UNIVERSITATEA DIN BUCUREȘTI
FACULTATEA DE CHIMIE
ȘCOALA DOCTORALĂ ÎN CHIMIE

Arii tematice - Doctorat in Chimie 2021
Thematic areas - PhD in Chemistry 2021

Topic : **Heterotrispin complexes**
Name of supervisor: **prof. dr. Marius Andruh**
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Background information: Coordination compounds constructed from three different spin carriers (2p-3d-4f; 3d-4d-4f, 3d-3d'-4f, etc.) represent a new class of magnetic materials of high interest in modern chemistry and materials science. Such compounds are still rare, and their synthesis is challenging for chemists. Two types of systems will be designed: coordination compounds containing: (a) three different paramagnetic metal ions and (b) two different metal ions and a nitronyl-nitroxide radical. An important problem to be solved consists in the analysis of the factors that influence the synergy between the three spin carriers, in order to improve the performances of the new magnetic materials (Single Molecule Magnets and Single Chain Magnets).

Special requirements from the student: The candidate is expected to have at least background knowledge in coordination chemistry (synthesis of new ligands and complexes; crystallogenesis; characterization of the new compounds using various spectroscopic techniques (FTIR, NMR), molecular magnetism.

References

1. J. Ribas, Coordination Chemistry, Wiley, 2008.
2. M. Andruh, *Chem. Commun*., **2018**, *54*, 3559.
3. M. Andruh, *Dalton Trans.*,**2015**, *44*, 16633.
4. S. Demir, I.-R. Jeon, J. R. Long, T. D. Harris, *Coord. Chem. Rev*., **2015**, *289-290*, 149.
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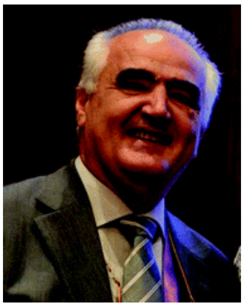

Topic : **Graphene derived catalysts for the valorisation of waste CO_2**
Name of supervisor: **prof. dr. Vasile I. Parvulescu**
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Background information: The thematic focuses on the investigation of the synthesis and modification of grafene structures with the aim to valorize CO_2. CO_2 is one of the main components of the greenhouse gases, its concentration in atmosphere presenting ascendant trends. CO_2 is the main product of burning of hydrocarbons, and a residual product of many chemical processes. Its negative effects are directly related to the property of CO_2 to adsorb and release radiant energy in the thermal infrared range. These properties are completed by a very high inertness of the C=O double bond in a good concordance to the symmetry of the molecule. Based on these, the diminution of the CO2 released concentrations is urgent and requires an efficient catalytic process. Efficiency means not only the removal of this pollutant but also its sustainable transformation into products of economic interest. The CO_2 hydrogenation to hydrocarbons is one of the very interesting alternatives for the valorization of this waste. In this line, the PhD thesis will follow the synthesis of graphene-based catalysts in which metal nano-particles and alloys of these will be deposited on surfaces of pure and doped graphene structures. The characterization of the catalysts will be carried out through multiple techniques (texture, XRD, Raman, ATR, HRTEM, XPS, EXAFS, etc). The collected results will be corelate to catalytic results in a range of various pressures and molar ratios. The kinetics of technological process will be investigated as well.

Special requirements from the student: The candidate is expected to have at least background knowledge in coordination organic chemistry, catalysis, chemistry of materials.

References

1. Greenhouse Gases: Refining the Role of Carbon Dioxide, Qiancheng Ma, (1998) NASA GISS: Science Briefs: *www.giss.nasa.gov*
2. H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan, K. P. de Jong, *Science*, (2012**)**, *335*, 835.
3. A. Primo, F. Neatu, M. Florea, V.I. Parvulescu, H. Garcia, *Nature Commun.***,** **5** (2014) 5291.
4. A. Primo, I. Esteve-Adell, J.F. Blandez, A. Dhakshinamoorthy, M. Álvaro, N. Candu, S.M. Coman, V.I. Parvulescu, H. García, *Nature Commun.***,** (2015), article number: 8561.
5. A. Primo, M. Puche, O.D. Pavel, B. Cojocaru, A. Tirsoaga, V.I. Parvulescu, H. Garcıa, Chem. Commun, 52 (2016) 1839.
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Topic : **Graphene based catalysts for chemo- and stereoselective reactions**

