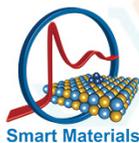


December 6-7, 2021
Rostov-on-Don, Russia



BOOK OF ABSTRACTS

International Workshop on
Synchrotron and Neutron Radiation



6-7 December, 2021, Rostov-on-Don

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Production of hybrid antibacterial coatings

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Modern methods of reducing microbiological contamination of surfaces are based on application of anti-adhesive and biocidal coatings.

Recently production of inorganic-organic hybrid coatings has received great development, which made it possible to create materials with unique characteristics due to the synergism of the properties of their constituent parts [1].

This work is devoted to the creation of antibacterial coatings based on transition metal oxides immobilized in a polymer matrix of chitosan using the method of non-stationary electrolysis.

The coatings formation was carried out on a prepared sample surface under the action of alternating asymmetric current of industrial frequency, representing two half-sine waves of different amplitudes. As a working electrode, AISI 304 grade steel macroelectrodes with geometric dimensions of 30x20x0.5 mm (on both sides) were used, counter electrodes were nickel. The metal oxides deposition was carried out from aqueous solutions of electrolytes containing cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$), nickel chloride ($\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$), surfactant, chitosan.

The surface morphology of the developed antibacterial coating has a crack-like structure. According to X-ray spectral microanalysis, the main elements are C, O, Co, Ni. Analysis of IR spectroscopy proved the immobilization of metal oxides in the polymer matrix of chitosan. According to TEM data, it was found that the hybrid coatings consist of CoO and Ni (OH)₂ phases.

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References

- [1] N. Choudhary, M. A. Islam, J. H. Kim (et al). Two-Dimensional Transition Metal Dichalcogenide Hybrid Materials for Energy Applications. Nano Today, vol 19, 16-40 (2018).

Operando FTIR diagnostics of nanocatalysts to optimize the parameters of the catalytic reaction

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In a catalytic reaction, researchers always strive to maximize the yield of the reaction product. However, these reactions are often carried out at constant gas flows and readily suboptimal conditions, such as catalytic reactor volume and dimensions, masses of catalyst, flow ratios, and other experimental conditions and setup parameters. Sometimes, one is trying to improve the catalyst itself when improvement of experimental conditions can have more impact on the reaction yield itself.

We suggest using machine learning (ML) algorithms to select the optimal values of CO and O₂ flows in a CO oxidation reaction catalyzed by alumina-supported Pd nanoparticles (Chimet S.p.A). For this aim, we carry out simultaneous MS and FTIR measurements. The experimental procedure consists in varying the gas flows at a constant temperature (433 K). A series of experiments were carried out with different catalyst contents: pure catalyst Pd/Al₂O₃ and diluted 5 and 10 times in Al₂O₃. At the same time, different proportions of carbon monoxide and oxygen were used (3:1, 2:1, 3:2). These experiments will form a database for training the algorithm. From the obtained FTIR spectra, we can determine the conversion by peak areas. Mass spectroscopy also allows us to estimate conversion, this requires calibration curves for each gas (Ar, O₂, CO, CO₂).

The essence of this research is the use of non-stationary values of gas flows to increase the yield of the reaction product and the most important thing from an environmental point of view is the rational use of gas during the reaction.

Composite porous nanoparticles based on UiO-66 with PEG shell and cyanine fluorescent dye as drug carriers

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Metal-organic frameworks (MOF) are a class of porous materials with a modular structure [1]. These compounds are used for tasks such as targeted drug delivery. UiO-66 has such critical properties for biomedical applications as low toxicity, nano-size, and stability. To improve the biological compatibility and stability of the aqueous dispersion, the surface of UiO-66 is coated with biocompatible polymers. In present work, the surface of UiO-66 was modified with polyethylene glycol (PEG) during synthesis [2]. The influence of the degree of PEG polymerization on the size, morphology and surface charge of UiO-66 nanoparticles has been investigated. Single-phase materials with a high degree of crystallinity were obtained. In addition, a large surface area is preserved. The high charge of the surface in an aqueous medium shows the possibility of creating a stable suspension. To visualize the distribution of particles with a modified surface in mice, a Cyanine5.5-NHS ester fluorescent label was used.

Thus, the materials obtained based on UiO-66 with a modified surface are promising as nano-containers for the delivery of biologically active substances.

This work was supported by Russian Science Foundation, (Project № 19-73-10069).

References

- [1] Yaghi O.M., O'Keeffe M., Ockwig N.W., Chae H.K., Eddaoudi M., Kim J. // Nature. 2003. V. 423. № 6941. P. 705.
- [2] Butova V.V., Burachevskaya O.A., Medvedev P.V., Gorban I.E., Kuzharov A.A. Trushina D.B., Soldatov M.A. // Journal of Surface Investigation. 2021. V. 15. № 5. P. 920 - 926.

Band gap estimation using descriptors dataset of materials and machine learning

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Artificial intelligence, Machine learning, Deep Learning

Artificial intelligence (AI) is the science of creating smart things, or in other words, performing human tasks by machines. Today computers reached significant success in computer vision, natural language processing, etc. The bottom line is that AI is not just machine learning (ML) or creating things. Generally speaking, AI is something that solves human problems in some way [1]. ML is a branch of AI that focuses on the use of models and algorithms to solve and recognize patterns using data and examples. If an artificial system can constantly learn, make decisions based on data rather than algorithms, and change its behavior, then this is ML system [2].

My report is devoted to the problem of band gap estimation of materials using a data set of descriptors. The data set is taken from the Materials Project [3] database using REST API requests. The data set consists of a total of 4608 samples of ABC3 stoichiometry materials and their band gaps. Data set was preprocessed to get a list of atomic-based descriptors generated from statistical information and distance metrics using Pymatgen (Python Materials Genomics) library. Then an exploratory data analysis was performed and the distribution for the values of the band gap was estimated. The quantity of metals was estimated from selected materials. Dataset was split into train and test parts with band gap non-zero values and XGBoost and Random Forest ML regressors were used. The mean absolute error (MAE) and the R2 score metric were used to estimate the quality of the prediction.

