

RuMex-2013

**3-rd Russian-Mexican workshop on
Nanoparticles, Nanomaterials and
Nanoprocessing**

October 14-17, 2013, Saint Petersburg, Russia

<http://nmr.phys.spbu.ru/rumex>

Book of Abstracts

Acknowledgements

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General Information

Saint Petersburg State University continues the Russian-Mexican workshops on Nanoparticles, Nanomaterials and Nanoprocessing (RuMex). The third meeting will be opened on Monday, October 14, 2013 and will be closed on Thursday, October 17, 2013.

The goal of the meeting is to provide a platform to establish the comprehensive and all-round cooperation between Russian and Mexican scientists in the field of nanomaterial science and technology.

Scientists from Russia and Mexico are invited to participate in the Workshop with oral reports and poster presentations. A special poster session will be organized for young scientists (including students and PhD students). The official language of the Workshop is English.

Previous RuMex workshops:

- 1st RuMex, Saint Petersburg, Russia, 24-26 June 2012
- 2nd RuMex, Ensenada, Mexico, 5-8 November 2012

Location

The 3rd RuMex workshop will take place at the Petergof Campus of Saint Petersburg State University. Petergof (known as Petrodvorets from 1944 to 2009) is a charming town, former summer residence of Russian Tsars, a place famous for its parks, palaces and fountains. Petergof is located at the south coast of the gulf of Finland at a distance of 30 km from the center of Saint Petersburg.

Saint Petersburg is the cultural capital of Russia, world-famous for its architecture, monuments, museums, and art galleries as well as for its theatres and concert halls.

Main Topics

The third meeting RuMex-2013 will cover:

- Producing and Characterizations of Nanoparticles and Nanostructured Thin Films
- Nanomaterials Applications in Electronics, Spintronics and Photonics
- Nanomaterials Applications in Biotechnologies and Medicine
- Nanomaterials for Energy Applications
- Nanoparticles in Catalysis
- Russian-Mexican cooperation in the field of nanomaterial science and technology

Organizers

Russian partners:

- Saint Petersburg State University
<http://www.spbu.ru>
- Faculty of Physics
<http://www.phys.spbu.ru>
- Faculty of Chemistry
<http://www.chem.spbu.ru>

Mexican Partners:

- National Autonomous University of México
<http://www.unam.mx>
- Center of Nanoscience and Nanotechnology
<http://www.cnyn.unam.mx>

Organizing Committee

- Dr. Marina Shelyapina (St Petersburg)
- Dr. Olga Pestova (St Petersburg)
- Dr. Vladimir Matveev (St Petersburg)
- Prof. Maria Khripun (St Petersburg)
- Dr. Vitalii Petranovskii (Ensenada)

Contact

Dr. Marina Shelyapina

Department of Quantum Magnetic Phenomena

V. A. Fock Institute of Physics, St. Petersburg State University

Ulyanovskaya st., 1 Peterhof, 198504, Saint Petersburg, Russia

Phone: +7(812) 428 44 69; Fax: +7 (812) 428 72 40

e-mail: RuMex@nmr.phys.spbu.ru

URL: <http://nmr.phys.spbu.ru/RuMex>

Social program

The Organizing Committee of the RuMex-2013 welcomes you cordially in Saint Petersburg. We hope you will enjoy your staying in the city and participation in the Workshop both scientifically and socially.

Monday, October 14

19:00 — Welcome reception

The reception will take place in the *Blue Hall* of the Institute of Physics

Tuesday, October 15

19:00 — Conference dinner

The dinner will take place in the restaurant «Krapiva» («The Nettle») situated on the territory of «Shuvalovka». Its specialty is dishes of author and national cuisine. The Russian village «Shuvalovka», located near Petergof, is a unique complex of buildings, made in the traditions of Russian wooden architecture of the XVIII and XIX centuries. The guests may enjoy not only traditional Russian cuisine but also visit the smithy and pottery studio, ethnographic hut, reconstituted from drawings Novgorod peasant's house of the XIX century, the mill and the Chapel Nativity of the Blessed Virgin.

Wednesday, October 16

9:30 - 17:00 — Excursions

We propose the participants to enjoy the walk & bus trip on the city and to discover the most famous attractions of Saint Petersburg: *Saint Isaac's Cathedral, Bronze Horseman, Rostral Columns, Saints Paul and Peter fortress* etc. ... and of cause to visit one of the most famous museums in the word the *Hermitage*.

19:00 - 22:00 — Concert in Jazz Philharmonic Hall

St. Petersburg State Jazz Philharmonic Hall was founded in 1989 by the outstanding jazz musician and composer, David Goloschokin. Since its opening Jazz Philharmonic Hall has hosted performances of such legendary jazzmen as David Baker, Richie Cole, Eddie Gomez, Herb Heller, Benny Golson, Monty Alexander, Wynton Marsalis and many others.

Wednesday, October 16, the Workshop participants may enjoy by "*Parade of the jazz guitarists*" (Gasán Bagirov, Andrey Ryabov, Ildar Kazahanov, Michael Edelstein and David Goloschekin).

Seating is arranged in tables, 2-6 people per table. There is also a dance floor. During the concert you can order refreshments, desserts, alcohol and non-alcohol beverages, light snacks.

Workshop program

Monday, October 14

- 10:00 **Registration**
- 11:00 **Opening**
- 11:20 D. Galvan (Invited lecture)
1H-MoS₂ nanoparticles grown on graphene and 1H-BN mono layers
- 12:00 **Coffee break**
- 12:20 A. Simakov (Invited lecture)
Selective oxidation of renewable wood compounds over supported gold catalysts
- 13:00 B. Acosta (Oral)
Highly Stable Au-Pd@Oxide Nanoreactors in the Reduction of 4-Nitrophenol
- 13:20 V. Evangelista (Oral)
Gold based nanoreactors decorated with ceria
- 13:40 K. Klyukin (Oral)
First-principles calculations of site occupation and hydrogen migration in magnesium
- 14:00 **Lunch**
- 15:20 M. Hernandez (Invited lecture)
External area assessment in hybrid materials with cellular regeneration properties
- 16:00 E. Serova (Oral)
Saint Petersburg State University: Academic mobility in science
- 16:20 **Poster session & Coffee**
- 19:00 **Welcome reception**

Tuesday, October 15

- 10:20 V. Petranovskii (Invited lecture)
*Synthesis of nanoparticles templated by zeolite matrices:
Advantages and disadvantages*
- 11:00 C. López-Bastidas (Invited lecture)
Plasmons in Metal Nanoparticles on Zeolite Template
- 11:40 O. Jaime-Acuña (Oral)
*Atomic and electronic structure of Cd_xZn_yS nanoparticles
supported on mordenite-type zeolite*
- 12:00 **Coffee break**
- 12:20 I. Zvereva (Invited lecture)
*Development of thermal analysis for the investigation of
nanostructural layered materials*
- 13:00 I. Rodionov (Oral)
Photocatalytic properties of perovskite-type layered oxides
- 13:20 P. Tolstoy (Oral)
*Introduction to center for magnetic resonance at St Petersburg
State University*
- 13:40 A. Gurinov (Oral)
*NMR study of Lewis and Brønsted acidic centers of aluminated
SBA-15 Silicas*
- 14:00 **Lunch**
- 15:20 E. Kurenkova (Oral)
*NQR/NMR studies in zero-field at Center for Magnetic
Resonance*
- 15:40 A. Shmyreva (Oral)
*Investigation of metal nanoparticles by the example of Co-59
NMR technic*

- 16:00 E. Charnaya (Invited lecture)
NMR studies of nanostructured sodium and sodium-potassium alloy
- 16:40 **Coffee break**
- 17:00 Optional visit and guided tour to CMR
- 19:00 **Conference Dinner**

Wednesday, October 16

- 9:30 **Excursions to the Hermitage, Peter & Paul Fortress, walk trip on the city**
- 19:00 **Concert at Jazz Philharmonic Hall**

Thursday, October 17

- 10:20 Round table on further perspectives of Russian-Mexican cooperation
- 12:00 Optional visit and guided tour to departments of physics and chemistry faculties
- 14:00 **Lunch**

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Abstracts

Lectures

1H-MoS₂ nanoparticles grown on graphene and 1H-BN mono layers

D. H. Galván, G. Alonso, S. Fuentes and J. F. Del Rosario

Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Carretera Tijuana-Ensenada, Km. 107, Ensenada, B. C., México.

Contact author: donald@cryn.unam.mx

ABSTRACT

A theoretical study has been performed on a *sandwich* made by MoS₂ nanoparticles grown on graphene and BN monolayers. The calculations reported in this study have been carried out by means of the tight binding method within the extended Hückel framework using YAeHMOP (Yet Another Extended Hückel Molecular Orbital Programs) computer package. The analysis performed includes Energy Bands, Total and Projected Density of States and Mulliken Population Analysis. For the energy Bands the new structure (*sandwich*) yield indication of a semiconductor with a reported energy gap $E_g \sim 0.12$ eV. In addition, total and Projected DOS in the vicinity of the Fermi level provides information of a hybridize band formed by C p-, S p-, B p- and N p-orbitals. On the other hand, Mulliken Population Analysis provides information that there is a redistribution of charge and depends upon selected configuration under investigation. Moreover, analyzing Average Net Charge of 1H-MoS₂ the study provides information that Mo is not in a trigonal-prismatic configuration as expected.