Name of supervisor: **prof. dr. Vasile I. Parvulescu**

Background information: Graphene have been attracting a huge interest in the last period. This interest is directly related to the applications have been demonstrate their efficiency, and catalysis is among these. The catalytic properties of these materials under both pure state and as supports for metal nano-particles or grafted molecules was already explored. The graphene properties also recommend them as catalysts for coupling reactions. These reactions are extremely important in organic synthesis and total organic synthesis in particular. Following this line, the PhD thesis will investigate chemo- and stereoselective C-C and C-N coupling reactions, including Henry synthesis. Various active 3d-4f nano-structure metal species deposited onto graphene surfaces either in amorphous and oriented state will be investigated. Also, oxygen and nitrogen functionalized graphene will be investigated. The characterization of the catalysts will be carried out through multiple techniques (texture, XRD, Raman, ATR, HRTEM, XPS, EXAFS, etc). the kinetics of the reactions will be also investigated taking into consideration the solvent nature.

Special requirements from the student: The candidate is expected to have at least background knowledge in coordination organic chemistry, catalysis, chemistry of materials.

References

1. H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan, K. P. de Jong, *Science*, **2012**, *335*, 835.
2. A. Primo, F. Neatu, M. Florea, V.I. Parvulescu, H. Garcia, *Nature Commun.***,** **5** (2014) 5291
3. N. Candu, A. Dhakshinamoorthy, N. Apostol, C. Teodorescu, A. Corma, H. Garcia, V.I. Parvulescu, J. Catal. 352 (2017) 59–66.
4. G. Sastre, A. Forneli, V. Almasan, V.I Parvulescu, H. Garcia, Appl. Catal. A: General 547 (2017) 52-59.
5. S.M. Coman, I. Podolean, M. Tudorache, B. Cojocaru, V.I. Parvulescu, M. Puche, H. Garcia, Chem. Comm. **53** (2017) 10271-10274.
6. P. Sazama, J. Pastvova, C. Rizescu, A. Tirsoaga, V.I. Parvulescu, H. Garcia, L. Kobera, J. Seidel, J. Rathousky, P. Klein, I. Jirka, J. Moravkova*,* V. Blechta, ACS Catal., 8 (2018) 1779-1789.

Topic: **Investigation on the retention mechanism in hydrophilic interactions based liquid chromatography: experimental parameters and data modeling.**

Name of supervisor: **prof. dr. Victor David**

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Background information: Hydrophilic interaction liquid chromatography (HILIC) is a rather new separation mechanism in liquid chromatography (LC), which is desiganted to separate various polar compounds on polar stationary phases. This mechanism represents an alternative possibility to the most used chromatographic mechanism, namely reversed-phase LC. The separation process under HILIC mechanism is influenced by nature of the stationary phase, and the composition of the mobile phase. Although some theoretical descriptions of analyte retention under this mechanism have been already published in the literature, the complete understanding of the retention behavior in HILIC mechanism is still debatable and this could have advantages in practice for its application to various types of samples investigated by LC.

References

1. S.C. Moldoveanu, V. David, *Selection of the HPLC Method in Chemical Analysis*, Elsevier, Amsterdam, The Netherlands; ISBN: 978-0-12-803684-6; 2017.
2. S.C. Moldoveanu, V. David, *Essentials in Modern HPLC Separations*, Editura Elsevier, Amsterdam, The Netherlands; ISBN: 978-0-12-385013-3; 2013.
3. Y.V. Kazakevich, High-performance liquid chromatography retention mechanisms and their mathematical descriptions; *Journal of Chromatography A*, 1126; 232-243 (2006).
4. R. Kaliszan, M.A. van Straten, M. Markuszewski, C.A. Cramers, H.A. Claessens, Molecular mechanism of retention in reversed-phase high-performance liquid chromatography and classification of modern stationary phases by using quantitative structure-retention relationships; *Journal of Chromatography A*, 855; 455-86 (1999).
5. B. Buszewski, S. Noga, Hydrophilic interaction liquid chromatography (HILIC) - a powerful separation technique; *Analytical and Bioanalytical Chemistry*, 402; 231-247 (2012).
6. A. Vailaya, C. Horváth, Enthalpy-entropy compensation in hydrophobic interaction chromatography; *Journal of Physical Chemistry*, 100; 2447-2455 (1996).

Topic: **Enthalpy – entropy compensation in liquid chromatography: experimental design and theoretical approaches.**

Name of supervisor: **prof. dr. Victor David**

Background information: Generally, two extra-thermodynamic correlations are frequently used to discuss the mechanistic similarities of chemical equilibria and reaction kinetics: enthalpy-entropy compensation (EEC) and linear free energy relationships (LFER). A few empirical studies have been applied to liquid-chromatography deriving from thermodynamic studies on various classes of compounds based on van't Hoff plots, but they are limited to the normal-phase and reversed-phase liquid chromatography. This topic is designated to extend the research in liquid chromatography for other important retention mechanisms, such as HILIC and ZIC-HILIC mechanism for various stationary phases and mobile phase compositions, and to compare the thermodynamic results with normal-phase and reversed-phase liquid chromatography.

