

Bogdanović, U., Pašti, I., Ćirić-Marjanović, G., Mitrić, M., Ahrenkiel, S.P., Vodnik, V.

Interfacial Synthesis of Gold-Polyaniline Nanocomposite and Its Electrocatalytic Application

(2015) ACS Applied Materials and Interfaces, 7 (51), pp. 28393-28403.

<https://doi.org/10.1021/acsami.5b09145>

ABSTRACT: Gold-polyaniline (Au-PANI) nanocomposite was prepared using a simple interfacial polymerization method, performed in an immiscible water/toluene biphasic system using tetrachloroaurate, AuCl<sub>4</sub><sup>-</sup> as an oxidant. The formation of Au nanoparticles (AuNPs) or Au-PANI nanocomposite can be controlled to a certain degree by varying the ratio of initial Au<sup>+</sup> and aniline concentrations. Under optimal condition (HAuCl<sub>4</sub>/aniline ratio is 1:2), green dispersion of Au-PANI nanocomposite is produced in aqueous phase, whose morphology, structure and physicochemical properties are investigated in details. The nanocomposite shows granular morphology with mostly rodlike AuNPs embedded in polymer. It was found that polyaniline in the composite is in the conducting emeraldine salt form, containing high amount of Au (28.85 wt %). Furthermore, the electrical conductivity of the nanocomposite was found to be four-fold higher than that of the polymer itself. In addition, the nanocomposite powder, isolated from the as-prepared aqueous dispersion, can later be easily redispersed in water and further used for various applications. Moreover, the obtained Au-PANI nanocomposite showed excellent electrocatalytic performance toward the electrochemical oxygen reduction reaction (ORR), with high ORR onset potential and good selectivity. This makes it a promising candidate for a new class of Pt-free ORR catalyst. © 2015 American Chemical Society.

Janićijević, J., Krajišnik, D., Čalija, B., Vasiljević, B.N., Dobričić, V., Daković, A., Antonijević, M.D., Milić, J.

Modified local diatomite as potential functional drug carrier - A model study for diclofenac sodium

(2015) International Journal of Pharmaceutics, 496 (2), pp. 466-474.

<https://doi.org/10.1016/j.ijpharm.2015.10.047>

ABSTRACT: Diatomite makes a promising candidate for a drug carrier because of its high porosity, large surface area, modifiable surface chemistry and biocompatibility. Herein, refined diatomite from Kolubara coal basin, which complied with the pharmacopoeial requirements for heavy metals content and microbiological quality, was used as a starting material. Inorganic modification of the starting material was performed through a simple, one-step procedure. Significant increase in adsorbent loading with diclofenac sodium (DS) was achieved after the modification process (~373 mg/g) which enabled the preparation of comprimates containing therapeutic dose of the adsorbed drug. Adsorption of DS onto modified diatomite resulted in the alteration of the drug's XRD pattern and FTIR spectrum. In vitro drug release studies in phosphate buffer pH 7.5 demonstrated prolonged DS release over 8 h from comprimates containing DS adsorbed on modified diatomite (up to 37% after 8 h) and those containing physical mixture of the same composition (up to 45% after 8 h). The results of in vivo toxicity testing on mice pointed on potential safety of both unmodified

(starting) and modified diatomite. All these findings favor the application of diatomite as a potential functional drug carrier. © 2015 Elsevier B.V. All rights reserved.

Milenković, D.A., Marković, J.M.D., Marković, Z.S.  
DFT investigation of the reaction of cyanidin with hydroxyl radical  
(2015) 2015 IEEE 15th International Conference on Bioinformatics and Bioengineering, BIBE 2015, art. no. 7367647, .