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Selective oxidation of renewable wood compounds over supported gold catalysts

A M. Estrada¹, O. Simakova², V. V. Costa³, B. Kusema²,
E. Smolentseva⁴, S. Beloshapkin⁵, V. Kriventsov⁶, I. Simakova⁶,
S. Fuentes⁴, E. Gusevskaya³, D. Yu. Murzin², A. Simakov⁴

¹*Posgrado en Física de Materiales, Centro de Investigación Científica y de Educación Superior de Ensenada (CICESE), Ensenada, B.C., 22860, (México),*

²*Process Chemistry Centre, Åbo Akademi University, FI-20500, Turku/Åbo (Finland),*

³*Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, MG (Brazil),*

⁴*Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, C.P. 22860, Ensenada, B. C., (México),*

⁵*Materials and Surface Science Institute, University of Limerick, Limerick (Ireland),*

⁶*Boreskov Institute of Catalysis, Novosibirsk (Russia). andrey@cnyn.unam.mx*

INTRODUCTION

The concept of biorefineries, which integrate biomass conversion to fuels, power and chemicals, is in line with green chemistry approach aiming at reducing and preventing pollutions. Depolymerization of lignocellulosic biomass results in the formation of low-molecular-mass components (sugars, phenols, furfural, various aromatic and aliphatic hydrocarbons, etc.), e.g. unique building blocks for further chemical synthesis [1–3]. Recent studies have shown that lignans are active as human health-promoting agents decreasing the risk of various cancers and cardiovascular diseases [4]. Studies of the lignans matairesinol (MAT) and oxidized MAT (oxoMAT) have shown that MAT has high radical scavenging activity, while oxoMAT exhibits high superoxide scavenging activity [5,6].

RESULTS

The aerobic selective oxidation of arabinose to arabinonic acid over Au and Au-Pd nanoparticles supported on oxides was studied. Gold metallic species seem to be responsible for activation of arabinose while an easy redox transformation of Pd species can provoke oxygen activation. Thus, gold species or Au-Pd alloy covered with thin PdO film manifest a synergetic effect in the selective arabinose oxidation by molecular oxygen. Gold nanoparticles supported on magnesium oxide were shown to be efficient heterogeneous catalysts for the liquid-phase oxidation of a wide range of alcohols using molecular oxygen as a sole oxidant in the absence of co-catalysts or additives. Various carbonylic monoterpenoids important for fragrance and pharmaceutical industries were obtained in good to excellent yields starting from biomass-based monoterpenic alcohols, such as isoborneol, perillyl alcohol, and carveol. The Au/MgO catalyst also performs a selective one-pot oxidative esterification of benzyl alcohol in alkali-free methanol solutions in the absence of any additive to give methyl benzoate in a virtually quantitative yield. In case of aerobic selective oxidation of the naturally occurring lignan hydroxymatairesinol (HMR) to another lignan oxomatairesinol (oxoMAT) Au and Au-Pd catalysts supported on metal oxides showed different activity and selectivity in the HMR transformation depending on the support acidity/basicity and the active phase. The highest activity was reached over Au supported on alumina with big transport pores displaying 100% selectivity to oxoMAT.

The study revealed the high performance of gold based catalysts in some reactions of practice interest in the processing of components of biorenewable wood.

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External Area Assessment in Hybrid Materials with Cellular Regeneration Properties

M. A. Hernandez^{1,a}, M. A. Salgado^{2,b}, V. Petranovskii^{3,c}

¹*Departamento de Investigación en Zeolitas, Posgrado en Agroecología, Instituto de Ciencias de la Universidad Autónoma de Puebla, México.*

²*Facultad de Ciencias Químicas, Universidad Autónoma de Puebla, México*

³*Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, B.C., México*

^a*vaga1957@gmail.com*, ^b*malicia.64@hotmail.com*,

^c*vitalii@cyn.unam.mx*

INTRODUCTION

Hybrid organic-inorganic nanostructures with a defined morphology and structure controlled at nanometric level with functions which can be chemically activated represent an interesting class of materials with potential applications such as optical, catalytic, and therapeutic purposes [1]. The nanoparticles distributed within the porous materials have certain advantages over its predecessors: high specific surface area, quantum effects, and the existence of surface defects that are suitable for certain specific reactions, Fig. 1. Here, the results of a comparative study of this kind are reported for the adsorption of N₂ at 77 K on a series of hybrid materials prepared by ion-exchange, and finally by annealing treatment route. The organic part of the hybrid material consists of nano particles from the plant called *Tournefortia hirsutissima sp.*, commonly known as *Soldierbush*, while the inorganic part consists of zeolites such as LTA, ZSM-5 and clinoptilolite, as well as montmorillonite, and a mixture of CaCO₃ and montmorillonite.

RESULTS AND DISCUSSION

Fig. 2 illustrates the organic nanoparticles formed on the surface of LTA zeolites. Compounds, identified in these particles are shown in the caption of the Fig. 3. N₂ sorption isotherms obtained at 76 K are shown on Fig. 4. The isotherms for the initial porous matrices are shown in Fig. 4a, and for the hybrid materials modified by organic nanoparticles in Fig. 4b.

The N₂ sorption isotherms for zeolites are essentially Type I curves according to the IUPAC classification, except for zeolites LTA, as they are of type VI. While the isotherms shown by NABE, CLINO and PZX are type IV in the same classification.

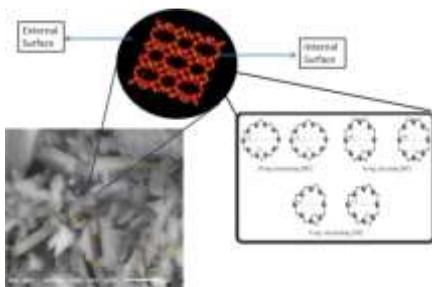


Fig. 1. External surface area of clinoptilolite zeolite.

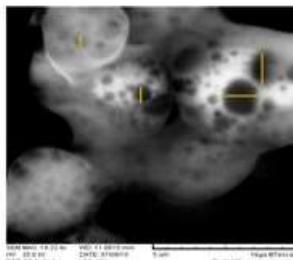


Fig. 2. SEM images of organic nanoparticles deposited on LTA.

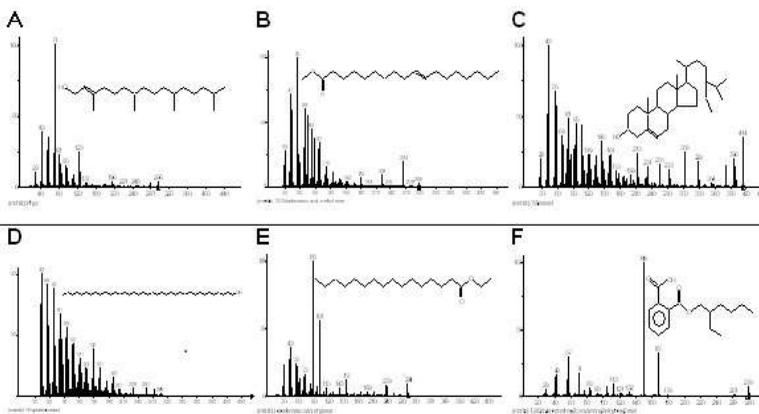


Fig. 3. Identified compounds: **A**. 3,7,11,15-Tetramethyl-2-hexadecen-1-ol, **B**. Hexadecanoic acid, ethyl ester, **C**. g-Sitosterol, **D**. 1-Heptatriacotanol, **E**. 9-Octadecenoic acid ethyl ester, **F**. 1,2 benzenedicarboxylic acid, mono.

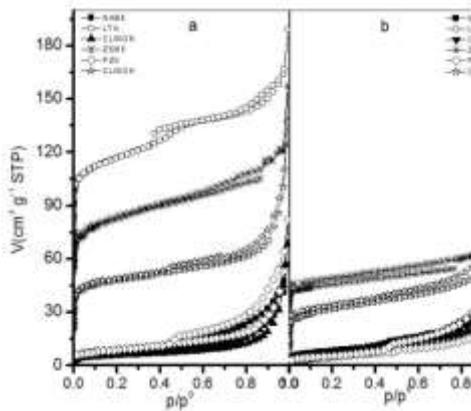


Fig. 4. N₂ Adsorption isotherms at 77 K: a) precursors and b) hybrid materials.

CONCLUSIONS

The formation of organic nanoparticles on inorganic supports led to a block in the porosity of the zeolite LTA, ZSM5 and NABE and PZX and this effect was not observed in the clinoptilolite.

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Synthesis of nanoparticles templated by zeolite matrices: Advantages and disadvantages

V. Petranovskii

Centro de Nanociencias y Nanotecnología,

Universidad Nacional Autónoma de México, Ensenada, B.C., México

vitalii@cny.n.unam.mx

ABSTRACT

Nanoparticles, because of their properties are very rarely used in the free form. Typically, for application necessary first immobilize them on any substrate, either directly synthesized thereon. In the case of catalysts for the practical application of particular importance is the developed surface, which provides the maximum available area of contact between the catalyst and the reaction medium.

Among the existing materials used as catalysts carriers, zeolites occupy a special place. They have crystal structure that makes their porosity uniform in size, unlike other oxide matrices. Thanks to this property zeolite matrix are called "molecular sieves" and are actually able to separate molecules, such as oxygen and nitrogen of the air. This uniform in size and distances between the cavities and channels porosity, making the zeolite voids "crystal space", allowing you to consider a set of clusters, similar in size and shape, and periodically arranged in a crystalline space, each holding one zeolite cavity as a superlattice [1]. Due to the presence of two periodic potentials - both between the atoms of the zeolite crystal, and a separate cluster, and between the centers of the clusters embedded in the zeolite structure having an order of magnitude longer periods compared with the interatomic such objects can and do have quite unusual physical properties, which makes them interesting objects for studying nonlinear optical and electrical phenomena.

Thus, nanoparticles and clusters deposited on the zeolite carrier may be used in various practical applications. Several processing techniques can be used for such synthesis.

The most used way of introducing of the required reagents for synthesis of nanoparticles of selected compound is the use of ion exchange properties of zeolites. Many metal-containing catalysts were prepared in this manner. However, not all elements of the Periodic Table exist in solution as cations. Also, the zeolites are sensitive to changes in pH. Therefore, the ion exchange may proceed parallel to the processes of aluminum leaching from the zeolite structure, which should be considered when preparing the catalyst.

Another example - a homogeneous porosity channels with a diameter of about one nanometer. On the one hand allows for very small nanoparticles, on the other hand creates problems in the diffusion of reactants and products. The solution to this problem is the synthesis of materials with hierarchical structures, in which both are present zeolite nanochannels and mesoporosity to ensure rapid diffusion of transport. These and other examples will be discussed and illustrated in the report.