References

- [1] John Markoff (2015). "Homo Roboticus? People and machines in search of mutual understanding".
- [2] Pedro Dominguez (2015). "The Supreme algorithm. How Machine Learning will Change our World".
- [3] The Materials Project. URL:<http://materialsproject.org>

Rational design of bimetallic Au- and Pd- based photocatalysts for methane-methanol conversion

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The aim of the work is to develop a smart system for the synthesis of bimetallic photocatalysts based on gold and palladium for the direct conversion of methane to methanol.

In the course of the research work, new ways of direct photocatalytic conversion of methane into liquid fuel on bimetallic catalysts would be developed. Bimetallic photocatalysts Pd-Au in the form of nanoparticles stabilized in a colloidal solution will be used as a prototype for research, with the help of which it is planned to refine the process. The developed system will make it possible to obtain nanoparticles with predetermined properties, which is a necessary step for solving the problem of optimizing catalysts for the direct conversion of methane into methanol.

Catalysts based on gold and palladium are promising materials for the conversion of methane to methanol, which is a process of enormous economic importance [1]. A number of studies suggest that the photostimulation of bimetallic catalysts in this reaction will improve this technology [2], which would significantly reduce the cost of the reaction and increase the economic feasibility of this process. Thus, the study of bimetallic nanoparticles is an urgent task for the development of effective catalysts for the conversion of methane to methanol.

References

[1] Agarwal, N. et al. Aqueous Au-Pd colloids catalyze selective CH₄ oxidation to CH₃OH with O₂ under mild conditions, *Science* 358, 223–227 (2017);

[2] Gondal, M. A., A. Hameed and A. Al-Suwaiyan, Photocatalytic conversion of methane into methanol using visible laser, *Applied Catalysis Vol* 243, pp 165 – 174 (2003).

Two-component ground normal state and pseudogap emergence in cuprate superconductors

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We are modeling the two-component ground normal state of systems with strong long-range electron-phonon interaction with the aim to study the pseudogap (PG) nature. Coexistence of two components, namely large bipolarons and delocalized carriers, is a feature of such system [1]. We consider quasiparticles (QPs) that emerge in cuprates in presence of additional charge ordering potential. We show that this potential transforms Bloch QPs into distributed wave packets with different momentums in areas with different potential. By modeling the carrier dispersion in the hole-doped cuprates and calculating the momentum-space trajectories of the new QPs we found that topology of the hole-doped cuprate dispersion forbids QPs with average momentums near antinode. Considering photoemission of carriers only from permitted QP states, we calculate antinodal angle-resolved photoemission spectrum (ARPES) that has all the features characteristic of the PG behavior in cuprates [2]. In the frames of the suggested approach we study also emergence of inhomogeneity in the PG width due to inhomogeneous distribution of dopant ions.

References

- [1] A. E. Myasnikova et al. (2019). Strong long-range electron-phonon interaction as possible driving force for charge ordering in cuprates. *J. Phys.: Condens. Matter*, 31, 235602 (2019).
- [2] M. Hashimoto et al. (2010). Particle-hole symmetry breaking in the pseudogap state of Bi2201. *Nat. Phys.*, 6, 414-418 (2010).

Porous Microcarriers as a Novel Platforms for Encapsulation, Storage, And Controlled Release of Reactive Oxygen Species

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Microencapsulation and targeted delivery of reactive oxygen species (ROS) open a venue for new non-toxic and biodegradable systems. Here, we employ polymeric carriers either as a container to encapsulate ROS with the possibility of a controlled release or as an agent to produce ROS under the action of NIR light directly to the site of interest. We show ordered arrays of microcontainers made of polylactic acid functionalised with carbon dots to encapsulate ROS and release it in response to NIR laser treatment with a high spatial resolution. Suspensions of polyelectrolyte microcontainers were employed to encapsulate zinc phthalocyanine PTD agent which produces singlet oxygen in response to NIR laser treatment. Both systems were tested in vitro and demonstrated a high level of biocompatibility with low cytotoxicity. The developed systems promise prospective delivery routes in many areas such as wound healing by time and site-specific release.

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Electrochemical Preparation of Magnetic Fe₃O₄@MIL-88A Nanocomposite

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In recent years, one of the trends in scientific research has been targeted drug delivery using various external forces, such as external electric, ultrasonic or magnetic fields. In such systems, under the influence of external forces, drugs move and accumulate in certain places. At the same time, systems containing magnetic nanoparticles are the most attractive due to their efficiency, easy handling, and relative cheapness.

Magnetic composites containing nanoscale organometallic coordination polymers or MOFs deserve special interest. It is due to the high porosity of this type of material, which makes them an extremely promising material for targeted drug delivery. First of all, this applies to non-toxic MOFs, such as MIL-88a, consisting of iron and fumaric acid.

In connection with the above, an attempt has been made in this work to obtain a magnetic nanocomposite based on MIL-88a. The preparation of such a composite consisted of two stages: the production of Fe₃O₄ magnetic nanoparticles and further synthesis of MIL-88a in the presence of magnetic nanoparticles. The peculiarity of this work is that both magnetic nanoparticles and MIL-88a were obtained by the electrochemical method.

Magnetic nanoparticles were obtained by electrolysis of a water-alcohol mixture with iron electrodes. As a result of the half-hour synthesis, magnetic nanoparticles were formed in the reaction medium, then centrifuged and dried (Figure 1 left).