<https://doi.org/10.1109/BIBE.2015.7367647>

ABSTRACT: Cyanidin, as one important plant pigment, was theoretically (at M05-2X/6-311+G(d, p) level of theory) investigated for its ability to scavenge potentially, highly damaging hydroxyl radical. The applied method successfully reproduces the bond dissociation enthalpy (BDE), the ionization potential (IP) and proton affinity (PA). The HAT mechanism is most favorable reaction pathway for antioxidative action of cyanidin in the gas phase. On the other hand, the SPLET mechanism is most favorable reaction pathway for antioxidative action of cyanidin in the aqueous phase. Mechanistic investigations of antioxidative action of cyanidin in reaction with the hydroxyl radical confirmed that HAT is the dominant reaction pathway in the gas phase, and that the 4' position is most reactive. © 2015 IEEE.

Amić, A., Marković, J.D., Jeremić, S., Gadanski, I., Lučić, B., Amić, D.  
Free radical scavenging potency of 3-hydroxyphenylacetic acid: A DFT study  
(2015) 2015 IEEE 15th International Conference on Bioinformatics and Bioengineering, BIBE 2015, art. no. 7367665, .

<https://doi.org/10.1109/BIBE.2015.7367665>

ABSTRACT: 3-Hydroxyphenylacetic acid (3-HPA) is one of the colon microbial metabolites of flavonoids produced in high concentrations (~300  $\mu$ M). In this work potency of direct inactivating of selected set of free radicals by 3-HPA was computationally investigated. All calculations were carried out using M05-2X functional with 6-311+G(d, p) basis set coupled with the SMD solvation model. Thermodynamics of three free radical scavenging mechanisms were studied considering electronic properties of 3-HPA and scavenged free radicals. On the basis of obtained results it can be safely predicted that 3-HPA is able to at least in situ effectively scavenge free radicals of different nature, thus contributing to protection from diseases mediated by oxidative stress. © 2015 IEEE.

Vojnović, M., Popović, M., Ristić, M.M., Vičić, M.D., Poparić, G.B.  
Rate coefficients for electron impact excitation of N<sub>2</sub>  
(2015) Chemical Physics, 463, pp. 38-46.

<https://doi.org/10.1016/j.chemphys.2015.09.014>

ABSTRACT: Rate coefficients for electron impact excitation of the nitrogen molecule have been determined. Calculations have been performed for all relevant non-elastic processes: rotational excitation, vibrational excitation, electronic excitation into singlet

and triplet states and particularly for dissociation and ionization. The rate coefficients have been determined for both equilibrium and non-equilibrium conditions in the presence of electric and magnetic fields. For the equilibrium conditions the Maxwellian electron energy distribution function has been used for determining rate coefficients in the energy region from 0 to 17 eV. In the case of the non-equilibrium conditions, where the homogenous electric and magnetic fields are present, we have calculated electron energy distribution functions needed for determining rate coefficients by use of a Monte Carlo simulation developed in our laboratory. The results for both equilibrium and non-equilibrium rate coefficients are presented in the paper and similarities and differences between them have been discussed. © 2015 Elsevier B.V. All rights reserved.

Ilić, G., Gaguly, R., Petković, M., Vidović, D.  
Oxidation of a P-C Bond under Mild Conditions  
(2015) Chemistry - A European Journal, 21 (51), pp. 18594-18597.

<https://doi.org/10.1002/chem.201503922>

ABSTRACT: The reactivity of phosphonium dication  $[(\text{Ph}_3\text{P})_2\text{C}-\text{P}(\text{NiPr}_2)]^{2+}$ ,  $12+$ , towards pyridine N-oxide (O-py) has been investigated. The resulting oxophosphonium dication  $[(\text{Ph}_3\text{P})_2\text{C}(\text{NiPr}_2)\text{P}(\text{O})(\text{O-py})]^{2+}$ ,  $22+$ , was surprisingly stabilized by a less nucleophilic O-py ligand instead of pyridine (py). This compound was then identified as an analogue of the elusive Criegee intermediate as it underwent oxygen insertion into the P-C bond through a mechanism usually observed for Baeyer-Villiger oxidations. This oxygen insertion appears to be the first example of a Baeyer-Villiger oxidation involving O-py. © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Blagojević, S.N., Čupić, Z., Ivanović-Šašić, A., Kolar-Anić, L.  
Mixed-mode oscillations and chaos in return maps of an oscillatory chemical reaction  
(2015) Russian Journal of Physical Chemistry A, 89 (13), pp. 2349-2358.