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Plasmons in Metal Nanoparticles on Zeolite Template

Catalina López-Bastidas, Elena Smolentseva, Vitalii Petranovskii and Roberto Machorro

Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Ensenada, B.C. México
clopez@cryn.unam.mx

Plasmons are collective excitations of the free electron density in metals. Their excitation energy is strongly correlated to the size, shape and environment of the metallic structure which have rendered them as a tool for sensing and many other applications. In this work we show how they can be used to obtain information on the particular system of noble metal nanoparticles supported by zeolite templates.

Zeolites are crystalline aluminosilicate materials comprised of a series of strictly uniform channels and cavities of nanosized dimensions repeating along the tri-directional structure of the lattice. A zeolite framework offers a unique method for creating stable three-dimensional artificial arrays of embedded nanoparticles, whose properties can be partially controlled.

The variety of zeolite structures permits the creation of diverse materials of reduced dimensionality, that is, super-lattices of zeolite-caged nanostructures. As the sizes of the particles are confined to the nanoscale, the ratio of surface to bulk atoms increases significantly. Mesoporous materials containing metal nanoparticles attract great attention in formation of materials used in catalysis and photochemistry, as well as in miniaturized electronic and optical devices.

The optical characterization of size and placement of the metal nanoparticles in the described systems is a sought after goal. The nondestructive nature of optical tools and the possibility of in-situ analysis makes them very attractive. Nevertheless there are still unsolved difficulties in modeling such a complex composite system and thus interpreting optical data from experiment. In this work we present optical spectra obtained experimentally and a simple average field

approach to calculate the optical spectra of the zeolite-metal system. We considered the three noble metals Ag, Au and Cu in Mordenite, Y-zeolite and β -zeolite with different molar ratios and protonation species. Experimental procedure is described in detail in [1, 2].

We employ an average field approach to describe the physics relevant to the optical response of the zeolite-metal system. The macroscopic dielectric response of the system will be described by an effective dielectric function obtained within the Maxwell Garnett approximation (MGA) [3]. The details of the theoretical modeling can be found in [4, 5].

In our approach the complex non-local in-homogeneous dielectric response of the zeolite + metal system is replaced by an effective homogeneous dielectric function which will permit us to study the effect some of the important physical mechanisms present can have on the optical properties observed. The model accounts for both the screening of the external field due to the zeolite itself and for the polarizability of the metallic inclusions due to the local field that excites them. We identify the main feature in the optical spectra as a localized surface plasmon excited on the metal nanoparticles. Its exact resonance energy depends on the characteristics of the zeolite template as well as on the annealing temperature and chemical composition. We observe that the molar ratio and type of zeolite are stronger factors in the plasmon energy shift than annealing which we relate to nanoparticle size. This is consistent with theoretical findings. We conclude that the screening of the interparticle interactions and excitation field by the zeolite matrix is a fundamental factor in the the plasmon shift.

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Development of Thermal Analysis for the Investigation of Nanostructural Layered Materials

Zvereva Irina

*St. Petersburg State University, 198504 Russia, St. Petersburg,
Universitetskiy pr.26.
irinazvereva@yandex.ru*

The presentation focuses on the investigation by methods of thermal analysis and calorimetry in area of properties of nanostructural layered oxides, processes of their multistage formation and thermal stability. It will be considered the wide range of oxides which belong to layered perovskite-type structures built of fragments of different structural types by the intergrowth of alternating layers (Ruddlesden-Popper, Dion-Jacobson and Aurivillius phases with various nano size thickness of perovskite slabs). Among objects of investigation there are nanostructural layered oxides promising for functional materials (photocatalysts, magnetic materials) as $A_2Ln_2Ti_3O_{10}$, $ALnTa_2O_7$ ($A = Li, Na, K, Rb, Cs$), $Gd_2SrFe_2O_7$, $Bi_2NdNbTiO_9$.

Main attention will be devoted to new data on quantitative characteristics of water intercalation in layered structure and ion-exchange reactions in the water medium obtained by thermogravimetry, simultaneous thermal analysis and differential scanning calorimetry. On the base of these sets of data the links to photocatalytic activity for $A_2Ln_2Ti_3O_{10}$ and $ALnTa_2O_7$ ($A = Li, Na, K, Rb, Cs$) will be discussed. Unexpected high photocatalytic activity of some layered oxides can be clear from point of a prominent role of the water intercalation into the interlayer space of the crystal structure.

The nature of the low-temperature phase transition obtained from the experimental values of heat capacity of layered oxides with magnetic ions has been investigated by electromagnetic properties measurements. This result gives rise to the assumption that the observed phase transition in layered oxides $Gd_2SrFe_2O_7$ and $Bi_2NdNbTiO_9$ is due to the 2D magnetic ordering of the paramagnetic ions

The comparison of thermodynamic properties of oxides with different thickness of perovskite blocks confirms the fact of additivity of thermodynamic functions of the layered structures built of fragments of various structural types by the intergrowth of alternating layers.

Brief review will be done on modern technical opportunities and equipment of Resource center “Thermogravimetric and Calorimetric Research” of Saint Petersburg State University.

NMR studies of nanostructured sodium and sodium-potassium alloy

E. V. Charnaya¹, C. Tien², M. K. Lee², D. Nefedov¹, Y. A. Kumzerov³,
J. Haase⁴, D. Michel⁴

¹*Physics Department, St. Petersburg State University, St. Petersburg
198504, Russia*

²*Physics Department, National Cheng Kung University, Tainan 70101,
Taiwan*

³*Ioffe Physiko-Technical Institute RAS, St. Petersburg 194021 Russia*

⁴*Faculty of Sciences and Geosciences, Leipzig University, Leipzig D-
04103, Germany*

E-mail: charnaya@mail.ru

Experimental data of NMR studies on metallic sodium and sodium-potassium alloy embedded into nanoporous matrices are presented. Size-effects and influence of nanoconfinement on the Knight shift, melting and freezing phase transitions, and spin relaxation in liquid and solid sodium and its alloy are revealed. Alterations in atomic mobility were evaluated within the framework of theoretical models of spin relaxation in solid and liquid metals.

Abstracts

Orals

Highly Stable Au-Pd@Oxide Nanoreactors in the Reduction of 4-Nitrophenol

Brenda Acosta^{1*}, Viridiana Evangelista¹, Sergio Fuentes²,
Andrey Simakov^{2**}

¹Posgrado en Física de Materiales, Centro de Investigación Científica y de Educación Superior de Ensenada (CICESE), Ensenada, B.C., 22860, México. ²Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México (CNyN-UNAM), Ensenada, BC, 22860, México.

* bracosta@cnyunam.mx; ** andrey@cnyunam.mx

INTRODUCTION

Nanoreactors, where catalytically active nanoparticles (nuclei) are encapsulated into porous shell (nuclei@shell), have become attractive due to their enhanced stability under reaction conditions [1]. The major publications are related with the study of gold based nanoreactors, where only few works are dedicated to multimetallic nuclei [2 - 3]. Because the effective use of Au-Pd nanoparticles in multiple catalytic reactions [4], it is interesting to synthesize and characterize Au-Pd@oxide nanoreactors.

EXPERIMENTAL METHOD

The Au-Pd@oxide nanoreactors were prepared via traditional bottom-up route. In brief, freshly prepared Au-Pd metallic nanoparticles using seed technique were encapsulated into silica shell by the Stöber method. Silica shell was then used as hard-template to form the zirconia porous shell. Finally silica was removed by the treatment with a concentrated base [5 - 6]. The Au-Pd@oxide nanoreactors during their preparation were characterized by TEM, STEM-EDS and UV-Vis *in situ* spectroscopy. Also, their catalytic performance was evaluated in the reduction of 4-nitrophenol into 4-aminophenol, model reaction commonly used to test nanoreactors [1 - 3].

RESULTS AND DISCUSSION

The effective contact of Au with Pd was revealed by the blue shift of

gold plasmon peak in UV-Vis spectrum as well as by STEM-EDS line technique (Fig. 1-Left). The successful encapsulation of the bimetallic nanoparticles into silica shell was confirmed by TEM images. The zirconia deposition onto the Au-Pd@SiO₂ structure was manifested by the changes in the surface morphology of the silica spheres found in the TEM images as well as the complete silica removal carried out further. The initial activity of nanoreactor was comparable with that of reference supported catalyst (see Fig. 1-Right). However subsequent catalytic runs manifested superior stability of nanoreactor.

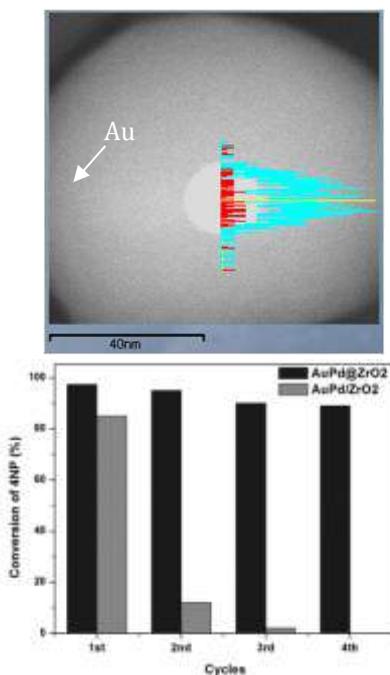


Fig.1. Left: TEM image of Au-Pd@SiO₂ with analysis of Au and Pd profiles by STEM-EDS line scanning technique. Right: conversion of 4-nitrophenol in 4 successive cycles of reduction using AuPd@ZrO₂ nanoreactors and reference supported catalyst.

CONCLUSIONS

The prepared samples of nanoreactors manifest high activity and

stability in the reduction of 4-nitrophenol into 4-aminophenol compared to the reference Au-Pd nanoparticles supported on oxides. Catalytic tests showed significant effect of both the shell nature and the nuclei. To the best of our knowledge this is the first study of Au-Pd@ZrO₂ nanoreactors.

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The authors would like to thank O. Callejas, E. Flores, F. Ruiz, J. Peralta and M. Sainz for technical assistance. This research project was partly supported by CONACyT (México) and PAPIIT-UNAM (México) through grants 179619 and 203813, respectively.