The resulting Fe₃O₄ nanoparticles were then added to the electrochemical system to produce MIL-88a. The synthesis took 30 minutes, with iron electrodes and an aqueous alcohol medium, but in the presence of fumaric acid. It led to forming a magnetic composite consisting of diamond-like MIL-88a particles coated with magnetic nanoparticles (Figure 1 right).

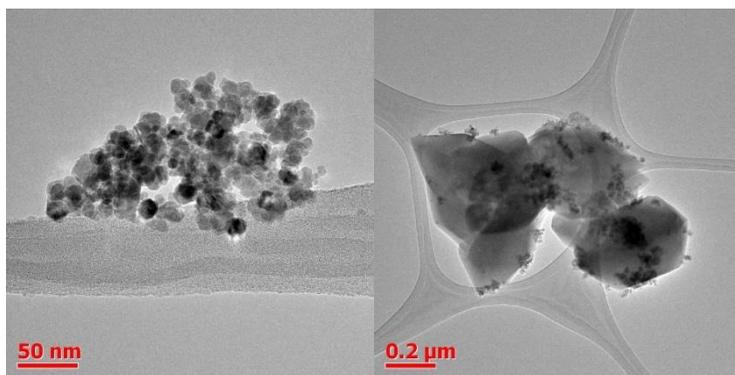


Figure 1. Transmission electron microscopy of magnetic nanoparticles (left) and magnetic composite Fe₃O₄@MIL-88A (right)

This work was supported by Russian Science Foundation, (Project № 19-73-10069).

Speciation of Ru Molecular Complexes in Homogeneous Catalytic System: Fingerprint XANES Analysis Guided by Machine Learning

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X-ray absorption spectroscopy is a powerful tool for the characterization of local atomic structure. Commonly, bond lengths and coordination numbers are extracted from the extended energy region of spectrum (EXAFS). However, for many diluted systems, such as homogenous catalysts, with a low concentration of the active component and under *in situ* or *operando* conditions, one cannot collect EXAFS data sufficient the quantitative analysis.

Considering the case of a homogenous ruthenium-based catalyst, where the ligand surrounding of ruthenium atoms can change from Br to CO depending on the reaction conditions, we establish here an effective machine learning (ML) approach based on the descriptor analysis of spectral features. After the training procedure, the algorithm predicts both the ligand surrounding of ruthenium and the distances to Br and CO ligands. The prediction quality of the approach was verified by means of a cross-validation procedure applied to the mixture of compounds and was validated for experimental spectra of reference RuBr₃ and [RuBr₂CO₃]₂ complexes. This work describes a practical route to improve classical fingerprint analysis and linear combination fit by more sophisticated data science algorithms.

Complex investigation of Markovka, Polujamki, Sayh Al Uhaymir 001, Dhofar 020 and Jiddat Al Harasis 055 ordinary chondrites

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Complex diagnostics of element and phase composition, Fe and Ni oxidation states in Markovka (H4 type), Polujamki (H4 type), Sayh Al Uhaymir 001 (L5 type), Dhofar 020 (H4/5 type), Jiddat Al Harasis 055 (L4-5 type) ordinary chondrites has been done using micro X-ray fluorescence (XRF) analysis, scanning electron microscopy (SEM), Mössbauer spectroscopy, synchrotron-based X-ray diffraction (XRD) and X-ray absorption near-edge structure (XANES) spectroscopy [1]. Mössbauer analysis has shown that the chondrites contain Fe in the form of olivine, pyroxene, goethite, hematite and troilite. The Fe-Ni-Co metal grains have been also found in Markovka and Polujamki. The phases obtained by Mössbauer analysis agree with the data determined by XRD. The other phases obtained by XRD refinement are clinopyroxene, chromite, maghemite, albite, anorthite and whitlockite. Fe and Ni *K*-XANES spectra have been used to estimate Fe and Ni oxidation states in the chondrites. The lowest $\text{Fe}^{3+}/\Sigma\text{Fe}$ values equal to 0.30 and 0.35 have been found for Sayh Al Uhaymir 001 and Polujamki. And the highest $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios equal to 0.61, 0.68 and 0.69 have been obtained for Jiddat Al Harasis 055, Markovka and Dhofar 020 samples. Element ratios from XRF analysis and magnetic susceptibility data have been used to compare investigated samples with the existing databases. The obtained multispectral data are of importance for the further understanding of meteoritic processes.

The research is supported by the grant 16.3871.2017/4.6 of the Ministry of Science and Higher Education of the Russian Federation.

[1] L.V. Guda, A.N. Kravtsova et al. Complex diagnostics of ordinary chondrites Markovka, Polujamki, Sayh Al Uhaymir 001, Dhofar 020 and Jiddat Al Harasis 055 by X-ray techniques and Mössbauer spectroscopy. *Meteoritics & Planetary Science* (in press). DOI: 10.1111/maps.13769.

Prediction of interatomic distances by experimental Pd nanoparticles XANES spectra using machine learning algorithms

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X-ray absorption near edge spectroscopy (XANES) is an advanced technique to obtain structural information of materials such as Pd nanocatalysts. In contrast to the extended X-ray absorption fine structure (EXAFS) this method allows collecting signal even from diluted samples, during fast measurements and from laboratory X-ray absorption spectrometer. However, XANES is not completed method of analysis, while the amount of data collected grows exponentially. The main goal of this work is to use EXAFS analysis to obtain structural parameters of Pd nanoparticles, cut spectrum to the only XANES region and apply machine learning (ML) algorithms to predict interatomic distances. Over 8000 X-ray absorption spectra (XAS) of Pd nanoparticles processed by standard first-shell Fourier analysis to construct training set. We demonstrate how ML algorithm choice and data included in the training set affect on quality of prediction.