<https://doi.org/10.1134/S0036024415130063>

ABSTRACT: The return maps, as an element of mathematical phenomenology appropriate for general examinations of complex dynamic states of the oscillatory systems were used to detect and explain the evolution of mixed-mode oscillations and chaos in a six-dimensional nonlinear reaction system of the Bray-Liebhafsky (BL) reaction, a well-studied nonlinear chemical reaction system that exhibits complex dynamic behavior. For this purpose principally different Poincaré sections were applied and different transition scenarios between periodic and aperiodic states were examined by numerical simulations. It is shown that emergence of new periodic patterns can be detected by return maps already within chaotic windows. Besides, we also show that the higher dimensionality of manifold gives the impression of having several layers of manifolds. © 2015 Pleiades Publishing, Ltd.

Čučulović, A., Veselinović, D.  
Desorption of  $^{137}\text{Cs}$  from *Brachythecium mildeanum* moss using acid solutions with pH 4.60-6.50  
(2015) Russian Journal of Physical Chemistry A, 89 (13), pp. 2473-2477.

<https://doi.org/10.1134/S003602441513004X>

ABSTRACT: The desorption of  $^{137}\text{Cs}$  from the moss *Brachythecium mildeanum* (Schimp.) was performed using the following solutions:  $\text{H}_2\text{SO}_4$  (I),  $\text{HNO}_3$  (II),  $\text{H}_2\text{SO}_4 + \text{HNO}_3$  (III) with pH values of 4.60, 5.15, and 5.75, respectively, as well as distilled water (D) with pH 6.50. After five successive desorptions, each lasting 24 h, 20.5–37.6%  $^{137}\text{Cs}$  was desorbed from the moss using these solutions, while 30.7% of the starting content was desorbed using distilled water. The first desorption removed the highest percent of the original content of  $^{137}\text{Cs}$  in the moss (11.3–18.4%). This was determined by measuring  $^{137}\text{Cs}$  activity. If the current results are compared with those obtained earlier it may be concluded that  $^{137}\text{Cs}$  desorption from mosses is not species-dependent. The obtained results indicate the necessity of investigating the influence of acid rain, or rather, of  $\text{H}^+$  ions, on desorption of other ions from biological systems, i.e., the role of  $\text{H}^+$  ions in spreading other polluting compounds and thus producing secondary environmental pollution. From the results of this study it follows that acid rain will lead, through  $\text{H}^+$  ion action, to a similar increasing pollution of fallout waters with other ionic compounds which may not be present in the water before the contact with the plants and thus enable the pollution spreading. In the investigated system, the replacement of  $\text{H}^+$  ions from acid rains by more dangerous radioactive ions occurred, increasing the concentration of the radioactive ions in the water, which demonstrates that the same process takes place in fallout water. © 2015 Pleiades Publishing, Ltd.

Radonjić, V., Krstić, J., Lončarević, D., Jovanović, D., Vukelić, N., Stanković, M., Nikolova, D., Gabrovska, M.  
Perlite as a potential support for nickel catalyst in the process of sunflower oil hydrogenation  
(2015) Russian Journal of Physical Chemistry A, 89 (13), pp. 2359–2366.

<https://doi.org/10.1134/S0036024415130294>

ABSTRACT: Investigation was conducted in order to elucidate the possibility of using perlite as support for preparation of nickel based precursor catalyst, potentially applicable in vegetable oil hydrogenation process. On three differently prepared expanded perlite, nickel catalyst precursors with identical  $\text{Ni}/\text{SiO}_2 = 1.1$  and  $\text{Ni}/\text{Mg} = 10/1$  ratios were synthesized by precipitation-deposition method. Different techniques, SEM micrography, He-pycnometry, calcimetry, Hg-porosimetry,  $\text{N}_2$ -physisorption,  $\text{H}_2$ -chemisorption and temperature programmed reduction, were used for characterization of obtained samples. Determining the precursor texture, morphology and reducibility shows a successfully deposited nickel phase on perlite support with promising properties for vegetable oil hydrogenation. Chosen precursor was reduced and passivated in paraffin oil and the obtained catalyst showed significant catalytic activity in the test of sunflower oil hydrogenation. © 2015 Pleiades Publishing, Ltd.