Special requirements from the student: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.

References

1. S.C. Moldoveanu, V. David, *Selection of the HPLC Method in Chemical Analysis*, Elsevier, Amsterdam, The Netherlands; ISBN: 978-0-12-803684-6; 2017.
2. S.C. Moldoveanu, V. David, *Essentials in Modern HPLC Separations*, Editura Elsevier, Amsterdam, The Netherlands; ISBN: 978-0-12-385013-3; 2013.
3. Y.V. Kazakevich, High-performance liquid chromatography retention mechanisms and their mathematical descriptions; *Journal of Chromatography A*, 1126; 232-243 (2006).
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5. B. Buszewski, S. Noga, Hydrophilic interaction liquid chromatography (HILIC) - a powerful separation technique; *Analytical and Bioanalytical Chemistry*, 402; 231-247 (2012).
6. A. Vailaya, C. Horváth, Enthalpy-entropy compensation in hydrophobic interaction chromatography; *Journal of Physical Chemistry*, 100; 2447-2455 (1996).

Topic: **Analytical issues for assaying target compounds having similar lipophilic character with respect to the complex matrices in which it exist .**

Name of supervisor: **prof. dr. Andrei-Valentin Medvedovici**
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Background information: Isolation of target compounds (at reduced levels) in complex matrices makes more often the analytical approach quite tedious, especially when the character of the analyte of interest is quite similar to the matrix constituents. Few examples can be mentioned: polyaromatic hydrocarbons in fat or vegetal oils, active ingredients with high log P in fatty creams or ointments or hydrophobic environments. Sample preparation in such conditions should consider some subtle differences in the properties of the target compounds with respect to the components of the matrix. In order to avoid random errors induced through multiple sample manipulation steps, automation should be strongly considered as a reliable solution. Bidimensional chromatography, with a first dimension oriented versus the rough isolation of the target compound, and a second direction oriented via its separation with respect to the residual co-extracted matrix should be envisaged. As long as the target analyte exists at low concentrations level in the initial sample, fraction transfer from one direction to the other should be attentively optimized in order to assist the overall sensibility of the approach.

Special requirements from the student: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.

Topic: **Liophilic additives in liquid chromatography**

Name of supervisor: **prof. dr. Andrei-Valentin Medvedovici**

Background information: Liophilic or chaotropic agents (ChA) are weakly hydrated ions (of inorganic or organic nature), with significant charge delocalization, symmetrical conformation (usually spherical), exhibiting lyophilic properties. ChA are used as additives in mobile phases for liquid chromatography (LC) for tuning retention (and consequently selectivity) and peak symmetry for ionized analytes separated under the RP or HILIC retention mechanisms. A coherent evaluation of advantages/disadvantages related to the use of ChA in liquid chromatography is necessary, including thermodynamic approaches. Behaviour of ChA based elution on new born stationary phases becoming recently commercially available is emphasized. The use of ChA in applications relating to various fields (i.e. pharmaceutical, forensic) will be considered.

Special requirements from the student: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.

Topic: **Green solvents in sample preparation techniques for bioanalytical applications**

Name of supervisor: **prof. dr. Andrei-Valentin Medvedovici**

Background information: Replacement of the usual organic solvents in mobile phases designed for RPLC elution by green solvents has been already studied in literature. However, the potential of using green organic solvents in protein precipitation processes related to bioanalytical sample preparation schemes were not yet considered. Their use in bioanalytical protein precipitation procedures should be closely related to phenomena relating to large volume injection in LC, having as declared aim to enhance on the overall method sensitivity. Approaches related to human whole blood and plasma processing have to be considered and studied in detail, ethyl lactate and propyl carbonate being the first choice among the green solvents successfully replacing methanol or acetonitrile. Evaluation should be based through residual matrix effects appearing in mild ionization techniques used for LC-MS/MS applications.

Special requirements from the student: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.

Topic: **Peak homogeneity in LC/DAD and LC/MS approaches**

Name of supervisor: **prof. dr. Andrei-Valentin Medvedovici**

Background information: Peak homogeneity represents a major concern when validating the selectivity/specificity of the stability indicating HPLC methods. Existing methods (included in softwares assisting the data acquisition) are based on the measurement of the cosine between vectors represented in the n-dimensional space defined by the UV-Vis or MS spectra acquired during peak elution. However, concentration/amount of the analyte reaching the detection area may induce errors with respect to the peak purity evaluation. Alternatives based on linear regression may be considered and should be tested with respect to the operational parameters used during spectral acquisition, similarity degree of spectra of the possible interfering compounds, spectral manipulation techniques (i.e. spectral derivatives) etc. Another feature of a major interest relates with the absolute differences in terms of retention time between the main compound and the interferent.