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Gold based nanoreactors decorated with ceria

Viridiana Evangelista^{1*}, Brenda Acosta¹, Sergio Fuentes²,
Andrey Simakov^{2**}

¹*Posgrado en Física de Materiales, Centro de Investigación Científica y de Educación Superior de Ensenada (CICESE), Ensenada, B.C., México,* ²*Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México (CNyN-UNAM), Ensenada, B.C., México.*

(*) vevangel@cnyun.unam.mx, (**) andrey@cnyun.unam.mx

INTRODUCTION

Yolk-shell nanoreactor consists of a nucleus, commonly the active phase, surrounded by a porous shell in a nucleus@void@shell arrangement, where the void allows free movement of the nucleus and free accessibility of their surface atoms to the components of the reaction media [1]. The reported size of shell pores is around 2.5-5 nm [2]. Therefore the size of Au nuclei should be above these values to prevent release of nuclei from the nanoreactors. On the other hand, the catalytic activity of Au nanoparticles drastically decreases when their size increases above 5 nm [3]. The catalytic activity of relatively large Au nuclei may be improved via covering or decorating them with some oxides, which promotes the formation of new active sites on the Au-oxide interface. The present work is dedicated to the design of Au@SiO₂ and Au@ZrO₂ nanoreactors where gold core is decorated with ceria.

EXPERIMENTAL

Four nanoreactors were prepared: Au@SiO₂, Au@ZrO₂, Au-Ce@SiO₂ and Au-Ce@ZrO₂ nanoreactors. Au NPs were synthesized using the Turkevich method and encapsulated into silica shell by the Stöber method. The decoration of Au core was carried out via injection of ceria precursor into void space of nanoreactors with consequent hydrolysis and thermal treatment. Finally Au-Ce@SiO₂ was coated by a zirconia shell and silica was removed by treatment with a strong base to obtain Au-Ce@ZrO₂ nanoreactors with a characteristic yolk-shell structure.

RESULTS

Analysis of *in situ* UV-Vis spectra, collected during thermal treatment of Au@SiO₂ nanoreactors prefilled with hydrolyzed ceria precursor, revealed red shift of plasmon peak of Au nuclei indicating the strong interaction of Au nuclei with formed ceria species. The preferable formation of ceria species around Au nucleus was confirmed by STEM analysis. Obtained Au-Ce@SiO₂ and Au-Ce@ZrO₂ samples show expectable high improvement of catalytic activity in CO oxidation and in the reduction of 4-nitrophenol due to formation of new active sites in the gold-ceria interface. The catalytic activity of Au-Ce@SiO₂ and Au-Ce@ZrO₂ nanoreactors decorated with ceria in CO oxidation was improved by ~4 and ~1.5 times, respectively, in comparison with that of non-decorated nanoreactors. In addition, it was found that the catalytic activity of Au-Ce@ZrO₂ in 4-nitrophenol reduction was further improved after 3 subsequent runs. The latter could be related with the partial reduction of ceria species under the reaction conditions.

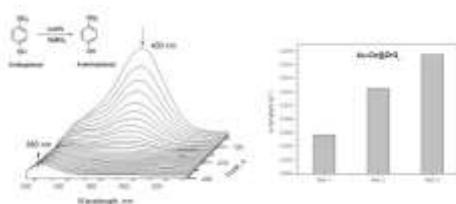


Fig. 1. UV-Vis spectra recorded *in situ* during 4-nitrophenol reduction in Au-Ce@ZrO₂ nanoreactors (left). Stability of Au-Ce@ZrO₂ nanoreactors in 4-nitrophenol reduction after 3 runs (right).

CONCLUSIONS

The proposed route allows the decoration of nuclei with ceria in Au@SiO₂ nanoreactors by formation of ceria species in the void space of nanoreactors via homogeneous hydrolysis of ceria precursor and this route could be applied for the synthesis of nanoreactors with Au nuclei modified with different materials in order to make them effective for different catalytic reactions in spite of relatively big size of the Au nuclei.

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First-principles calculations of site occupation and hydrogen migration in magnesium

Konstantin Klyukin¹, Marina G. Shelyapina¹ and Daniel Fruchart²

¹ Faculty of Physics, St. Petersburg State University, Ulyanovskaya 1, Petrodvorets, St. Petersburg, 198504 Russia

² Institut Néel, CNRS, 25 avenue des Martyrs, BP 166, 38042 Grenoble Cedex 9, France

konstantin.klyukin@gmail.com

INTRODUCTION

Magnesium hydride has attracted a lot of attention as a hydrogen storage material. But applications of pure MgH₂ are limited by a high temperature of hydrogen release and slow sorption kinetics. Nevertheless, it was found that a limited dissociation rate of hydrogen on the magnesium surface may be improved by additions of transition metals catalyst (TM). Investigations by means of in situ X-ray [1] and neutron [2] diffraction of Mg/Nb thin films and nanocrystallites have shown that hydrogen penetrates within Mg through Nb “gates”. But the role of the interface border between Mg and TM remains unclear. In our previous theoretical investigations [3] of Mg/Nb thin films we have found that Nb additives stabilize the Mg bcc structure on interface border. Also we have studied H-induced [4] transitions in Mg upon the hydrogenation.

In this contribution we report on the results of first-principles calculations of hydrogen diffusion pathways in different structures of magnesium, which may occurs near the Mg/Nb interface border upon the hydrogenation.

THEORETICAL METHOD

Calculations were performed within the framework of density functional theory using the plane-wave pseudopotential method and the Perdew–Burke–Ernzerhof GGA exchange and correlation potential as implemented in Quantum Espresso package. To locate the minimum energy path (MEP) for hydrogen, where the forces perpendicular to the

path vanish, nudged elastic band (NEB) method was applied. The configuration with the maximal energy along the MEP was obtained via climbing image implementation of the NEB method.

RESULTS AND DISCUSSION

We have considered 3 possible structures of MgH_x , which may occur at low hydrogen concentration [4]: hcp- MgH_x , bcc- MgH_x , fcc- MgH_x . According to DFT calculations it was found that the hydrogen atoms prefer to occupy octahedral interstitial sites in the hcp structure of Mg and tetrahedral ones in the fcc and bcc structures.

To understand the atomic migration process of hydrogen in Mg, we have considered different diffusion pathways between tetrahedral and octahedral sites. Then the activation barriers were found as the difference between the optimized transition states and the ground states.

It was found that in hcp- MgH_x the hydrogen atom moves between the two adjacent tetrahedral sites and then a jump towards neighboring octahedral occurs. Activation barriers are 0.16 eV/cell and 0.12 eV/cell for this two-step transition. In the case of bcc- MgH_x diffusion of hydrogen occurs by a direct hop between two neighboring tetrahedral sites, but H atom does not move along a straight-line trajectory, from one tetrahedral site to a nearby tetrahedral site it moves by a curved path distorted toward the octahedral site. The activation barrier for such transition is equal to 0.08 eV/cell. In fcc- MgH_x diffusion of hydrogen occurs by a hop from the tetrahedral site into the metastable octahedral site and then to the nearest tetrahedral site. The activation barrier for such transition is equal to 0.25 eV/cell.

For all described pathways the simple estimation of the diffusion coefficient was performed. Preliminary results have shown that the bcc structure of Mg hydride has the lowest activation barrier and the highest diffusion rate.

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Research was carried out using computational resources provided by Resource Center "Computer Center of SPbU" (<http://cc.spbu.ru/en>).

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Atomic and electronic structure of Cd_xZn_yS nanoparticles supported on mordenite-type zeolite

O. E. Jaime-Acuña^{1, *}, O. Raymond², H. Villavicencio³,
J. A. Díaz-Hernández², V. Petranovskii²

^{1,2} *Centro de Investigación Científica y Educación Superior de Ensenada, Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada CP 22860, Baja California, México,*

² *Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, Baja California 22860, México,*

³ *Dirección Nacional de Informática Educativa del Ministerio de Educación de Cuba, La Habana, Cuba.*

ojaime@cryn.unam.mx

INTRODUCTION

The atomic structure and composition of the ternary Cd_xZn_yS semiconductor nanoparticles grown on synthesized mordenite-type zeolite (MOR) is analyzed herein. Semiconductor–MOR composite materials have been synthesized in two different ways, either by ion exchange of Na-MOR with Zn and Cd ions, or by direct synthesis through a variant of the sol-gel technique; both followed by sulfidation treatment with H₂S flow. Morphology, chemical composition and crystallographic structure of the composites were characterized using X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electron diffraction (ED). Electronic structure of semiconductor nanoparticles was studied by X-ray photoelectron spectroscopy (XPS). Optical response was characterized using UV-Vis optical absorption, and photoluminescence spectroscopic techniques. The grown nanoparticles on MOR surface proved to be core-shell type, with a core of ZnS surrounded by a shell of CdZnO-CdZnS. The structural and optical properties of the synthesized materials make them promising candidates for applications in the fields of optoelectronics and

photocatalysis.

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Photocatalytic Properties of Perovskite-Type Layered Oxides

Ivan Rodionov, Irina Zvereva

*Saint-Petersburg State University, Faculty of Chemistry, Department of
Chemical Thermodynamics and Kinetics,
Petrodvorets, Universitetskiy pr. 26, Saint-Petersburg, 198504 Russia
chimikus@yandex.ru*

Photocatalysts for decomposition of water into hydrogen and oxygen under light irradiation have been the subject of extensive investigation since the discovery of this process till the present day. This is due to the obvious practical interest in the using of solar energy to produce hydrogen as an ecological clean fuel. However, the efficiency of discovered photocatalysts is still low for many commercial purposes, so the design of new photocatalytic systems is an actual problem. To drive an uphill reaction such as overall water splitting, there is need in effective separation of oxidation and reduction sites to prevent undesirable back reactions. Such separation is possible in photocatalysts with complex structure, e.g. layered oxides.