Milenković, A., Smičiklas, I., Šljivić-Ivanović, M., Vukelić, N.  
Concurrent  $\text{Co}^{2+}$  and  $\text{Sr}^{2+}$  sorption from binary mixtures using aluminum industry waste: Kinetic study  
(2015) Russian Journal of Physical Chemistry A, 89 (13), pp. 2461–2465.

<https://doi.org/10.1134/S0036024415130269>

ABSTRACT: Multi-component sorption studies are essential to identify the applicability of red mud as a lowcost sorbent for the simultaneous removal of metal ions from wastewaters. Sorption kinetics of Co<sup>2+</sup> and Sr<sup>2+</sup> ions was investigated, at different total concentrations of mixtures and different molar ratios of two cations. Kinetics of metal sorption from binary systems was found to be well described by pseudo-second order rate model. Equilibrium sorbed amounts and equilibrium times for Co<sup>2+</sup> sorption increased with the increase of its total concentration in the mixture, whereas pseudo-second order rate constants exhibited the opposite trend. Sr<sup>2+</sup> sorption was strongly suppressed in the presence of Co<sup>2+</sup> ions, and the removal efficiency decreased with increasing concentration and mole fraction of Co<sup>2+</sup>. Red mud can be used for simultaneous Co<sup>2+</sup> and Sr<sup>2+</sup> removal from mixtures of lower initial concentration, otherwise Co<sup>2+</sup> sorption is dominant. © 2015 Pleiades Publishing, Ltd.

Bolić, B., Mijušković, A., Popović-Bijelić, A., Nikolić-Kokić, A., Spasić, S., Blagojević, D., Spasić, M.B., Spasojević, I.  
Reactions of superoxide dismutases with HS-/H<sub>2</sub>S and superoxide radical anion: An in vitro EPR study  
(2015) Nitric Oxide - Biology and Chemistry, 51, pp. 19-23.

<https://doi.org/10.1016/j.niox.2015.09.008>

ABSTRACT: Interactions of hydrogen sulfide (HS-/H<sub>2</sub>S), a reducing signaling species, with superoxide dismutases (SOD) are poorly understood. We applied low-T EPR spectroscopy to examine the effects of HS-/H<sub>2</sub>S and superoxide radical anion (O<sub>2</sub><sup>-</sup>) on metalcenters of FeSOD, MnSOD, and CuZnSOD. HS-/H<sub>2</sub>S did not affect FeSOD, whereas active centers of MnSOD and CuZnSOD were open to this agent. Cu<sup>2+</sup> was reduced to Cu<sup>+</sup>, while manganese appears to be released from MnSOD active center. Untreated and O<sub>2</sub> treated FeSOD and MnSOD predominantly show 5 d-electron systems, i.e. Fe<sup>3+</sup> and Mn<sup>2+</sup>. Our study provides new details on the mechanisms of (patho)physiological effects of HS-/H<sub>2</sub>S. © 2015 Elsevier Inc. All rights reserved.

Jovanović, S., Petrović, B., Petković, M., Bugarčić, Ž.D.  
Kinetics and mechanism of substitution reactions of the new bimetallic [PdCl(bipy)]<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>H<sub>2</sub>N)]Cl<sub>4</sub> complex with important bio-molecules  
(2015) Polyhedron, 101, art. no. 11535, pp. 206-214.