Special requirements from the student: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.

Topic : **Biosensors based on nanostructure materials**

Name of supervisor: **prof. dr. Camelia Bala**
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Background information: This project deals with the development of biosensors, sensitive and selective, able to work in complex media for applications in clinical laboratory, water monitoring, drug discovery and food quality control. The research will focus more specifically on biosensors modified with different materials: metal nanoparticles, metal oxide nanoparticles, metal and carbon quantum dots, graphene, carbon nanotubes, nanowires, nanocomposites, mesoporous silica, porous silicon, that expand sensitivity. Biosensors are analytical devices combining a transducer with a biorecognition element being able to transform a biochemical event on the transducer surface directly into a measurable analytical signal. The emergence of nanostructured materials has opened new horizons in the development of next-generation biosensors; being able to control the design of the electrode interface at the nanoscale combined with the intrinsic characteristics of the nanomaterials engenders novel biosensing platforms with improved capabilities. In recent years, biosensors devices made with different materials and working with different modes have attracted particular interest due to their multiple applications, from clinical labs, to food analysis, environmental applications, protein engineering, drug discovery, and security applications.

Special requirements from the student: The candidate is expected to have Master degree in Chemistry, Biochemistry, Physics or affine sectors. Previous experience in sensing, biosensing and biomolecular assay development will be considered as a strong asset. The candidates should be highly motivated to do research, to be communicative, creative, eager to learn and able to work independently as well as part of the team.

References

1. A. P. F. Turner, Chem. Soc. Rev., 2013, 42, 3184

2. S. Azzouzi, L. Rotariu, A. M. Benito, W. K. Maser, M. Ben Ali, C. Bala, Biosens. & Bioelectron, 2015, 69, 280

3. L. Rotariu, F. Lagarde, N. Jaffrezic-Renault, C. Bala, TRAC-Trends in Analytical Chemistry, 2016, 79, 80-87.

5. M. Braik, L.-G. Zamfir, L. Rotariu, C. Curutiu, M. C. Chifiriuc, M. Ben Ali, C. Bala, Sensors and Actuators B: Chemical, 2018, 273

6.O.-M. Istrate, L. Rotariu, C, Bala, Chemosensors, 2021, 9(4), 74

Topic : **Affinity sensors**

Name of supervisor: **prof. dr. Camelia Bala**

Background information: the topic is addressing the sensors based on affinity reactions by integrating a biological material (e.g., cell receptors, antibodies, nucleic acids, etc.), a biologically derived material (e.g., recombinant antibodies, engineered proteins, aptamers, etc.) or a biomimetic analogue (e.g., synthetic receptors, biomimetic catalysts, combinatorial ligands, molecularly imprinted polymers, etc.) closely associated with or integrated within a physicochemical transducer, which may be optical (e.g. Surface Plasmon Resonance-SPR), electrochemical, piezoelectric or magnetic. The project will focus on complementary intersection between molecular recognition, nanotechnology and supramolecular chemistry to improve the analytical performance and robustness of devices. The application will be driven by the label-free detection of low molecular weight molecules with application in medical diagnosis (point-of-care devices), on-site detection of pollutant (food and environment monitoring).

Special requirements from the student: The candidate is expected to have Master degree in chemistry, biochemistry, physics or affine sectors. Previous experience in sensing, biosensing and biomolecular assay development will be considered as a strong asset. The candidates should be highly motivated to do research, to be communicative, creative, eager to learn and able to work independently as well as part of the team.

References

1. M. Puiu, A. Idili, D. Moscone, F. Ricci, C. Bala, Chem. Commun., 2014, 50(64), 8962
2. L.-G. Zamfir, P. Fortgang, C. Farre, M. Ripert, G. De Crozals, N. Jaffrezic-Renault, C. Bala, P. Temple-Boyer,
3. C. Chaix, Electrochimica Acta, 2015, 164, 62
4. G. M. Danila, M. Puiu, L. Gabriel Zamfir, C. Bala, Analytical Chemistry, 2019, 91(23), 14812
5. M Puiu, V Mirceski, C. Bala, Current Opinion in Electrochemistry 2021, 100726

Topics :

1. New stationary phases for ion exchange chromatography.
2. Non-conventional stationary phases for environmental analysis.