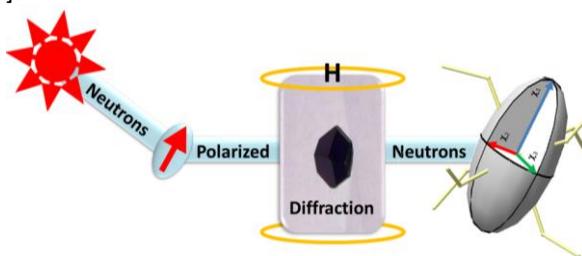
Polarized Neutron Diffraction and molecular magnetic anisotropy

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PND has proved to be particularly suitable for the study of magnetic molecular compounds and the determination of the spin density. This provides unique information on the paths of magnetic interactions and the nature of magnetic intra-or intermolecular coupling [1-2]. In this talk, we show on recent examples how we can go beyond the spin density reconstruction and use the local susceptibility tensor approach to study the magnetic anisotropy in molecular compounds [3].



This makes PND an excellent tool to help in the design of molecular-based magnets and especially single-molecule magnets for which strong uniaxial magnetic anisotropy is required.

References

- [1] B. Gillon, C. Mathonière, E. Ruiz, S. Alvarez, et al. *J. Am.Chem. Soc.*, 2002, 124(48), 14433–14441 ([link](#))
- [2] C. Aronica, E. Jeanneau, H. El Moll, D. Luneau, B. Gillon, et al., *Chem. Eur. J.*, 2007, 13, 3666-3674 ([link](#))
- [3] A. Gukasov and P. J. Brown, *J. Phys-Condens. Mat.* 2002, 14, 8831-8839.([link](#))
- [7] K. Ridier, B. Gillon, A. Gukasov, G. Chaboussant, A. Cousson, D. Luneau, A. Borta, J.-F. Jacquot, R. Checa, Y. Chiba, H. Sakiyama, M. Mikuriya *Chem. Eur. J.* **2016**, 22, 724-735 ([link](#))
- [8] O. Iasco, Y. Chumakov, F. Guegan, B. Gillon, M. Lenertz, A. Bataille, J. F. Jacquot, D. Luneau *Magnetochemistry* **2017**, 3 ([link](#))
- [9] F. Guégan, J. Jung, B. Le Guennic, F. Riobé, O. Maury, B. Gillon, J-F. Jacquot, Y. Guyot, C. Morell, D. Luneau *Inorg. Chem. Front.*, **2019**, 6, 3152–315 ([link](#))

Using synchrotron radiation to solve polynuclear structures of cobalt and nickel complexes

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Co(II, III) and Ni(II) coordination compounds are used in various fields, such as magnetochemistry, optics, medicine and catalysis [1,2]. The series of 36-nuclear Ni(II) complexes with substituted malonic acids, which are capable of exhibiting ferromagnetic behavior, were synthesized. The anionic framework is also capable of encapsulating various cations[3].

Complexes based on cobalt(III) with biologically active acylhydrazones are used as bactericidal agents [4]. Were obtained complexes, which are containing a large number of metal centers and bulky ligands in the unit cell.

Bulky ligands, a large unit cell, a large amount of solvent and small crystal size complicate the task of solution the structure using laboratory Moka and Cuka sources. The influence of a high-intensity synchrotron source on the solution of the exact structure of the complexes will be shown.

References

- [1] M. Carraro. and S. Gross (2014) *Materials*, 2014, vol. 7, p. 3956-3989;
- [2] L. Ungur, J.-P. Costes et al. (2013) *Inorg. Chem.*, vol. 52, p. 6328-6337;
- [3] A.V. Vologzhanina, E.N. Zorina-Tikhonova, A.K. Matyukhina (2017) *Russ. J. of Coord. Chem.*, vol. 43, p. 801-806;
- [4] D.S. Raja, N.S.P. Bhuvanesh, K. Natarajan (2012) *Dalton Trans.*, vol. 41, p. 4365-4378;

Potential application of metal-organic frameworks in the different remediation technologies

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Abstract

Metal-organic frameworks have attracted much attention in recent years, especially as newly developed porous materials. As such, they possess a wide array of potential applications including materials for adsorption and advanced oxidation processes. In this presentation, these potential applications of metal-organic frameworks are examined, and an outlook will be proposed. Finally, their applications will be presented for Fenton-like oxidation of organic pollutants and adsorption of potentially toxic elements by MOF composites for high and selective removal contaminants.

Drug carrier based on zirconium metal-organic frameworks

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Metal-organic frameworks (MOFs) are a class of porous materials that possess an adjustable three-dimensional crystal structure with a high specific surface area, chemical flexibility, tunable functional and structural characteristics [1].

UiO-66 and UiO-66-NH₂ were chosen as the carrier for the bioactive compound since they have a good biocompatibility [2]. D,L-Leucine was chosen as the model compound to be loaded into the pores due to its different functional groups: methyl, carboxylic and amino groups. We obtained nanoparticles of size 30-70 nm with specific surface areas of 1395 and 1000 m²/g for UiO-66 and UiO-66-NH₂, respectively. The materials obtained were characterized using various physical and chemical research methods. Experimental data showed successful loading of the preparation in an amount of 7-10 wt%. Analysis of IR spectra suggested the mechanism of interaction between leucine molecules and porous matrix through bond formation between CH₃-groups of leucine and benzene rings of linkers by CH- π interaction [3].

References

- [1] Rowsell, J. and O. Yaghi, *Metal-organic frameworks: A new class of porous materials*. Microporous and Mesoporous Materials, 2004. **73**: p. 3-14.
- [2] Cunha, D., et al., *Rationale of Drug Encapsulation and Release from Biocompatible Porous Metal–Organic Frameworks*. Chemistry of Materials, 2013. **25**(14): p. 2767-2776.
- [3] Butova, V.V., et al., *Loading of the Model Amino Acid Leucine in UiO-66 and UiO-66-NH₂: Optimization of Metal–Organic Framework Carriers and Evaluation of Host–Guest Interactions*. Inorganic Chemistry, 2021. **60**(8): p. 5694-5703.