We present a comparative study of photocatalytic activity of layered perovskite-type oxides based on original results. Series of Ruddlesden-Popper ($A_2Ln_2Ti_3O_{10}$ and $ANdTiO_4$, where $A = H, Li, Na, K$; $Ln = La, Nd$) and Dion-Jacobson ($ANdTa_2O_7$, where $A = H, Li, Na, K, Rb, Cs$ and $ANdNb_2O_7$, where $A = Rb, Cs$) phases were synthesized and characterized by XRD, SEM, UV-VIS diffuse-reflectance spectroscopy, BET, TGA. Photocatalytic activity was determined from the hydrogen evolution rate in aqueous suspensions under UV-irradiation in the presence of isopropyl alcohol as a sacrificial electron donor. Dependence of photocatalytic activity of complex oxides on their characteristics, such as BET surface area, particle morphology, band gap energy and water intercalation ability is discussed.

Our study showed that the maximum photocatalytic activity ($263 \mu\text{L/h}$) along with the highest apparent quantum efficiency (2%) is achieved by $RbNdTa_2O_7$ (Table I). On the example of this complex oxide it was

shown, that during the photocatalytic reaction in the presence of isopropyl alcohol acetone and hydrogen are formed at equal rate. In the absence of isopropyl alcohol hydrogen generation rates over $\text{RbNdTa}_2\text{O}_7$, $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ increase in the same order as they do in its presence. Correlation between photocatalytic activity and BET surface area for samples containing the same alkali metal was demonstrated by the triple-layered Ruddlesden-Popper titanate series $\text{A}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ (A = H, Li, Na, K; Ln = La, Nd). The ability of water intercalation of a layered oxide was found to be related to high photocatalytic activity, but not to be the only feature determining it.

Table I. Photocatalytic activity of layered oxides compared with other characteristics

| Sample | Hydrogen evolution rate ω_v , $\mu\text{L}/\text{h}$ | Band gap energy E_g , eV | BET surface area S , m^2 | Apparent quantum efficiency, % | Water intercalation |
|--|---|----------------------------|-------------------------------------|--------------------------------|---------------------|
| HNdTa_2O_7 | 45 | 4.36 | 3.9 | 0,27 | yes |
| $\text{LiNdTa}_2\text{O}_7$ | 6 | 4.49 | 4.3 | 0,043 | - |
| $\text{NaNdTa}_2\text{O}_7$ | 104 | 4.38 | 5.0 | 0,61 | yes |
| KNdTa_2O_7 | 42 | 4.38 | 1.2 | 0,25 | - |
| $\text{RbNdTa}_2\text{O}_7$ | 263 (40*) | 4.54 | 0.8 | 2,02 | - |
| $\text{CsNdTa}_2\text{O}_7$ | 183 | 4.40 | 2.0 | 1,08 | - |
| $\text{RbNdNb}_2\text{O}_7$ | 207 | 3.70 | 1.5 | 0,28 | - |
| $\text{CsNdNb}_2\text{O}_7$ | 152 | 3.64 | 0.5 | 0,21 | - |
| $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ | 80 | 3.54 | 11 | 0,11 | yes |
| $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ | 1 | 3.64 | 0,9 | 0,001 | - |
| $\text{Na}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ | 5 | 3.50 | 1.2 | 0,007 | - |
| $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ | 175 (18*) | 3.58 | 4.5 | 0,24 | yes |
| $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ | 39 | 3.51 | 7.2 | 0,053 | yes |
| $\text{Li}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ | 1 | 3.65 | 1.6 | 0,001 | - |
| $\text{Na}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ | 9 | 3.50 | 2.0 | 0,012 | - |
| $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ | 113 (9*) | 3.54 | 3.0 | 0,15 | yes |
| TiO_2 P25 | 96 | 3.10 | 50 | 0,08 | - |

* - measured in the absence of isopropyl alcohol.

ACKNOWLEDGMENT

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Introduction to Center for Magnetic Resonance at St.Petersburg State University

Peter Tolstoy¹

*¹Center for Magnetic Resonance, St.Petersburg State University,
198504 Peterhof, Universitetskij pr. 26
peter.tolstoy@spbu.ru*

The Center for Magnetic Resonance at St.Petersburg State University (<http://cmr.spbu.ru>) is a newly established core facility with one of the widest sets of magnetic-resonance-based techniques available in Russia. The Center provides access to the instrumentation, expertise, and infrastructure to carry out and support fundamental, applied and innovative research projects utilizing NMR, NQR and EPR spectroscopy as well as magnetic resonance microimaging.

Equipment of the Center allows one to give theoretical and practical courses, classes and seminars for students and employees of St.Petersburg State University in order to strengthen the curriculum in the area of magnetic resonance spectroscopy and in order to train qualified users of modern spectral methods. On commercial basis, all services of the Center could be provided to external users, such as medical, pharmacological and forensic organisations, as well as museums, technological and research centers, industry etc.

In this presentation we will give an overview of the available equipment, techniques and show examples of research projects carried out in the Center as well as some works done independently by its employees.

NMR Study of Lewis and Brønsted Acidic Centers of Aluminated SBA-15 Silicas

Andrey A. Gurinov¹, Yulia A. Rozhkova¹, Arnošt Zukal², Jiří Čejka²
and Ilya G. Shenderovich¹

¹*Department of Physics, St. Petersburg State University, Ulianovskaya 1, 198504 St. Petersburg, Russian Federation;* ²*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i. Dolejškova 3, CZ-182 23 Prague 8, Czech Republic*
andrey.gurinov@spbu.ru

INTRODUCTION

The main advantage of ordered mesoporous silicas is that they offer extremely high surface areas, whose catalytic function can be selectively varied. One can either deposit or bind covalently active species to the inner surfaces or incorporate active sites into/onto the silica walls. Probably the most elaborated example of such modification is alumination. Most of the authors support the view that it creates strong Brønsted acid groups due to interaction of the oxygen atoms of surface silanol groups with neighboring aluminum atoms. It is not clear how many different types of Lewis acid sites can coexist on aluminated surfaces.

POST-SYNTHESIS ALUMINATION OF SILICAS

If calcined SBA-15 material containing octahedrally coordinated extra-framework aluminum is treated with a solution of NH_4OH , aluminum is inserted into tetrahedral framework positions. Successive grafting of alumina on SBA-15 has led to a gradual filling of the cavities of a corona surrounding the mesopores. Generally, the post-synthesis modification can vary the density and the accessibility of surface hydroxyl groups.

NMR STUDY

The following types of measurements have been proposed and carried out in order to characterize purely siliceous and aluminated SBA-15

silicas: (1) solid state ^{27}Al MAS NMR; (2) ^{15}N MAS NMR at 130 K at a submonolayer and high loading of pyridine- ^{15}N to identify different adsorption-active sites; (3) ^{15}N static NMR at 300 K at a submonolayer loading of pyridine- ^{15}N to estimate the surface roughness from the residual ^{15}N chemical shift anisotropy; (4) ^1H MAS NMR at 300 K in the presence and absence of pyridine- d_5 ; to analyze the effect of the grafting on the accessibility of silanol groups.

^{27}Al MAS NMR spectra show the modification of the local environment of the Al atoms dependent on the Si/Al ratio. Three distinct signals are observed that can be assigned to octahedral, pentahedral, and tetrahedral aluminum atoms. At high Si/Al ratios most of the aluminum atoms are tetrahedral, indicating the formation of framework aluminum species. On the other hand, at lower Si/Al ratios formation of loosely bonded species is clearly shown by the presence of octahedral and pentahedral aluminum.

^1H and variable temperature ^{15}N NMR spectra of these materials loaded with pyridine can be summarized as following. The corona around the mesopores of non-aluminated material has a reach network of cavities that are easily accessible for nitrogen but not for pyridine. Aluminum chlorhydrol most effectively reacts with silica surface in a strongly confined geometry of micropores instead of forming a homogeneous film at the surface.

The most intriguing result of the current study is that gaseous nitrogen can occupy Lewis acid sites and hinder the interaction of the aluminum with any other electron donor. As a result aluminated surface saturated with nitrogen does not exhibit any Brønsted or Lewis acidity. At room temperature it takes days before pyridine replaces nitrogen at the Lewis acid sites.

Evacuation at 420 K removes the adsorbed nitrogen. Such surface exhibits up to two types of Brønsted and Lewis acid groups each. Isolated silanol groups are responsible for the physisorption of pyridine on surface. The proton donating ability of silanol groups interacting with aluminum is sufficient to protonate pyridine. At low aluminum content the surface contains Lewis acid sites of a high acidity which are

attributed to tetracoordinated aluminum. An increase of aluminum content results in the appearance of Lewis acid sites of a lower acidity attributed to pentacoordinated aluminum.

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NQR/NMR Studies in Zero-Field at Center for Magnetic Resonance

Elena Kurenkova

Saint Petersburg State University, Center for Magnetic Resonance
e.kurenkova@spbu.ru

INTRODUCTION

The popularity of nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) in zero-field techniques stems from sensitivity of these methods to molecular structure and local environment. NQR is used to the study of crystalline materials (mono- and polycrystalline, amorphous, ordered and disordered compounds) containing atoms whose nuclei have an electric quadrupole moment. The method allows one to obtain information about the local structure of the material, the distribution of electron density in the proximity of the nucleus, mobility of molecules and groups of atoms in a molecule, phase transitions, inter- and intramolecular interactions etc. NMR in zero-field is a powerful tool to investigate magnetic and superconducting materials. This application gives information about hyperfine interactions and local electronic structure etc.

The most often studied nuclei are ^{59}Co , ^{57}Fe , ^{61}Ni , ^{55}Mn for magnetically ordered systems and $^{35,37}\text{Cl}$, $^{63,65}\text{Cu}$, $^{121,123}\text{Sb}$, ^{75}As etc nuclei for NQR applications.

EQUIPMENT AVAILABLE AT CMR

As NQR/NMR in zero-field measurements require a dedicated instrument, Center for Magnetic Resonance (CMR) [1] is equipped with Redstone NMR/NQR spectrometer (Tecmag, Houston, TX) with two-channel transmitter and one-channel receiver modules controlled by TNMR software.

Frequency range of this spectrometer covers all major nuclei in most of chemical environments, while short dwell time makes it suitable for study of many fast-relaxing magnetically ordered materials.

