Systems, Research Centre Juelich, D-52425 Juelich, Germany

**Bucura F.**

National Institute for Cryogenic and Isotopes Technologies, 1000 Rm. Valcea, Romania

**Cayirtepe I.**

Bilkent University, 06800 Bilkent, Ankara, Turkey

**Chakarova K.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Che M.**

Université Pierre et Marie Curie & Institut Universitaire de France, Paris, France

**Cherkezova-Zheleva Z.**

Institute of Catalysis, BAS, 1113 Sofia, Bulgaria

**Chimentao R.**

Universitat Rovira i Virgili, 43005 Tarragona, Spain

**Dimitriev Y.**

University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

**Dimitrov M.**

Institute of Organic Chemistry with Centre of Phytochemistry, BAS, 1113 Sofia, Bulgaria

**Dornheim M.**

Institute for Materials Research, 21502 Geeshacht, Germany

**Drenchev N.**

Faculty of Chemistry, University St. Kl. Ohridsky, 1126 Sofia, Bulgaria

**Drenchev B.**

Faculty of Chemistry, University St. Kl. Ohridsky, 1126 Sofia, Bulgaria

## *List of Participants*

**Faria J. L.**

Laboratory of Catalysis and Materials,  
University of Porto, Portugal

**Georgescu V.**

Institute of Physical Chemistry "I. G.  
Murgulescu", RA, 060021 Bucharest,  
Romania

**Grbic B.**

Institute of Chemistry, Technology and  
Metallurgy, 11001 Belgrade, Serbia and  
Montenegro

**Grigorova E.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Hadjiivanov K.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Iordanova R.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Ivanov B.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Ivanova E.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Ivanova S.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Ivanova Sv.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Jantschi L.**

Technical University of Cluj-Napoca,  
400020 Cluj-Napoca, Romania

**Kantcheva M.**

Bilkent University, 06800 Bilkent, Ankara,  
Turkey

**Kassabova N.**

University of Chemical Technology and  
Metallurgy, 1756 Sofia, Bulgaria

**Kelder E. M.**

Delft University of Technology, The  
Netherlands

**Khristov M.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Khristova M.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Khrussanova M.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Klimev H.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Koleva V.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Konova P.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Kostadinova D.**

Laboratoire de Matériaux catalytiques et  
catalyse en Chimie organique, France

**Kostova N.**

Institute of Catalysis, BAS, 1113 Sofia,  
Bulgaria

**Kovacheva A.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Kraleva E.**

Institute of Catalysis, BAS, 1113 Sofia,  
Bulgaria

## *List of Participants*

**Krapchanska M.**

University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

**Lambescu S.**

Metallurgical Research Institute, 060543 Bucharest, Romania

**Linares-Solano A.**

University of Alicante, Spain

**Machado B.**

Laboratory of Catalysis and Materials, University of Porto, Portugal

**Malovic L.**

Faculty of Forestry, 11030 Belgrade, Serbia and Montenegro

**Mancheva M.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Mandzhukova Ts.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Markova -Velichkova M.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Matic Sl.**

Faculty of Technology and Metallurgy, University of Belgrade, 11000 Belgrad, Serbia and Montenegro

**Mihaylova A.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Milanova M.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Mitov M.**

South-West University, 2700 Blagoevgrad, Bulgaria

**Naydenov A.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Nedjar Z.**

Engineering laboratory of Processes and Environment, Mentouri Constantine University, Algeria

**Nenad N.**

Institute of Chemistry, Technology and Metallurgy, 11001 Belgrade, Serbia and Montenegro

**Newton M.**

The European Synchrotron Radiation Facility, Grenoble, France

**Nickolov R.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Nickolov P.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Niculescu V. C.**

National Institute for Cryogenic and Isotopes Technologies, 1000 Rm. Valcea, Romania

**Nikolic G.**

Faculty of Technology, University of Niš, 16000 Leskovac, Serbia and Montenegro

**Palcheva R.**

Institute of Catalysis, BAS, 1113 Sofia, Bulgaria

**Panaitescu C.**

University Politehnica Bucharest, Faculty of Industrial Chemistry, Romania

**Paneva D.**

Institute of Catalysis, BAS, 1113 Sofia, Bulgaria

## *List of Participants*

**Pavlova L.**

University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

**Pejov L.**

Institute of Chemistry, St. Ciril and Methodius University, 1000 Skopje, Macedonia

**Pejova B.**

Institute of Chemistry, St. Ciril and Methodius University, 1000 Skopje, Macedonia

**Penkova A.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Petrov K.**

Institute for Electrochemistry and Energy Systems, BAS, 1113 Sofia, Bulgaria

**Popova E.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Popovici I. C.**

Chemistry Department, Ovidius University, 124 Constantza, Romania

**Preda A.**

National Institute for Cryogenic and Isotopes Technologies, 1000 Ramnicu Valcea, Romania

**Predeanu G.**

Metallurgical Research Institute 060543 Bucharest, Romania

**Radev I.**

Institute of Electrochemistry and Energy Systems, BAS, 1113 Sofia, Bulgaria

**Radev D.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Radic N.**

Institute of Chemistry, Technology and Metallurgy, 11001 Belgrade, Serbia and Montenegro

**Rohr C.**

Metallurgical Research Institute 060543 Bucharest, Romania

**Shinova E.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Sisu C.**

National Institute for Cryogenics and Isotopes Separation, 1000 Rm. Valcea, Romania

**Slavescu V.**

Metallurgical Research Institute 060543 Bucharest, Romania

**Solano A. L.**

Carbon Materials and Environment Research Group, Inorganic Chemistry Department, University of Alicante, Spain

**Spasov L.**

Institute of Catalysis, BAS, 1113 Sofia, Bulgaria

**Spasova I.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Spasov T.**

Faculty of Chemistry, University St. Kl.Ohridsky, 1126 Sofia, Bulgaria

**Stambolova I.**

Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

**Stankulov T.**

Institute of Electrochemistry and Energy systems, BAS, 1113 Sofia, Bulgaria

**Starcevic G.**

NIS-Oil Refinery, 26000 Pancevo, Serbia and Montenegro

## *List of Participants*

**Stefchev P.**

Central Laboratory of Solar Energy and  
New Energy Sources, 1784 Sofia, Bulgaria

**Stoyanova D.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Stoyanova R.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Šubrt J.**

Institute of Inorganic Chemistry, Academy  
of Sciences of the Czech Republic, 250 68  
Řež, Czech Republic

**Suzer S.**

Bilkent University, 06800 Bilkent, Ankara,  
Turkey

**Tenea E.**

Institute of Physical Chemistry "I. G.  
Murgulescu", RA, 060021 Bucharest,  
Romania

**Todorova S.**

Institute of Catalysis, BAS, 1113 Sofia,  
Bulgaria

**Tsanev Al.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Tyuliev G.**

Institute of Catalysis, BAS, 1113 Sofia,  
Bulgaria

**Tzvetkova P.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Uzunov I.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Uzunov K.**

University of Chemical Technology and  
Metallurgy, 1756 Sofia, Bulgaria

**Vasilchina H.**

Institute of Electrochemistry and Energy  
Systems, BAS, 1113 Sofia, Bulgaria

**Vassileva P.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Wagemans R.**

Debye Institute, Utrecht University, The  
Netherlands

**Yavari A.**

Institut National Polytechnique de  
Grenoble, 38402 France, Metropolitan

**Yoncheva M.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria

**Zhecheva E.**

Institute of General and Inorganic  
Chemistry, BAS, 1113 Sofia, Bulgaria





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