DFT study of different Cu-oxo species formation in Cu-SSZ-13 catalyst.

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Zeolites are extensively used in heterogeneous catalysis as their inner cavities offer a confined environment providing high selectivity for a wide range of reactions [1]. Recent studies indicate the presence of two major Cu-sites in activated Cu-SSZ-13, namely redox-resistant Z_2Cu^{II} species hosted in 6MR of the CHA framework and redox-active $ZCu^{II}OH$ complexes hosted in the proximity of 1Al sites in 8MR [2]. In recent work by Pappas et al. [3] the linear combination between the reducibility of the Cu sites in Cu-CHA catalysts and methanol productivity was observed. Moreover, on the basis of XAS analysis and previously reported spectroscopic finding two different mechanism of Cu-oxo species has been proposed. The first one assumes the formation of $Cu^{II}_xO_y$ from $ZCu^{II}OH$ precursors, while the second one assumes some internal pathways [3]. In the present work the proposed mechanisms and its particular steps has been verified from the computational point of views. In such a way we have provided an estimation of Gibbs energy for each reaction step, considering high-T and low-T activation modes. It has been shown that formation of Cu-oxo sites is more thermodynamically feasible at high temperatures, because of lower energy required to form intermediates. Also, we found that the second reaction step leading to the formation of dimeric four-fold coordinated thermodynamically more favorable in the low temperature range. This agreed well with XANES/EXAFS analysis that declares higher relative fraction of four-fold coordinated species at 200 °C [3].

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References

- [1] J. S. McEwen, T. Anggara et al., *Catal. Today* **184** (2012) 129-144.
- [2] E. Borfecchia, K. A. Lomachenko et al., *Chem. Sci.* **6** (2015) 548-563.
- [3] D. K. Pappas, E. Borfecchia et al., *J. Am. Chem. Soc.* **139** (2017) 14961

Investigation of the binding sites of ethylene and 1-MCP in HKUST-1 both experimental and theoretical

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Metal organic frameworks (MOFs) are crystalline nanoporous materials comprised of small metal-containing clusters connected by polyfunctional organic ligands [1]. The ligands act as spacers, creating an open porous three-dimensional structure, with high pore volume and surface area. Recently, a Cu-based HKUST-1 MOF was shown effective for storage and release of ethylene and 1-methylcyclopropene implying the potential applications in food industry [2]. Here, we investigate ethylene and 1-MCP adsorption and desorption potteries of HKUST by means of in situ infrared spectroscopy and theoretical calculations.

Experimental infrared spectra were obtained for a commercial HKUST-1 sample (Basolite C300) in DRIFTS mode. The sample was activated in Ar at 180 °C for one hour to remove water coordinated to Cu ions and then exposed to 10% C₂H₄/Ar or 1-MCP flow at room temperature. The shift of the C-H wagging mode by 30 cm⁻¹ was observed indicating ethylene binding to unsaturated Cu-centers. The results were complemented by adsorption energies of ethylene and 1-methylcyclopropene on Cu-sites and corresponding vibrational frequencies calculated at DFT level of theory.

The results shed light on ethylene and 1-MCP binding to HKUST-1 for potential use as mediator and, respectively, inhibitor of fruit ripening.

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References

- [1] Zhou, H. C., Long, J. R., and Yaghi, O. M. Introduction to metal–organic frameworks. 2012, 112, 673–674
- [2] Chopra S., Dhupal S., Abeli P., et al. Metal-organic frameworks have utility in adsorption and release of ethylene and 1-methylcyclopropene in fresh produce packaging. Postharvest Biol. Tec. 2017, 130, 48-55

Eu³⁺-doped BaGdF₅ nanophosphors for CT and XPDT application

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One of the promising areas of deeply located malignant tumors treat is X-ray photodynamic therapy (XPDT) [1]. Nanocomposites for XPDT usually consist of two components: nanophosphor and photosensitizer. The nanophosphor re-emits X-ray radiation into visible light, the photosensitizer absorbs it and produces reactive oxygen species (ROS). In addition, nanophosphors containing heavy metals can be visualized by computed tomography (CT). In this work, we synthesized Eu³⁺-doped BaGdF₅ nanocomposites covered with various thicknesses SiO₂-shell and impregnated with a methylene blue photosensitizer. The core-shell morphology was confirmed by TEM and the possibility of tunable shell size was reported. The nitrogen adsorption/desorption isotherms showed a high porosity of the formed shell. This fact made it possible to facilitate the conjugation of nanophosphor and methylene blue with the formation of a promising composite for XPDT. On the other hand, the nanophosphor citrate-coating increased its biocompatibility and demonstrated a high CT contrast in the liver and spleen after intravenous injection.

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References

[1] Pogue, B.W.; Wilson, B.C. Optical and x-ray technology synergies enabling diagnostic and therapeutic applications in medicine. *J Biomed Opt* 2018, 23, 1-17

In situ FTIR as instrument for Pd nanoparticles structure investigation

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Fourier transform infra-red spectroscopy (FTIR) is known as a technique mostly sensible to the light molecules. In particular, CO is often used as probe molecule to estimate catalytic properties of nanocatalysts [1], but structural characterization involves wide range of techniques including synchrotron radiation [2]. Usage of FTIR to investigate both structural parameters and properties of adsorbed gases might significantly simplify laboratory characterization of materials. This work is a first step in development a method to derive structural information of Pd nanoparticles under exposure of H₂ and small flow of carbon monoxide using *in situ* DRIFTS spectroscopy. The set of structural features of CO region were investigated over different hydrogen flows, supported by DFT calculations and compared with X-ray absorption spectroscopy data.