Name of supervisor: **prof. dr. Irinel Adriana Badea**
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Background information: Nowadays the quality of water is a social concern even if the term “quality” is not very familiar to many people. You are thirsty, in a big city, in front of clear water running from a marvelous drinking fountain and suddenly you see the notice: “Non-potable water”. When you read them, it is not only frustration but resignation, too. And the question “why?” rises without any chance to a direct answer. Small species in term of both chemistry and biology sciences are responsible for the quality of water. No matter the purpose of the water is, the term of “good water” hides a huge scientific activity related to the monitoring of physical, chemical and biological properties. Usually ion-exchange resins are the first choice for this purpose due to their ion-exchange capacity, good selectivity and effortless regeneration. In quest of the high selectivity of the ion-exchange process new materials should be developed and characterized, and this is the aim of the topics proposed.

Special requirements from the student: The candidate is expected to have at least background knowledge of Analytical Chemistry (level Master degree)

Reference

1. Christian, G. D., Dasgupta, P. K., Schug, K.A. Analytical Chemistry, 7th Edition, Wiley Global Education, 2013.

Topic: ***Transition-metal-containing LDH-based catalysts for bio-oil hydrodeoxygenation***

Name of supervisor: ***prof. dr. habil. Ioan-Cezar Marcu***
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Background information: Layered double hydroxides (LDH), a class of anionic clays, which can be found in nature as minerals and can also be synthesized, are currently generating an increasing attention among scientists working in catalysis [1]. Indeed, due to their special lamellar structure, these synthetic inorganic materials exhibit a set of unique properties that make them suitable for the catalysis domain, either as catalyst precursors, catalyst supports or as actual catalysts [2]. Hydrodeoxygenation is an important step in the conversion of biomass-derived oxygenates to fuels and chemicals consisting in selective deoxygenation of the intermediates derived from the fast pyrolysis step to transform them into high-value finished products [3]. To achieve this, bifunctional catalysts are needed, LDH derived materials being privileged [4]. Thus, our objective is to synthesize different multifunctional transition-metal-containing LDH-derived oxide materials and to investigate their catalytic properties in hydrodeoxygenation of some model oxygenated compounds.

Special requirements from the student: Heterogeneous Catalysis and Basic Chemical Technology.

References

1. G. Fan, F. Li, D.G. Evans, X. Duan, Catalytic applications of layered double hydroxides: recent advances and perspectives, Chem. Soc. Rev. 43 (2014) 7040-7066.

2. Marcu, I.C., Urdă, A., Popescu, I., Hulea, V., Layered Double Hydroxides-based Materials as Oxidation Catalysts. In Sustainable Nanosystems Development, Properties and Applications, M.V. Putz, M.C. Mirica (Eds.), IGI Global: Hershey, PA, USA, 2017, Ch. 3, p. 59-121.

3. A.M. Robinson, J.E. Hensley, J.W. Medlin, Bifunctional catalysts for upgrading of biomass-derived oxygenates: A Review, ACS Catal. 6 (2016) 5026–5043.

4. W.Y. Hernández, J. Lauwaert, P. Van Der Voort, A. Verberckmoes, Recent advances on the utilization of layered double hydroxides (LDHs) and related heterogeneous catalysts in a lignocellulosic feedstock biorefinery scheme, Green Chem. 19 (2017) 5269–5302.

Topic: **Oxidative dehydrogenation of light alkanes over transition-metal-based mixed oxides catalysts**

Name of supervisor: **prof. dr. habil. Ioan-Cezar Marcu**

Background information: Oxidative dehydrogenation (ODH) of light alkanes may offer a promising alternative for the production of the corresponding alkenes compared to the simple dehydrogenation as the ODH has the advantage of an exothermic reaction, without thermodynamic limitations and with a low risk of catalyst deactivation through coking because the reaction is run in an oxidative environment [1, 2]. Nevertheless, the main difficulty in obtaining high alkene yields by ODH of light alkanes arises from the fact that the alkene is more reactive than the corresponding alkane, thus being prone to further oxidation to produce carbon oxides. Indeed, the ODH of light alkanes proceeds through sequential (Alkane → Alkene → COx) and parallel (Alkane → COx) oxidation steps, the secondary reactions, i.e. the deep oxidation of both alkane and alkene, being more thermodynamically favorable than the oxidative dehydrogenation. Consequently, our objective is to design transition-metal-based oxide catalysts [3, 4] which significantly accelerate only the chosen sequence of elementary steps and suppress all other possible elementary steps, parallel or consecutive, in ethane and propane conversion.

Special requirements from the student: The candidate is expected to have at least background knowledge of the Principles of Heterogeneous Catalysis, including variable-valence oxide catalysts, and Basic Chemical Technology.