<https://doi.org/10.1016/j.poly.2015.09.021>

ABSTRACT: The new dinuclear bimetallic complex, [PdCl(bipy)]<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>H<sub>2</sub>N)]Cl<sub>4</sub> (bipy is 2,2'-bipyridine), has been prepared and characterized by elemental microanalysis, IR, <sup>1</sup>H NMR spectroscopy and MALDI-TOF mass spectrometry. Substitution reactions of the studied complex with selected biologically important ligands such as: thiourea (Tu), l-methionine (l-Met), l-cysteine (l-Cys), l-histidine (l-His) and guanosine-5'-monophosphate (5'-GMP), were studied under the pseudo-first order conditions as a function of concentration and temperature using stopped-flow and UV-Vis spectrophotometry. The reactions were monitored in 0.1 M NaCl<sub>4</sub> at pH 5.0, in the presence of 40

mM NaCl. All fast reactions were monitored by stopped-flow at three temperatures (288 K, 298 K, 308 K) to determine the activation parameters, while the reactions studied by UV-Vis spectrophotometry were tested only at 298 K. Observed order of reactivity of the used ligands is: Tu > l-Met > l-Cys > l-His > 5'-GMP. Substitution reactions of the investigated bimetallic complex with Tu, l-Cys and l-His were followed by degradation to the corresponding substituted mononuclear complexes of palladium (II) and platinum (II), [Pd(bipy)(Nu)<sub>2</sub>] and [Pt(bipy)(Nu)<sub>2</sub>] (where Nu = Tu, l-Cys, l-His), by releasing of the bridge ligand, 1,6-diaminohexane. In contrast, during the substitution reactions with l-Met and 5'-GMP, the structure of starting bimetallic complex was preserved and the process of degradation can be halted. The proposed pathways of the substitution reactions of [PdCl(bipy)]<sub>2</sub>(μ-(NH)<sub>2</sub>(CH)<sub>2</sub>)<sub>6</sub>H<sub>2</sub>N] [PtCl(bipy)]<sub>2</sub>Cl<sub>4</sub> complex with all selected ligands were confirmed by 1H NMR spectroscopy at 295 K. Additionally, the two pK<sub>a</sub> values of studied diaqua complex, [Pd(H<sub>2</sub>O)(bipy)]<sub>2</sub>(μ-(NH)<sub>2</sub>(CH)<sub>2</sub>)<sub>6</sub>H<sub>2</sub>N] [Pt(H<sub>2</sub>O)(bipy)]<sub>2</sub>]<sup>4+</sup>, were determined by spectrophotometric pH titration. The large negative values for the entropy of activation, ΔS<sup>‡</sup>, support an associative substitution mechanism. © 2015 Elsevier Ltd.

Prekodravac, J., Marković, Z., Jovanović, S., Budimir, M., Peruško, D., Holclajtner-Antunović, I., Pavlović, V., Syrgiannis, Z., Bonasera, A., Todorović-Marković, B.

The effect of annealing temperature and time on synthesis of graphene thin films by rapid thermal annealing  
(2015) Synthetic Metals, 209, pp. 461-467.

<https://doi.org/10.1016/j.synthmet.2015.08.015>

ABSTRACT: In this paper, we performed synthesis of graphene thin films by rapid thermal annealing (RTA) of thin nickel-copper (Ni/Cu) layers deposited on spectroscopic graphite as a carbon source. Furthermore, we investigated the effect of annealing temperature and annealing time on formation and quality of synthesized graphene films. Raman spectroscopy study showed that annealing at lower temperatures results in formation of monolayer graphene films, while annealing at higher temperatures results in formation of multilayer graphene films. We used Raman mapping to determine the distribution of graphene sheets. Surface morphology of graphene thin films was investigated by atomic force microscopy and scanning electron microscopy with EDS probe. © 2015 Elsevier B.V. All rights reserved.

Rožić, L., Grbić, B., Petrović, S., Radić, N., Damjanović, L., Vuković, Z.

The tungsten heteropolyacid supported on activated bentonites as catalyst for selective oxidation of 2-propanol This article is dedicated to the memory of Prof. Željko Grbavčić, who recently passed away.  
(2015) Materials Chemistry and Physics, 167, pp. 42-48.