Investigation of orientation-dependent magnetic properties of monocrystals is possible with the use of goniometer. Main technical specifications of the spectrometer and detection probe are collected in the tables below:

Spectrometer

| | |
|--------------------|-------------------|
| Frequency range | 0.5 MHz - 500 MHz |
| Pulse length range | 10 ns - 43 s |
| Dwell time | 300 ns - 21 ms |
| Temperature range | 4 K – 400 K |

Probe

| | |
|-----------------------|------------|
| Frequency range | 27-120 MHz |
| Maximal input power | 500 W |
| Goniometer resolution | 0.1° |

Spectrometer also includes two a low-noise preamplifiers (gain not less than 30 dB, noise not more than 1.2 dB) and a system to reduce the dead- time of the preamplifier.

EXAMPLES

In this presentation we will give a brief overview of applications of NQR/NMR in zero-field and show several examples, demonstrating the information content of such studies. In particular, we will discuss the followings examples:

- ^{57}Fe NMR in metallic iron with different size of crystallites including nanoparticles
- Detection of explosives using NQR spectroscopy
- Techniques for amplification of weak NQR/NMR signals

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Investigation of metal nanoparticles by the example of Co-59 NMR technic

Shmyreva A. A.¹

¹198504, Saint-Petersburg State University, Center for Magnetic Resonance
E-mail: annshmyreva@gmail.com

INTRODUCTION

In recent years there has been increasing interest in the metal nanoparticles. These particles occupy an intermediate position between the bulk materials and molecules and exhibit new chemical and physical properties which are characterize only this state of the substance. From a practical standpoint, metal nanoparticles interesting for the catalytic activity and high activity in solid-state reactions. Among the plurality of magnetic nanoparticles the most attractive are the cobalt nanoparticles and cobalt-based alloys. This is due to the fact that cobalt-containing nanomaterials have the highest practical importance magnetic characteristics (the coercive force and saturation magnetization), as compared with other magnetic materials. [1]

EXPERIMENT

A set of cobalt -containing composite materials based on cobalt -containing nanoparticles stabilized by different matrix were studied. Nanoparticles were synthesized using the thermal decomposition of metal compounds [2]. As a reference sample a sample of bulk cobalt powder was used. Major studies were carried out on the spectrometer, which was fully developed and assembled at the University of Parma. Measurements were performed in zero magnetic field at 77 K according to the method of spin-echo ($p1 - \tau - p2$).

RESULTS AND DISSCUSSION

The samples prepared using different starting cobalt-containing compounds and/or different preparation conditions of the material and having a different particle size have lines in the NMR spectrum at

frequencies: 217-218 MHz and 224 - 228 MHz.

The frequencies of the main lines of the spectrum of cobalt nanoparticles are close to the frequencies observed in the spectrum of bulk sample of cobalt. Based on the position of the lines in the spectra suggests the presence of nanoparticles in the phase close to the hcp structure of bulk cobalt.

For a number of samples the integral intensity of the NMR signals is proportional to the amount of cobalt metal and does not correspond to the total content of cobalt, introduced during preparation (Fig. 1). This means that part of the cobalt in the nanocomposites there is in the form of oxides, and the NMR method can be used for rapid (operational) control for certain procedures of nanoparticles synthesis.

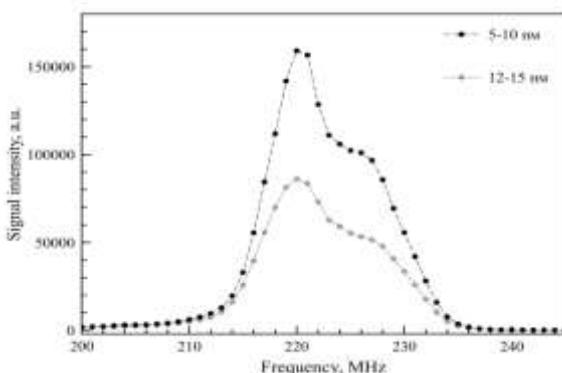


Fig.1. Cobalt in nanodiamond matrix, 50% , size of nanoparticles 5-10 nm – circles. Cobalt nanoparticles without matrix, 5%, size of nanoparticles 12-15 nm – rhombs. T=77 K.

Comparing the NMR spectra of bulk cobalt powder and cobalt nanoparticles without the matrix and the behavior of the spectral lines with the change of RF field amplitude one can assume a non-uniform magnetic structure of nanoparticles [3]. Takes into account that the size of cobalt nanoparticles without matrix is approximately three orders of magnitude smaller than particle size of bulk cobalt powder and considering a sharp increase in the proportion of surface atoms (from ~ 0.05 % to ~ 50%) can be expected that the nanoparticles of given size

characterized by a core-shell structure.

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Abstracts

Posters

Exfoliation of protonic forms complex layered perovskite-like titanates HLnTiO_4 and $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Nd}$) promoted by VOSO_4

L.D. Abdulaeva, O.I. Silyukov, I.A. Zvereva

*Saint-Petersburg State University, Petrodvorets, Universitetskiy pr. 26,
Saint-Petersburg, 198504 Russia*

Lilian_chem@mail.ru

Protonic forms of complex layered perovskite-like titanates have attracted great attention due to their particularly interesting and variable properties, such as high ionic conductivity and photocatalytic activity [1]. These compounds consist of sheets of transition-metal oxides with the thickness less than 2 nm and protons in the interlayer space. Protonic forms could be obtained by the treating initial alkali metal containing layered compounds in acid medium [2]. Such protonated compounds are interesting in terms of their application as precursor for low-temperature reactions.

The present work reports results of the treatment of protonic forms of layered oxides HLnTiO_4 and $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Nd}$) belonging to the Ruddlesden-Popper phases in $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ water solution. We have observed that such treatment leads to the exfoliation and then to self-assembly of protonic form particles, where $(\text{VO})^{2+}$ cations are adsorbed on the surface. There are several examples of similar exfoliation under the reaction with organic bases [3].

Characterization by SEM, powder XRD and TGA have been performed for the determination of the structure, content and stability of synthesized oxides.

Exfoliated $(\text{VO})_x\text{H}_{1-2x}\text{LnTiO}_4$ and $(\text{VO})_x\text{H}_{2-2x}\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Nd}$) for the first time have been prepared by treatment in VOSO_4 solution. The morphology of exfoliated particles significantly changes compared with the morphology of the initial compounds HLnTiO_4 and $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ (Fig.1). VOSO_4 causes exfoliation and reassembling of protonic particles. In case of $(\text{VO})_x\text{H}_{1-2x}\text{LnTiO}_4$, particles are made up of interconnected flat crystallites with thickness below 10 nm (Fig.1, b).

Exfoliated compounds contain significant amounts of adsorbed $(VO)^{2+}$ cations (more than 15% mass) according to the X-ray microanalysis. In case of three-layer perovskite-like oxide $H_2Ln_2Ti_3O_{10}$, the treatment with $VOSO_4$ aqueous solution leads to the compounds with significant amount of exfoliated surface layers, but in general, it keeps the particle morphology of the precursor (Fig. 1, d).

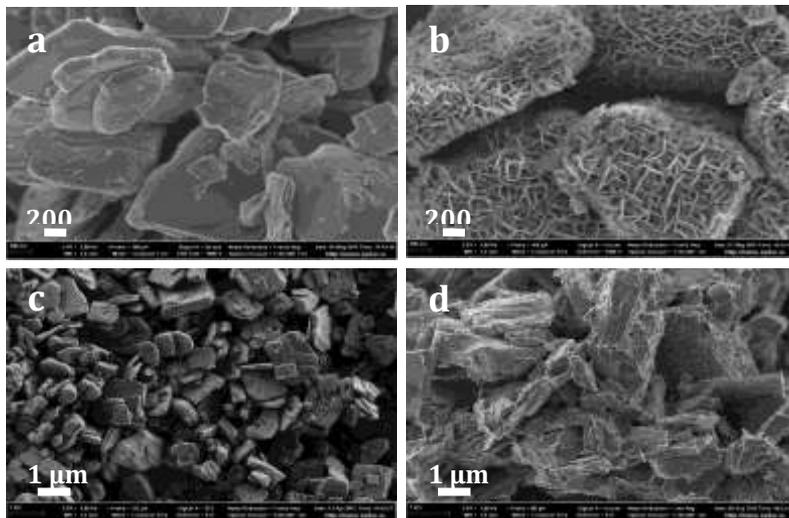


Fig. 1: a) initial $HLaTiO_4$; b) $(VO)_xH_{1-2x}LaTiO_4$;
c) initial $H_2La_2Ti_3O_{10}$; d) $(VO)_xH_{2-2x}La_2Ti_3O_{10}$

ACKNOWLEDGMENT

Powder X-ray study was carried out in the X-ray Diffraction Centre, SEM study – in the Interdisciplinary Resource Center for Nanotechnology, TGA – in Center for Thermogravimetry and Calorimetry of Saint Petersburg State University. This work has been supported by the RFBR (Grant 12-03-00761).

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Structural Transformations in Aqueous Solutions of Lithium, Sodium and Cesium Chlorides

Khlynova Oksana¹, Davidian Anna¹,
Kudrev Andrey¹, Myund Lyubov¹, Khripun Maria¹

¹ Saint-Petersburg State University
AGDavidian@yandex.ru

The aim of this work is to study structural transformations of the solvent in aqueous solutions of lithium, sodium, and cesium chlorides as the concentration of a salt changes.

The data acquired from studying of alkali metal chlorides shows the difference in the changes of dominant forms, which is determined by the nature of a salt, concentration of the solution, and the hydrating power of the salt ions. From a practical point of view, alkali metal chlorides are closely related to medicine and physiology, and it is essential to know how various salt concentrations can impact a drug effect on the body.

The IR absorption spectra of the first overtone of stretching vibrations of water ν_{OH} (5400 - 7500 cm^{-1}) were measured, depending on the concentration of aqueous solutions of LiCl, NaCl and CsCl in the range 0 – 12.98 M, 0 – 6.61 M and 0 – 4.53 M, respectively. The spectra were recorded on a Spectrum BX spectrometer in steps of 2 cm^{-1} at room temperature (25°C). The test solution was placed in a glass cell with a layer thickness of 0.1 cm.