References

1. F. Cavani, N. Ballarini, A. Cericola, Oxidative dehydrogenation of ethane and propane: How far from commercial implementation?, Catal. Today 127 (2007) 113-131.

2. C.A. Gartner, A.C. van Veen, J.A. Lercher, Oxidative dehydrogenation of ethane: common principles and mechanistic aspects, ChemCatChem 5 (2013) 3196-3217.

3. A. Chieregato, J.M. López Nietob, F. Cavani, Mixed-oxide catalysts with vanadium as the key element for gas-phase reactions, Coord. Chem. Rev. 301-302 (2015) 3-23.

4. E.W. McFarland, Horia Metiu, Catalysis by doped oxides, Chem. Rev. 113 (2013) 4391-4427.

Topic: **Transition-metal-based mixed oxides catalysts for volatile organic compounds abatement**

Name of supervisor: **prof. dr. habil. Ioan-Cezar Marcu**

Background information: Control of volatile organic compounds (VOC), including methane [1], emissions has become a major concern of the chemical and petrochemical industries commitment towards the environment. In this context, it is necessary to develop new eco-friendly techniques to limit and control these emissions which can affect the climate change, the growth of plants and the health of human beings [1]. Catalytic total oxidation is a suitable alternative to conventional incineration due to its practical applications both for pollution abatement and power generation. Precious metals have been widely reported in the literature as very active catalysts for the complete oxidation of short-chain hydrocarbons and VOC, but they are expensive, easily sintered and volatile at moderate temperatures [2]. Many efforts have been devoted to the replacement of noble metals by transition metals to obtain highly active metal oxide catalysts for methane combustion [2, 3]. Mn-, Co- or Cu oxides and their mixtures prepared by different methods, proved to be very promising catalysts in the combustion of VOC [2] and methane [3] as cheap and environmentally friendly systems. Consequently, our objective is to design transition-metal-based mixed oxide catalysts active for the total oxidation of methane as a model molecule for VOC.

Special requirements from the student: The candidate is expected to have at least a background knowledge of the Principles of Heterogeneous Catalysis, including oxide-based catalysts, and Basic Chemical Technology.

References

1. P. Kustrowski, A. Rokicinska, T. Kondratowicz, Abatement of volatile organic compounds emission as a target for various human activities including energy production, Adv. Inorg. Chem. 72 (2018) 385-419.
2. M.S. Kamal, S.A. Razzak, M.M. Hossain, Catalytic oxidation of volatile organic compounds (VOCs) - A review, Atmos. Environ. 140 (2016) 117-134.
3. J. Chen, H. Arandiyan, X. Gao, J. Li, Recent advances in catalysts for methane combustion, Catal. Surv. Asia 19 (2015) 140–171.

Topic: **Layered double hydroxide-based catalysts for fine organic synthesis**

Name of supervisor: **prof. dr. habil. Ioan-Cezar Marcu**

Background information: Layered double hydroxides (LDH), a class of anionic clays, which can be found in nature as minerals and can also be synthesized, are currently generating an increasing attention among scientists. Due to their special lamellar structure, these synthetic inorganic materials exhibit a set of unique properties that make them suitable for the catalysis domain, either as catalyst precursors, catalyst supports or as actual catalysts [1]. The LDH-based materials can show both acid-base and redox properties, depending on their composition [2]. Indeed, they can incorporate in their structure 2 or more cations in different proportions, which generate the multifunctional catalytic sites needed to synthesize in a single step a valuable compound, which traditionally needs at least 2 or 3 steps to be obtained [3].

Our objectives are to synthesize LDH materials with different cationic compositions so as to generate different types of catalytic sites, and to study their catalytic behavior in various multistep organic transformations.

Special requirements from the student: The candidate is expected to have at least a background knowledge of the Principles of Heterogeneous Catalysis, Basic Organic Synthesis, and Basic Chemical Technology.

References

1. Marcu, I.C., Urdă, A., Popescu, I., Hulea, V., Layered Double Hydroxides-based Materials as Oxidation Catalysts. In Sustainable Nanosystems Development, Properties and Applications, M.V. Putz, M.C. Mirica (Eds.), IGI Global: Hershey, PA, USA, 2017, Ch. 3, p. 59-121.
2. Cavani, F., Trifiro, F., Vaccari, A., Hydrotalcite-type anionic clays: Preparation, properties and applications, Catalysis Today 11 (1991) 173 - 301.
3. Sels, B.F., De Vos, Dirk E., Jacobs, P.A., Hydrotalcite-like anionic clays in catalytic organic reactions, Catal. Reviews, 43(4) (2001) 443-488.