<https://doi.org/10.1016/j.matchemphys.2015.09.040>

ABSTRACT: This paper provides the correlation between the catalytic activity and selectivity of catalysts with various loadings of

heteropolyacids over bentonite in the vapour phase 2-propanol oxidation. The catalysts are characterised by energy dispersive spectroscopy, differential scanning calorimeter, ammonia temperature programmed desorption, infrared spectroscopy and a nitrogen adsorption/desorption method. Energy dispersive spectroscopy results have shown satisfactory agreement regarding chemical composition that corresponds to the desired content of heteropolyacids on bentonite. Thermal analysis confirmed the thermal stability of catalysts under the investigated region of oxidation reaction. NH<sub>3</sub>-TPD spectra demonstrated that all catalysts include two types of acidic sites: weak adsorption centres up to 390 K and a broad distribution of stronger acidic sites at higher temperatures. The catalysts were active in the vapour-phase conversion of 2-propanol to acetone in the temperature region of 343-553 K. An increase of HPW loading improves selectivity towards acetone formation. © 2015 Elsevier B.V.

Damjanović, L., Gajić-Kvašček, M., Durdević, J., Andrić, V., Marić-Stojanović, M., Lazić, T., Nikolić, S.

The characterization of canvas painting by the Serbian artist Milo Milunović using X-ray fluorescence, micro-Raman and FTIR spectroscopy (2015) Radiation Physics and Chemistry, 115, pp. 135-142.

<https://doi.org/10.1016/j.radphyschem.2015.06.017>

ABSTRACT: A canvas painting by Milo Milunović "The Inspiration of the poet" was studied by energy dispersive X-Ray fluorescence (EDXRF), micro-Raman and Fourier transform infrared (FTIR) spectroscopy in order to identify materials used by the artist and his painting technique. Study is performed combining in situ non-destructive method with the preparation and study of cross-section samples and raw fragments of the samples. Milo Milunović, an eminent painter from Balkan region, made a copy of the Nicolas Poussin's original painting in Louvre in 1926/27. Obtained results revealed following pigments on the investigated canvas painting: vermilion, minium, cobalt blue, ultramarine, lead white, zinc white, cadmium yellow, chrome-based green pigment and several earth pigments - red and yellow ocher, green earth and umber. Ground layer was made of lead white mixed with calcium carbonate. © 2015 Elsevier Ltd.

Stoševski, I., Krstić, J., Vokić, N., Radosavljević, M., Popović, Z.K., Miljanić, Š.

Improved Poly(vinyl alcohol) (PVA) based matrix as a potential solid electrolyte for electrochemical energy conversion devices, obtained by gamma irradiation (2015) Energy, 90, pp. 595-604.

<https://doi.org/10.1016/j.energy.2015.07.096>

ABSTRACT: PVA (Poly(vinyl alcohol)) matrixes were developed for potential application in electrochemical energy conversion devices, like batteries, alkaline fuel cells and electrolyzers. They were prepared by  $\gamma$ -irradiation of aqueous PVA solutions, followed by different post irradiation treatments. By immersion in an electrolyte they become membranes with high ionic conductivities. The treatments were shown as the key factor determining the conductivity, through affecting their structure. An improved structure has large fractional free volume, and allows high electrolyte uptake and thus

high conductivity (0.30 S cm<sup>-1</sup>-0.34 S cm<sup>-1</sup>). The structure, as well as the conductivity, has not been changed even after a period of 14 months, although the membranes have been exposed to strong alkaline medium. Besides high and long-term conductivity of the KOH doped membranes, other important properties for application in the devices were investigated, like thermal stability and gas crossover through the membranes. The 10%PVA25kGy membrane doped with saturated LiNO<sub>3</sub> solution was tested in a rechargeable aqueous Li-ion battery. Due to its high conductivity it allowed an electrode material to have the same coulombic efficiency as it would have in liquid LiNO<sub>3</sub>, showing good compatibility with the material. All these properties make the membranes attractive candidates for possible application in the electrochemical devices. © 2015 Elsevier Ltd.

Vasić, M.M., Minić, D.M., Blagojević, V.A., Žák, T., Pizúrová, N., David, B., Minić, D.M.