It was found that variation in concentration of selected alkali metal chlorides determines the change in the shape of the contour $\nu_{\text{OH}}^{02}(\text{H}_2\text{O})$. The resulting spectral data were processed by methods of principal component analysis and multivariate curve resolution - alternating least squares. The solution concentration dependence of intensity and frequency was compared with solubility polytherms of the salts. The results are interpreted in terms of a phenomenological model of the structure of electrolytes aqueous solutions.

Sol-gel synthesis of nanostructured complex perovskite-type layered ferrites

I. Chislova, V. Panchuk, I. Zvereva

*Saint-Petersburg State University, Petrodvorets, Universitetsky pr. 26,
Saint-Petersburg, 198504 Russia
i.v.chislova@gmail.com*

There are not so many sufficient examples of the synthesis by low temperature “soft chemistry” methods of highly dispersed powders, fibers, thin films of compounds with complex cationic composition.

In this report we present the results for nanodispersed perovskite-like ferrites GdFeO_3 , GdSrFeO_4 , $\text{Gd}_2\text{SrFe}_2\text{O}_7$ synthesized by sol-gel technique. GdSrFeO_4 and $\text{Gd}_2\text{SrFe}_2\text{O}_7$ belong to Ruddlesden-Popper phases and exemplify the 1/1 and 2/1 intergrowths of ABO_3 Perovskite (P) and AO Rock-Salt (RS) type slabs.

At the present time there is no information of the synthesis conditions and physicochemical properties for nanodispersed layered oxides GdSrFeO_4 and $\text{Gd}_2\text{SrFe}_2\text{O}_7$. As for the complex oxide GdFeO_3 - with perovskite type of structure it was recently reported that this compound obtained by ceramic technology shows multiferroic properties at 2.5 K [1].

The magnetic properties of these oxides in nanocrystalline state and their dependence on the size of particles have not been investigated yet. The size of particles is also very important for increasing the catalytic activity. Thus it is very necessary to obtain the complex oxide GdSrFeO_4 that was used as a catalyst [2] and more stable oxide $\text{Gd}_2\text{SrFe}_2\text{O}_7$, which has not been studied in detail.

Complex oxides GdFeO_3 , GdSrFeO_4 and $\text{Gd}_2\text{SrFe}_2\text{O}_7$ were synthesized by sol-gel technology and by high temperature solid state reactions. The sol-gel technology was performed by using citrate-nitrate techniques in case of GdFeO_3 , GdSrFeO_4 , $\text{Gd}_2\text{SrFe}_2\text{O}_7$ and glycine-nitrate techniques in case of GdFeO_3 . Determination of the temperature of formation of complex oxides GdSrFeO_4 and $\text{Gd}_2\text{SrFe}_2\text{O}_7$ has been performed by

differential thermal analysis. Methods of powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used for the determination of the structure and morphology of synthesized samples. The decrease in size of particles from 10 μm , obtained by high temperature ceramic synthesis, to 50–200 nm, obtained by sol-gel technology, was demonstrated (Fig.1). Photon correlation spectroscopy have been used for evaluation average particle size and size distribution. Photon correlation spectroscopy data are consistent with scanning electron microscopy at the maximum amount - the length of the particles.

The valent state of iron atoms in complex perovskite-like ferrites have been investigated using Mössbauer spectroscopy. Heterovalent state of iron atoms (Fe^{+3} and Fe^{+4}) was determined only in layered oxide GdSrFeO_4 . It was shown that iron atoms of complex ferrites obtained by sol-gel technology were in different oxygen surrounding, that hasn't been detected for the same compounds synthesized by high temperature solid state reactions.

The results indicate that complex ferrites obtained by sol-gel method exists not only in ultradispersed state but also in heterovalent iron state with oxygen vacancies that is necessary for catalysis.

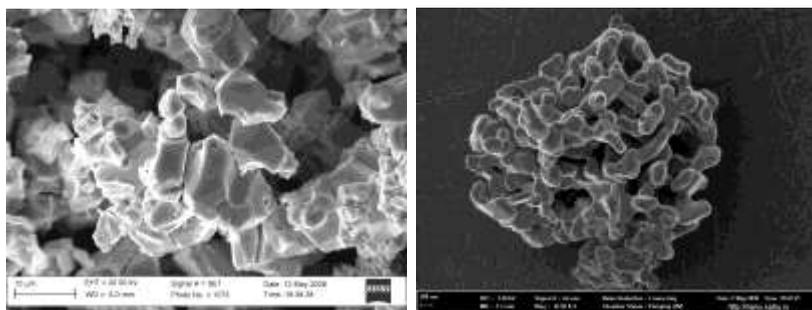


Fig. 1. Microphotographs of perovskite-like layered oxide $\text{Gd}_2\text{SrFe}_2\text{O}_7$ synthesized by ceramic (left) and sol-gel technology (right)

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A theoretical Study of Cluster Inclusions on Siliceous Mordenite and Erionite Zeolites

Joel Antúnez-García, Donald H. Galván, Vitalii Petranovskii

*Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México (CNyN-UNAM). Ensenada, B.C. México
jantunez@cny.n.unam.mx*

ABSTRACT

A theoretical study of the configuration and electronic properties of different composites obtained by the inclusion of certain clusters inside the main channel or cavity of both siliceous mordenite (MOR) and erionite (ERI) zeolites, is presented in this work in terms of periodic density functional theory method. Composite materials have been built by the insertion of copper oxides Cu_2O_x ($x=1-4$) and copper Cu_x ($x=2,4,6,8$) clusters in the crystalline structure of MOR and ERI zeolites. Results indicate that regardless of the clusters which are considered inside of zeolite frameworks, the mechanism of reducing the forbidden band gap observed in the composites, is the same. However, the proportion and participation of distinct orbitals at the Fermi level, and charge response of distinct equivalent sites of the frameworks, depends upon the local environment on which clusters are embedded.

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Study of hydroxyapatites structure by electron paramagnetic resonance

Anastasia Kultaeva, Stanislav Sukharzhevskii, Artem Antipov

Department of Quantum Magnetic, Faculty of Physics, Saint-Petersburg State University

anastasia.kultaeva@gmail.com

INTRODUCTION

The problem of determining the age is fundamental to such scientists as historians, archaeologists and geologists. For the dating of organic objects, which are more than the upper limit of the radiocarbon method can be applied EPR dating. The dating of tooth enamel - one of the most remarkable achievements of the EPR method. The suitability for the dating of teeth depends on the mineral hydroxyapatite.

PROBLEM OF DATING

Despite the prevalence of the EPR - dating until now there is no definite method for the dating of the bones. To construct this method solved problems following items:

- study of nature paramagnetic centers in hydroxyapatite by EPR – spectra (Fig. 1);
- determination of sample preparation methods;
- establish the structural features of hydroxyapatite in the enamel of the tooth.

CONCLUSIONS

In the course of work have been obtained the electron paramagnetic resonance spectra, which indicating that the tooth enamel - the crystal with partially – oriented.

Such structural peculiarities have a hydroxyapatite crystal in bone tissue (Fig. 2).

These results may allow to create a model for dating of bone tissue in paleontological objects.

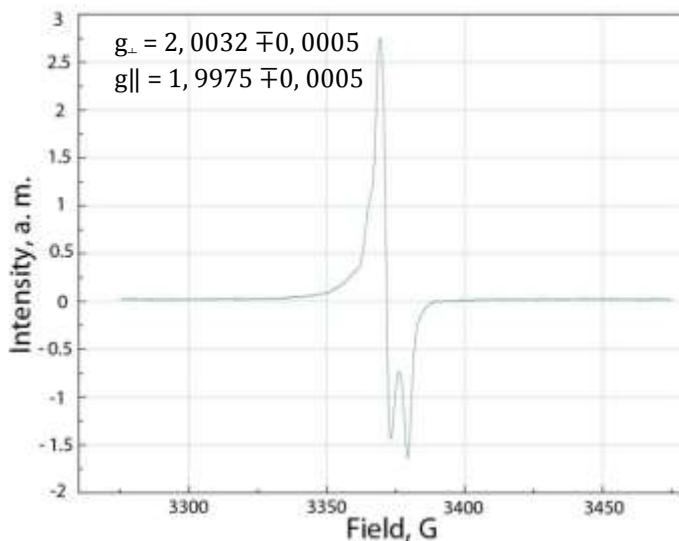


Fig. 1. ERP-spectra of CO_2^- in tooth enamel.



Fig. 2. Hydroxyapatite crystal of bone tissue.

ACKNOWLEDGMENT

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***Ab Initio* Calculation of ^{29}Si NMR Chemical Shift in Mordenite**

Y.M. Zhukov, M.G. Shelyapina

Dept. of Quantum Magnetic Phenomena, St Petersburg State University
yuri.m.zhukov@gmail.com

Electronic structure calculation is a key point, which helps to understand physical basis for formation of zeolites. Experimentally the electron structure can be tested by nuclear magnetic resonance (by measuring chemical shifts at magnetic nuclei). Here we report on the results of our calculations of ^{29}Si NMR chemical shifts in mordenite

The ^{29}Si NMR magnetic shielding constants are subsequently calculated using the coupled perturbed Hartree-Fock method with gauge including atomic orbitals (GIAO). The mordenite was modeled by a neutral fully protonated species [1]: the cluster $[\text{Si}_5\text{H}_{12}\text{O}_{16}]$ (see Fig.1).

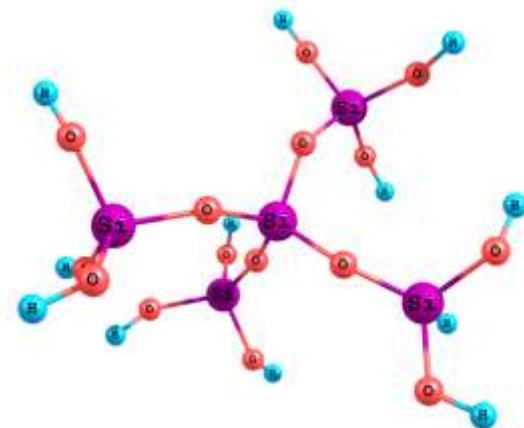


Fig.1. The $[\text{Si}_5\text{H}_{12}\text{O}_{16}]$ cluster representing a fragment of the mordenite cage.