References

- [1] Balandin, A. A. *Adu. Catal. Relat. Subj.* 1969, 19, 1.
- [2] A. L. Bugaev, A. A. Guda, K. A. Lomachenko, A. Lazzarini, V. V. Srabionyan, J. G. Vitillo, A. Piovano, E. Groppo, L. A. Bugaev, A. V. Soldatov, V. P. Dmitriev, R. Pellegrini, J. A. van Bokhoven and C. Lamberti "Hydride phase formation in carbon supported palladium hydride nanoparticles by in situ EXAFS and XRD" *Journal of Physics: Conference Series* 2016 712 (1) 012032 DOI: 10.1088/1742-6596/712/1/012032

Removal of heavy metals from water by porous materials

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The removal of pollutants from the industrial wastewater is a vital problem for human health because of their toxicity and limited drinking water resource. The fact that water pollutants could not be fully removed by conventional methods. To improve the existing methods, and to develop novel approaches to mitigate water pollution and offer eco-friendly durable approach, scientific community paid great attention and huge efforts. Recently, active carbon and zeolites adsorbent shown promising results; especially for water remediation in sustainable way. Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc.

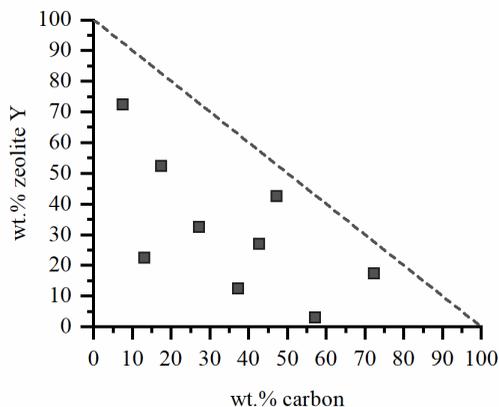


Figure 1. Weight fractions of sorbents generate according to IHS scheme.

The present work is focused to remediate heavy metals polluted wastewater using porous materials. Active carbon (VXC-72), and two types of zeolites (zeolite-Y and zeolite ferrierite) were chosen as cheap and commercially available

materials. The model wastewater contained Zn, As, Pb, Ni, Mn, Cd and Cu. Ten different mixtures containing the three sorbents in different fractions degenerated according improved Latin Hypercube Sampling (IHS) scheme were prepared (fig. 1). The setup based on infusion system was developed to fulfil the following conditions: low cost, operation in flow conditions, tunability and scalability. The polluted water was passed thorough the absorbent drop-wise at fixed rate of 6 drops per minute.

The elemental analysis of filtered water was carried out using Atomic Absorption Spectroscopy (AAS). The analysis of heavy metal concentrations in sorbents was performed by means of X-ray fluorescence (XRF) spectroscopy as well. All materials show good sorption for Cd and Cu. Ni and Zn were filtered with worse performance. The overall filtration quality decreased with increasing fraction of zeolite ferrierite. In addition, the dependency of total time of filtration was observed. The difference in time was attributed to the fact that that the sorbents were getting wet and were increasing its resistance to the flow in different way. Future development of the project will include automatization of the flow rates by using remotely controlled syringes, determination of the pH effect, the role of the total mass of the sorbent and the geometry of the filter.

Characterization of novel valence tautomeric cobalt complex using temperature- and time-resolved XANES studies

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This study is devoted to optical and X-ray structure characterization of novel (N-cyclohexyl-2-iminopyridine)(3,6-di-*tert*-butyl-*o*-benzosemiquinonato)(3,6-di-*tert*-butyl-catecholato)(Co₂) cobalt complex. Valence tautomeric (VT) transition from the high-spin Co^{II} to low-spin Co^{III} state was observed for Co₂ complex in both solid and liquid form. X-ray pump-probe study was performed at the Super-XAS beamline of the Swiss Light Source (Villigen, PSI). For the first time, we demonstrate a low-temperature nanosecond pump-probe XANES experiment revealing the valence tautomeric transition in a solution of Co complex.

The solid sample at room temperature was characterized as the LS Co^{III} state while the optical absorption spectra and Co K-edge XANES spectra in the toluene solution confirmed the HS Co^{II} state. At 213 K we registered a transient laser pump – X-ray probe signal in the Co₂ toluene solution that reproduced the difference between temperature stabilized HS and LS states. The relaxation kinetics to the ground state occurred with a time constant of 250 ± 50 ns. Our results indicate that reversible transition in the studied complex could be induced both under the influence of temperature and laser radiation. This study opens new perspectives for the pump-probe experiments for liquid samples at low temperatures.

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High-pressure *operando* investigation of Pd-MOFs for CO₂ hydrogenation

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Current investigation is devoted to the development of novel types of Zr-based metal-organic frameworks (MOFs) for catalytic applications. Using Pd-functionalized UiO-67 we have conducted an experiment on CO₂ hydrogenation. The local environment of Pd and Zr atoms in the catalysts was followed by *operando* XANES and EXAFS spectroscopies. The overall stability of UiO-67 was monitored by X-ray diffraction.

The CO₂ hydrogenation was run at different temperatures (240, 200, and 170 °C) and pressures (1 and 8 bar), controlling the conversion and selectivity to methanol by *online* mass spectrometer. Fourier analysis of the EXAFS data collected under reaction conditions showed that interatomic Pd-Pd distances are increased for all samples, being larger at lower temperatures and high pressures. Analysis of XANES spectra was performed using the MCR-ALS procedure to determine the number of pure species formed during treatment conditions, their spectra and concentration profiles. The whole experimental dataset was deconvolved into three components: metallic phase of palladium and two mixed palladium hydride and carbide phases. The hydride phase was stronger at high pressure and low temperatures, but was removed upon flushing in He, while the carbide phase was stable even after flushing. To reproduce the observed changes, the theoretical spectra were calculated using FDMNES code for the Pd surface with various adsorbed species placed in different configurations. The highest similarity with the experimental data was observed for bridge CO, which is the most probable reaction intermediate.