Topic: **Organic functionalized nanometric assemblies for multivalent applications**

Name of supervisor: **prof. dr. habil. Petre Ioniță**
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Background information: This research topic is a blend between organic and materials chemistry, with the aim to obtain by synthesis nanometric assemblies that contain functional organic molecules [1-3]. These assemblies may be formed from pure organic compounds brought together by non-covalent interactions or may be hybrid structures of inorganic-organic type (such are nanoparticles), functionalized with organic compounds. The organic part will have specific properties, like paramagnetic, fluorescent, acid-base or redox. Depending on that, multivalent applications can be envisaged.

Special requirements from the student: The candidate is expected to have at least background knowledge in organic reactions and synthesis, column chromatography, organic physical chemistry (spectroscopy). Supramolecular, materials or nanoparticles chemistry will be an asset.

References

1. N. Erathodiyil, J. Ying. *Functionalization of inorganic nanoparticles for bioimaging applications*. Acc. Chem. Res. 2011, 44, 925. DOI: 10.1021/ar2000327
2. S. E. Lohse, C. J. Murphy. *Applications of colloidal inorganic nanoparticles: from medicine to energy*. J. Am. Chem. Soc. 2012, 134, 15607. DOI: 10.1021/ja307589n
3. R. Thiruppathi, S. Mishra, M. Ganapathy, P. Padmanabhan, B. Gulvas. *Nanoparticle functionalization and its potentials for molecular imaging.* Adv. Sci. 2017, 4, 1600279. DOI: 10.1002/advs.201600279

Topic: **Stable free radicals and radicaloids derived from DPPH**

Name of supervisor: **prof. dr. habil. Petre Ioniță**

Background information: The chemistry of stable free radicals is well known now-a-days [1]. A free radical is a chemical entity that contains an unpaired electron (free electron) and usually has a high reactivity due to its open-shell structure. The DPPH stable free radical (2,2-diphenyl-1-picrylhydrazyl) is a violet-colored organic compound that can be involved into redox or acid-base processes (as example, reduction yields the yellow hydrazine, and the addition of a base led to the corresponding red anion); these reversible processes are easily followed by such color-changes [2]. The aim of this research is the synthesis, characterization and the study of novel DPPH-derivatives, mainly containing a betainic structural moiety (zwitterion) that may behave as a hetero-diradical [3].

Special requirements from the student: The candidate is expected to have at least background knowledge in organic reactions and synthesis, column chromatography, organic physical chemistry (spectroscopy). Free radicals chemistry will be an asset.

References

1. R. G. Hicks. *Stable radicals: fundamentals and applied aspects of odd-electron compounds*. John Wiley & Sons, Ltd. Chichester, UK, 2010.
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Topic: Metal–organic framework-derived porous materials for catalysis

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Background information: Effective transformation of biopolymers from biomass (eg cellulose, hemicellulose and lignin) into added value compounds relies heavily on the development of cascade chemical reactions, where the use of multifunctional solid catalysts is indispensable. In this context, advances in material science and catalysis have provided some innovative strategies for the development of new catalytic materials with well-defined structures and efficient physico-chemical characteristics. Metal-organic frameworks (MOFs), for instance, have emerged as promising materials in the areas of gas storage, magnetism, luminescence and catalysis owing to their superior properties of highly crystalline structures. However, MOFs' stability to thermal or humidity is greatly less than carbons because they are constructed from assembly of ligands with metal ions or clusters by coordination bonds. Transforming MOFs into carbons is bringing a novel potential for MOFs to reach industrialization, and carbons with controlled pore size and surface-doping are one of the most important porous materials. As compared with other carbons such as activated carbons, carbon nanotubes and graphene, MOF-derived carbons showed at least two merits: (a) the pores and shape can be easily controlled by MOF precursors; (b) heteroatoms can be easily doped with controllable configuration by the selected linkers for MOFs and carbonization condition [1, 2]. Applying MOF-derived carbons in biomass valorization to biofuels and biochemicals, which is one of the main aim of this research, is of a great potential considering their large surface areas with abundant active sites and defects in the structure.

Special requirements from the student: The candidate is expected to have at least background knowledge in coordination chemistry, catalysis, chemistry of materials.