The cluster represents a 5-ring fragment of the mordenite cage. The coordinates of Si, Al and O atoms are taken from the refined single crystal x-ray structure [2]. To make cluster electrically neutral, on the one hand, and to balance the electron density distribution inside the cluster, on the other hand, all broken bonds of outer oxygen atoms were “closed” by hydrogen atoms. Hydrogen atoms were placed at an

appropriate O–H distance (0.91 Å) along the bonds to the next Si or Al atom in the crystal.

The GIAO-HF calculations were carried out with using different basis sets: 3-21G, 6-31G, 6-311G. For better description of hydrogen bonds diffuse functions were used. In Table I we listed the calculated chemical shift at the ^{29}Si nucleus for the central Si atom of the $[\text{Si}_5\text{H}_{12}\text{O}_{16}]$ cluster simulating the mordenite and in tetramethylsilane, the usual ^{29}Si NMR experimental reference.

Table I. The calculated values of the ^{29}Si NMR chemical shift.

| Basis set | Chemical shift (ppm) | |
|-----------|----------------------|---|
| | tetramethylsilane | $[\text{Si}_5\text{H}_{12}\text{O}_{16}]$ cluster |
| 3-21G | 538.4415 | 641.3212 |
| 3-21+G | 556.1157 | 643.7153 |
| 6-31G | 484.6132 | 539.2029 |
| 6-31+G | 479.8453 | 538.3731 |
| 6-311G | 431.8416 | 500.7993 |
| 6-311+G | 434.1884 | 501.5059 |

Calculations showed that the chemical shift is rather sensitive to the basis set choice: its value decreases with increasing the basis quality. However, addition of diffuse functions does not have any significant impact. The results of our simulations are consistent with experimental data for aluminocilicates with Si atom coordinated by four other Si atoms [3].

ACKNOWLEDGMENT

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^1H NMR study of hydrogen diffusion in the transition metal alloys lattice

Anna Vyvodtceva¹, Marina Shelyapina¹, Alexei Privalov²,
Franz Fujara², Daniel Fruchart³

¹*Faculty of Physics, St Petersburg State University, 198504, 1
Ulyanovskaya st., St Petersburg, Russia*

²*Institute für Ferstkoerperphysik, TU Darmstadt, 64289,
Hochschulstarsse 6, Darmstadt, Germany*

³*MCMF Institut Néel, CNRS, BP 166, 38042 Grenoble Cedex 9, France
anna.vyvodtceva@nmr.phys.spbu.ru*

Metal hydrogen systems have been extensively studied last decades due to their ability to be used as hydrogen storage materials. A good hydrogen storage material has to fulfill a number of criteria, such as a high hydrogen storage capacity, a low hydrogen desorption temperature, a high hydrogen sorption kinetics, a reversibility of the hydrogen sorption reaction etc. Despite a comparatively low hydrogen storage capacity (up to 3.8 wt% for selected compositions) Ti-V-Cr alloys exhibit low temperature of the hydrogen release and rather high hydrogen sorption kinetics [1].

Kinetic properties of hydrogen storage materials are governed by their microstructure. To investigate the hydrogen mobility in the metal lattice nuclear magnetic resonance (NMR) method was used. NMR relaxometry probes internal field fluctuations on an atomic scale so that its measurements can be very sensitive to small changes in the system under observation. One area where NMR is substantially independent is in diffusion measurements. The onset of diffusion of hydrogen has a clear effect on NMR observations. Diffusion constants of hydrogen can be measured directly using NMR with only limited information of other properties of the Me-H system. Furthermore, with knowledge of host metal structure, diffusion mechanisms can be identified.

In this contribution we report on the results of our experimental study of the hydrogen diffusion in Ti-V-Cr alloys of various compositions ($\text{TiV}_{0.8}\text{Cr}_{1.2}\text{H}_{5.29}$, $\text{Ti}_{0.5}\text{V}_{1.9}\text{Cr}_{0.6}\text{H}_{5.03}$ and $\text{Ti}_{0.33}\text{V}_{1.27}\text{Cr}_{1.4}\text{H}_{1.13}$). The

hydrogen diffusion coefficients (D) were measured by ^1H NMR in ultra-high static field gradient instrument [2] at frequency 100 MHz with low field gradient of 51.27 T/m. Such a technique allows us to measure proton self-diffusion coefficients even for short spin-spin relaxation times T_2 , when the pulsed field gradient method is not applicable. To enable application of long diffusion times and, thus, small diffusion coefficients, the stimulated echo sequence was used.

Sometimes the apparent self-diffusion coefficient measured in experiments is lower than the real one. This is the case if the diffusion is restricted by geometry factors of studied samples, usually by the size of pores, inside which particles diffuse [3]. In our case this restriction factor is the crystallite size. To eliminate this effect we have also measured the diffusion coefficients with varying times between pulses to optimize the experiment conditions.

All hydrides exhibit rather slow hydrogen diffusion ($D = 1\div 3 \times 10^{-11} \text{m}^2/\text{s}$). Such low values of the hydrogen diffusion coefficient are quite typical for transition metal hydrides with a high hydrogen concentration [4]. It was found that the activation energy increases in the series $\text{Ti}_{0.5}\text{V}_{1.9}\text{Cr}_{0.6}\text{H}_{5.03} < \text{TiV}_{0.8}\text{Cr}_{1.2}\text{H}_{5.29} < \text{Ti}_{0.33}\text{V}_{1.27}\text{Cr}_{1.4}\text{H}_{1.13}$. The measurements have shown that D is independent on mixing time which means that diffusion is unrestricted.

ACKNOWLEDGMENT

This project is supported by German-Russian Interdisciplinary Science Center (G-RISC).

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Nanospecies obtained by thermal reduction of Cu^{2+} - Ag^+ - Zn^{2+} trimetallic system on mordenite

Inocente Rodríguez-Iznaga¹, [Vitalii Petranovskii](mailto:vitalii@cnyn.unam.mx)² and Felipe Castellón Barrasa²

¹*Instituto de Ciencia y Tecnología de Materiales (IMRE) - Universidad de La Habana. Cuba.* ²*Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada 22800, México.*

Contact Authors: vitalii@cnyn.unam.mx, inocente@imre.oc.uh.cu

INTRODUCTION

New materials of diverse uses can be obtained from modified zeolite with metal nanospecies prepared via ion-exchange with cations of such metals as Cu, Zn and Ag. Reports are mainly known for monometallic systems. Significant differences in the metal nanospecies are observed even in binary systems [1,2], which in line influences to their properties. The aim of this work was to study the ternary (Cu^{2+} - Ag^+ - Zn^{2+})/Mordenite system and to evaluate the mutual influence of these cations on the obtained nanospecies of copper and silver during thermal reduction in hydrogen flow.

EXPERIMENTAL

Synthetic Na-Mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio equal to 13, supplied by Zeolyst International, was firstly exchanged with Cu^{2+} , Zn^{2+} or Ag^+ from 0.1 M solutions of corresponding nitrates. Exchange was done during 24 h, with solid/solution ratio of 1g/5mL; the solutions were replaced after 12 h. Cu^{2+} and Zn^{2+} exchange was performed at 100°C; Ag^+ was exchanged at room temperature. To obtain trimetallic forms, CuMor and ZnMor were treated with mixed in 5:1 ratio $\text{Zn}(\text{NO}_3)_2/\text{AgNO}_3$ and $\text{Cu}(\text{NO}_3)_2/\text{AgNO}_3$ solutions, respectively, under the similar conditions at room temperature. The resulting samples are referred as AgCu-ZnMor and AgZn-CuMor. The Cu, Ag and Zn content in CuMor, AgMor and ZnMor samples was 3.9%, 13.8% and 1.8%, respectively; in AgZn-CuMor -- 3.2%, 0.7% and 0.9% and in AgCu-ZnMor -- 1.6%, 0.7% and 1.4%, respectively. These samples were reduced in H_2 flow at 50–450°C

during 4 h, after this they were cooled in H₂ to room temperature. The samples, before and after the reduction, were studied by XRD and UV-Vis diffuse reflectance spectroscopy.

RESULTS AND DISCUSSION

XRD patterns of the CuM, AgM and trimetallic samples reduced at 250°C -450°C show new peaks at 38.11° and 44.29°, corresponding to metal Ag, and at 43.2° and 50.3° corresponding to metal Cu. Reduced ZnM do not show any new peaks in all temperature range used. These peaks are not present in the trimetallic and AgM forms reduced at 150°C, while for CuM metal Cu is present. This suggests that the aggregation of the reduced Cu species is limited in the trimetallic systems. UV-vis spectra of the reduced trimetallic samples show that a 320 nm band, associated with Ag₈ clusters starts from 100°C only, while it is very intense for AgM reduced at 50°C and 100°C, which suggest the limited formation of Ag clusters in trimetallic systems. Also, a decrease of Cu²⁺ band (800-850nm) is observed, not typical for CuMor reduced at this temperature. This suggests that Zn²⁺ and Ag⁺ facilitate Cu²⁺ reduction in the trimetallic systems. From 125°C the plasma resonance band of nanometer size colloidal copper particles at 550 nm, the quasi-colloidal silver particles band at 400 nm, and other band at 290 nm associated with Ag clusters begin to appear in the UV-Vis spectra of trimetallic samples. The intensity of the Cu plasma resonance band increase with the temperature, while the intensity to the silver clusters and quasi-colloidal particles decrease. From 300°C the silver clusters disappear completely, and the optical properties of the samples start to be similar to the so called “metal blacks”, that is finely dispersed metals with structureless absorption over UV-Vis range [1,3].

CONCLUSIONS

Hydrogen reduction of Cu²⁺-Ag⁺-Zn²⁺ trimetallic system in mordenite was studied. The Ag⁺ and Cu²⁺ reduction is sensitive to the presence of co-cations. The temperature range of Ag and Cu aggregation and nanoparticles formation is significantly influenced. The use of trimetallic system leads to the diversity in obtained reduced species both for Cu and Ag.

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