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**Nitrogen K-edge simulation and electronic structure investigation
for the f-elements organic extractants study**

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One of the most important problems in atomic industry is a huge amount of spent nuclear fuel and radioactive waste that should be buried. But preliminary recycling allows to critically reduce the radioactivity of the waste. Recycling process includes several steps of different elements separation. We deal with the problem of Am and Cm separation by liquid-liquid extraction with using of organic ligands as extractants. Am and Cm have the same ionic radii, stable oxidation states and similar electronic structure. Such a similarity in chemical properties and behaviour of these atoms makes the separation process very difficult.

Organic ligands based on the 1,10-phenantroline have suitable extraction parameters for Am/Cm separation. However, adding different functional groups in phenanrolines structure changes ligands properties (for example, selectivity, efficiency, radiolytic stability). We performed a thorough examination of the ligands electronic structure by quantum chemistry calculations realized in ORCA (versions 4.2 and 5.0). In order to understand the electronic structure, we analyzed atomic charges, ESP, distribution of electronic density by D4 RI-MP2/cc-PCVTZ RIJCOSX approach after geometry optimization by D4 TPSSH cc-PCVTZ RIJCOSX level of theory. We also compared characteristics obtained via RI-MP2 and DFT TPSSH methods using core-optimized and def2 groups of basis sets.

Moreover, we performed the nitrogen K-edge XANES analysis for a set of ligands with different functional substitutional groups for the core-electrons state research. TDDFT D4 TPSSH CPCM approach was used for the spectra simulations. We also compared set of functionals (B3LYP, TPSSH, PBE0, wB97x) in this task.

Applying machine learning algorithms and adaptive sampling approach for predicting binding energy of CO adsorbed on Pd nanoparticles

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FTIR spectroscopy of adsorbing molecular probes is a powerful technique for studying the surface morphology of noble-metal catalysts, such as Pd nanoparticles (NPs). However, experimental FTIR spectra are also significantly affected by coverage. Thus, estimation of the coverage as a function of P,T is desired for reliable interpretation of spectra.

As the first step for this, a precise approximation of adsorbate binding energy is required. In this work, we suggested the use of Machine Learning (ML) algorithms for binding energy prediction for CO adsorbed on the Pd₅₅ nanocluster. Due to a high dependency of binding energy from the nature of adsorbing site (top, bridge, or hollow) and its local coordination (e.g. bridge on particle edges, or regular Pd(100) and Pd(111) facets), we used radial distribution functions (RDF) as a descriptor for ML.

To prepare a training set, adaptive sampling was utilized in combination with DFT calculations. It allowed decreasing the number of required energy calculations compared to the randomly generated set. 6 ML algorithms were tested, and it SVM and Extra Trees algorithms shown the best precision (mean absolute error ca. 0.1 eV). We also compared RDF with such descriptors as mean Pd-C distances, coordination and generalized coordination numbers, angular distribution functions, and RDF was the most efficient. Finally, an energy surface was constructed for the Pd₅₅ and Pd₄₄ nanocluster using the trained SVM algorithm.

Thus, an approach that can rapidly and accurately predict binding energies for CO adsorbed on Pd NPs was developed.

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Sorption of calcium phosphates on a composite hydrogel for biomedical application

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Biodegradable composites have attracted a lot of interest in the last decade. They are widely used in medicine, including bone surgery. For orthopedics, the presence of calcium phosphates in the composite allows for a significant increase in biocompatibility, especially on the surfaces [1]. Our work aimed to study the possibility of obtaining composite hydrogel-calcium phosphate, depending on the protein in the composition of the hydrogel. As objects, we selected hydrogels based on polyvinylpyrrolidone with an average model weight with the addition of protein (zein, legumin, and pumpkin globulin), ascorbic acid, and xanthan gum. They were obtained under the influence of ultraviolet (UV) irradiation. All hydrogels were initially tested for swelling and rehydration. To study mineralization and adsorption, SBF solutions and a mixture of $\text{Ca}(\text{OH})_2$ and H_3PO_4 solutions were used. We also applied sequential immersion of hydrogels in solutions of calcium hydroxide and $(\text{NH}_4)_2\text{HPO}_4$. The waiting time was 24 hours in each case. According to the data of X-ray phase analysis, it was found that in composites with globulin and zein, calcium phosphate with a monetite structure crystallizes on the surface, and in the case of legumin, whitlockite is formed. The shape and size of the crystals are studied by an optical microscope. The results of the work allow us to conclude that samples with legumin are the most promising for further research because whitlockite is a more biocompatible calcium phosphate than monetite.

References

[1] Ramírez Caballero S. (2018) Composites made of bioceramic and chitosan physical hydrogel as potential bone substitutes (2018).

Porous calcium carbonate particles - structural aspects and prospects in drug delivery

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In last decades, porous inorganic particles were extremely investigated as potential drug carriers for controlled drug delivery purposes. Among them, nanostructured calcium carbonate in vaterite crystalline modification attracts a special attention owing to its biocompatibility, solubility at a slightly acidic pH, low toxicity, and good absorption capacity to a wide range of compounds.