Thermal stability and mechanism of thermally induced crystallization of Fe<sub>73.5</sub>Cu<sub>1</sub>Nb<sub>3</sub>Si<sub>15.5</sub>B<sub>7</sub> amorphous alloy

(2015) *Acta Physica Polonica A*, 128 (4), pp. 657-660.

<https://doi.org/10.12693/APhysPolA.128.657>

**ABSTRACT:** Investigation of thermal stability of the alloy revealed stepwise crystallization process, manifested by two distinct complex exothermic peaks in differential scanning calorimetry curves. Kinetic parameters of individual crystallization steps were found using the Kissinger and Vyazovkin methods. Structural characterization of thermally treated samples showed formation of different iron-based phases including  $\alpha$ -Fe(Si), Fe<sub>2</sub>B, Fe<sub>16</sub>Nb<sub>6</sub>Si<sub>7</sub> and Fe<sub>2</sub>Si and some metastable intermediary species. Morphology characterization of the surface and cross-section of the thermally treated samples showed granulated structure composed of several different phases and indicated occurrence of impingement effects during crystal growth. Value of estimated lifetime suggested very high stability against crystallization at room temperature and abrupt decrease of lifetime with temperature increase.

Jovanović, S., Bogojeski, J., Petković, M., Bugarčić, Z.D.

Interactions of nitrogen-donor bio-molecules with dinuclear platinum(II) complexes

(2015) *Journal of Coordination Chemistry*, 68 (17-18), pp. 3148-3163.

<https://doi.org/10.1080/00958972.2015.1048240>

**ABSTRACT:** Substitution reactions of the dinuclear Pt(II) complexes, [Pt(en)Cl]<sub>2</sub>(-pz)]<sup>2+</sup> (1), [Pt(dach)Cl]<sub>2</sub>(-pz)]<sup>2+</sup> (2) and [Pt(dach)Cl]<sub>2</sub>(-4,4-bipy)]<sup>2+</sup> (3), and corresponding aqua analogs with selected biologically important ligands, viz. 1,2,4-triazole, L-histidine (L-His) and guanosine-5-monophosphate (5-GMP) were studied under pseudo-first-order conditions as a function of concentration and temperature using UV-vis spectrophotometry. The reactions of the chloride complexes were followed in aqueous 25 mmol L<sup>-1</sup> Hepes buffer in the presence of 40 mmol L<sup>-1</sup> NaCl at pH 7.2, whereas the reactions of the aqua complexes were studied at pH 2.5. Two consecutive reaction steps, which both depend on the nucleophile concentration, were observed in all cases. The second-order rate constants for both reaction steps indicate a decrease in the order 1 > 2 > 3 for all

complexes. Also, the pKa values of all three aqua complexes were determined. The order of the reactivity of the studied ligands is 1,2,4-triazole > L-His > 5-GMP. <sup>1</sup>H NMR spectroscopy and HPLC were used to follow the substitution of chloride in the dichloride 1, 2, and 3 complexes by guanosine-5-monophosphate (5-GMP). This study shows that the inert and bridging ligands have an important influence on the reactivity of the studied complexes. © 2015 Taylor & Francis.

Vujković, M., Mitrić, M., Mentus, S.  
High-rate intercalation capability of  
NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C composite in aqueous  
lithium and sodium nitrate solutions  
(2015) Journal of Power Sources, 288, pp. 176-186.

<https://doi.org/10.1016/j.jpowsour.2015.04.132>

ABSTRACT: (Graph Presented). The nanodispersed NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C composite containing 20-25 wt.% of in-situ formed carbon, was synthesized by gel combustion procedure followed by a heat treatment at 650, 700 and 750 C. The samples calcined at 700 and 750 C displayed crystalline nasicon structure. They were subjected to the investigation of intercalation/deintercalation kinetics in aqueous NaNO<sub>3</sub> and LiNO<sub>3</sub> solutions, using cyclic voltammetry and galvanostatic charging/discharging measurements. As regards to the effect of electrolyte composition, the reactions were evidenced to be roughly twice faster in sodium nitrate than in lithium nitrate solution. Among the samples treated at 700 and 750 C, better performance was evidenced for the sample treated at lower temperature. Coulombic capacity in NaNO<sub>3</sub> solution at charging rate 1C amounted to ~70 mAh g<sup>-1</sup> and ~55 mAh g<sup>-1</sup> for the sample calcined at 700 and 750 C, respectively, and displayed surprisingly slight dependence on charging rate up to even 100C. © 2015 Elsevier B.V. All rights reserved.