References

1. T.Wang, H.-K. Kim, Y. Liu, W. Li, J. T. Griffiths, Y. Wu, S. Laha, K. D. Fong, F. Podjaski, C. Yun, R. V. Kumar, B. V. Lotsch, A. K. Cheetham, S. K. Smoukov, *J. Am. Chem. Soc.*, 2018, 140, 6130.
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Topic: Valorization of biomass wastes to functional catalytic materials

Name of supervisor: **prof. dr. habil. Simona Margareta Coman**

Background information: An important challenge for biorefinery operations is the production of bio-based fuels and chemicals in an economical, ethical and environmentally friendly way. This requires complete and efficient valorization of non-edible feedstock, the transition from a *linear economy* to a *circular economy* being the key of a sustainable development. Currently, humins - carbonaceous insoluble by-products, typically formed during the acid-catalyzed dehydration of carbohydrates, are used for low-value applications, such as combustion to supply heat in biorefineries [1]. Nevertheless, humins could be valorized by their conversion to chemicals [2], or as functional carbon materials for soil improvement or CO_2 sequestration [3]. However, although the potential of humins waste valorization is huge the research in this area is still in infancy. In this line, the PhD thesis will follow the synthesis of humins by saccharides dehydration and their use to produce functional materials with catalytic efficiency for fine chemicals production.

Special requirements from the student: The candidate is expected to have at least background knowledge of organic chemistry, catalysis, chemistry of materials.

References

1. T. Hoang, E. Van Eck, W. Bula, J. Gardeniers, L. Lefferts, K. Seshan, *Green chemistry*, 2015, *17*, 959.
2. S. Agarwal, D. v. Es, H. J. Heeres, *J. Anal. Appl. Pyrol*., 2017, *123*, 134.
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Topic: Catalytic amino acids production from biomass-derived intermediates

Name of supervisor: **prof. dr. habil. Simona Margareta Coman**

Background information: As the basic building blocks of proteins, amino acids play an essential role in life and are widely used in food and feed supplements, as precursors to biodegradable plastics, pharmaceutical products, and elsewhere. Although the current production of amino acids mainly relies on microbial cultivation processes, the issues associated with the scale limitations of microbial processes, the strict need for sterile operating conditions, and the complexity of their separation have stimulated efforts to develop efficient chemical approaches to produce amino acids and their derivatives [1-3]. As an alternative, chemocatalytic approaches to produce amino acids from renewable feedstocks such as bio-based sugars could offer a rapid and potentially more efficient means of amino acid synthesis. However, to date, the efforts have been limited by the development of facile chemistry and associated catalyst materials, and therefore, sustainable approaches for their direct synthesis from abundant and renewable feedstocks are still quite rare. The main aim of this work is to develop sustainable catalytic approaches for direct synthesis of amino acids from both biomass-derived α-hydroxyl acids and glucose.

Special requirements from the student: The candidate is expected to have at least background knowledge of organic chemistry, catalysis, chemistry of materials.

References

1. S. J. Zuend, M. P. Coughlin, M. P. Lalonde, E. N. Jacobsen, *Nature*, 2009, 461, 968.
2. M. Zhang, S. Imm, S. Bähn, H. Neumann, M. Beller, *Angew Chem Int Ed Engl*, 2011, 50, 11197.
3. H. Yan, J. Suk Oh, J.-W. Lee, C. Eui Song, *Nat Commun*, 2012, 3, 1212.

Topic: Liquid crystals with luminescent properties

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Background information: Liquid crystals, anisotropic fluids with a partial degree of ordering, a unique combination of typical properties of both the liquid state and the solid state, are commonly used in various applications, ranging from the manufacturing of LCDs to different molecular sensors and detectors, optical switches, spatial light modulator, etc. Metallomesogens (liquid crystals based on metal complexes) are a special class of liquid crystals which bring together the properties of anisotropic fluids (anisotropy of physical properties and fast orientational response to external fields) specific to liquid crystals (LC) with the particular properties of metals (geometry of coordination, electronic, magnetic or the purely structural role, depending on the metal ion). As the luminescent liquid crystals can find useful application in emissive display devices, the required photophysical properties of such materials can be achieved by a judicious combination of metals and ligands. The project will focus on the design and preparation of new candidates as luminescent liquid crystals based on d- or f-metals with high thermal stability, lower transition temperatures and LC properties according to envisaged application (nematic and columnar phases).

Special requirements from the student: The candidate is expected to have at least background knowledge in synthetic organic chemistry, coordination chemistry and basic spectroscopic techniques (NMR, IR, UV-VIS).

References:

1. Handbook of Liquid Crystals, Second Edition, Eds. J.W. Goodby, P.J. Collings, T. Kato, C. Tschierske, H.F. Gleeson, P. Raynes, Wiley-VCH Verlag, (2014).
2. X. Wu, M. Zhu, D. W. Bruce, W. Zhu and Y. Wang, *J. Mater. Chem. C*, 2018,**6**, 9848-9860.
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