The investigation of the vaterite particles formation in the wide size range and the analysis of their structure are the main purpose of current research. We show the possibility of the controlled synthesis of the vaterite particles as a result of mass crystallization from supersaturated aqueous solutions in a range from 400 nm to 5 μ m. We studied the structural features and porosity of the polycrystalline vaterite particles depending on the presence of the organic additives in the reaction mixture such as bovine serum albumin and cosolvents such as ethylene glycol or glycerol. To enhance encapsulation capacity of a low molecular weight compounds, we applied several loading approaches including sorption from water/alcohol mixture and freezing-induced loading. The efficacy of the developed vaterite particles loaded with anesthetic and sedative-hypnotic medicines were shown in vivo for intranasal delivery.

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Machine Learning application XANES analysis of Pd nanocatalysts

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Machine learning (ML) algorithms are a promising analytic tool that has found applications in many areas of science. This method has proven itself for tasks with a large number of parameters and is effective for big data processing. At the same time, near edge X-ray absorption spectroscopy (XANES) is a powerful tool widely used to determine the atomic and electronic properties of catalysts [1]. However, XANES analysis has not completed procedure of analysis, since there is no unambiguous method for determining the structural parameters, while the amount of experimental data increases exponentially every day. We offered 2 options for solving this problem. On the one hand, in many cases, the analysis of XANES data requires the construction of theoretical models with a huge number of variable parameters. Application of ML to fit theoretical experimental data opens up new horizons for determining the structural parameters of the investigated substance. We applied the Extra Trees method for the time-resolved XANES spectra of Pd NPs. The evolution of structural parameters was obtained and compared with the method of principal component analysis (PCA) and multivariate parametric interpolation [2,3]. We constructed a training set based on theoretical XANES spectra calculated in the FDMNES program for Pd NPs with different interatomic distances and in the presence of hydrogen and carbon-containing particles. On the other hand, it is used as an adjunct to extended-region X-ray absorption spectroscopy (EXAFS) analysis. We have labeled over 300 EXAFS spectra using a single-sphere analysis method. Then the Extra trees training was carried out for only XANES spectral regions, using tagged data. This approach made it possible to predict interatomic distances (Figure 1) with accuracy ~ 0.004 Å, that does not exceed EXAFS standard analysis accuracy.

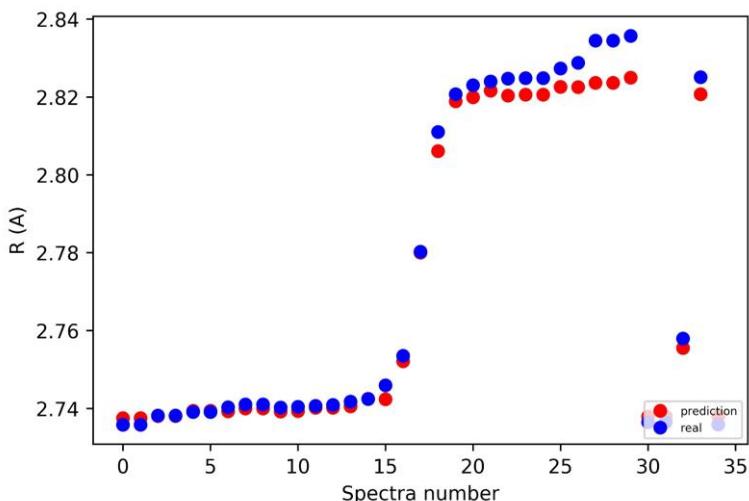


Figure 1 – Predicted values of RPD-Pd (red) and extracted by standard 1st shell Fourier analysis (blue)

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References

- [1] Guda, A. A., Guda S.A., Lomachenko K.A. et al. Quantitative structural determination of active sites from in situ and operando XANES spectra: From standard ab initio simulations to chemometric and machine learning approaches // *Catal. Today*. 2019, 336, pp. 3–21.
- [2] Martini A., Guda S. A., Guda A. A., et. Al. PyFitit: the software for quantitative analysis of XANES spectra using machine-learning algorithms // *Computer Physics Communications*, 2020 250, p. 107064
- [3] Smolentsev, G., Soldatov, A. V. Quantitative local structure refinement from XANES: multi-dimensional interpolation approach // *J. Synchrotron Radiat.*, 2006,13, pp. 19-29.

Preparation of Co, Mn, Ni oxide coatings on a ferritic stainless steel

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One of the most significant problems with the operation of solid oxide fuel cells (SOFC) is connected with the degradation of metal interconnectors. The reason is the formation of a chromia subscale that forms during high temperature oxidation causes serious problems leading to premature performance degradation [1]. Applying electrically conductive coatings is a simple and effective method to protect interconnectors from corrosion processes.

In the present study, nitrate electrolyte has been developed to obtain Co, Mn, Ni spinel coatings using non-stationary electrolysis method.

The coating formation was carried out on a prepared sample surface under the action of alternating asymmetric current of industrial frequency, representing two half-sine waves of different amplitudes. As a working electrode, AISI 304 grade steel macroelectrodes with geometric dimensions of 30x20x0.5 mm (on both sides) were used, counter electrodes were nickel. The metal oxides deposition was carried out from aqueous solutions of electrolytes containing cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$), nickel chloride ($\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$), manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), boric acid (H_3BO_3).

The morphology of the coating surface has a crack-like character. X-ray spectral microanalysis data showed that the main elements of the protective coating are oxygen, cobalt, nickel, manganese and traces of iron. Thus, the possibility of using the method of non-stationary electrolysis to obtain protective coatings based on oxide compounds of cobalt, nickel, manganese on the surface of stainless steel is shown.

References

- [1] S. N. Hosseini, F. Karimzadeh, M. H. Enayati, N. M. Sammes . Oxidation and electrical behavior of CuFe_2O_4 spinel coated Crofer 22 APU stainless steel for SOFC interconnect application. Solid State Ionics, 289 , 95-105 (2016).

BOOK OF ABSTRACTS

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