Šljukić, B., Vujković, M., Amaral, L., Santos, D.M.F., Rocha, R.P., Sequeira, C.A.C., Figueiredo, J.L.  
Carbon-supported Mo<sub>2</sub>C electrocatalysts for hydrogen evolution reaction  
(2015) Journal of Materials Chemistry A, 3 (30), pp. 15505-15512.

<https://doi.org/10.1039/c5ta02346g>

ABSTRACT: Molybdenum carbide (Mo<sub>2</sub>C) nanoparticles supported on two different carbon materials, carbon nanotubes and carbon xerogel, were prepared and characterised using X-ray diffraction, thermogravimetric analysis, scanning and transmission electron microscopy, nitrogen sorption and X-ray photoelectron spectroscopy. The analyses showed similar composition (ca. 27 wt% of Mo<sub>2</sub>C) and crystallite size (22-28 nm) for the two samples, but significantly different morphologies and specific surface areas. These were subsequently tested as electrocatalysts for hydrogen evolution reaction (HER) in acid media. Using linear scan voltammetry and electrochemical impedance measurements the main reaction parameters were determined, including Tafel slope, charge transfer coefficient and exchange current density. Capacitance properties were examined and correlated with the electrocatalysts activity for HER. The stability of the two materials

was also investigated and proved to be very good. © The Royal Society of Chemistry 2015.

Etinski, M., Petković, M., Ristić, M.M., Marian, C.M.  
Electron-Vibrational Coupling and Fluorescence Spectra of Tetra-,  
Penta-, and Hexacoordinated Chlorophylls *c*<sub>1</sub> and  
*c*<sub>2</sub>  
(2015) Journal of Physical Chemistry B, 119 (32), pp. 10156-10169.

<https://doi.org/10.1021/acs.jpccb.5b05079>

ABSTRACT: Chlorophylls (Chls) are a group of pigments related to light absorption, excitation energy, and electron transfer in photosynthetic complexes. Given the importance of intramolecular nuclear motion for these electronic processes, many experimental studies were performed in order to relate its coupling to electronic coordinates of these pigments, but a detailed analysis is still lacking for isolated Chls *c*<sub>1</sub> and *c*<sub>2</sub>. To gain insight into the intramolecular motion and fluorescence spectra of these two pigments in tetra-, penta-, and hexacoordinated states, we performed a quantum chemical study based on density functional theory and multimode harmonic approximation with displaced, distorted, and rotated normal modes. In order to benchmark the employed methods, we simulated the high-resolution fluorescence spectra of tetracoordinated Chls a, b, and d and compared them with available experimental spectra obtained with fluorescence line-narrowing techniques. Although the experimental spectra were obtained for ligand coordinated Chls, qualitatively good agreement was found between the simulated and experimental spectra. Almost all resonances were reproduced in the spectroscopically interesting region from 200 to 1700 cm<sup>-1</sup>. The significance of mode distortion and rotation for the simulated spectra is discussed. The fluorescence spectra of Chls *c*<sub>1</sub> and *c*<sub>2</sub> consist of a group of peaks in the 200-450 cm<sup>-1</sup> spectral range, a group of weak peaks from 700 to 1000 cm<sup>-1</sup>, and a large group of strong peaks from 1100 to 1600 cm<sup>-1</sup>. Ligand effects are also addressed, and a mode is identified as a sensitive probe for the coordination state of Chls *c*<sub>1</sub> and *c*<sub>2</sub>. © 2015 American Chemical Society.

Dobrota, A.S., Pašti, I.A., Skorodumova, N.V.  
Oxidized graphene as an electrode material for rechargeable metal-ion batteries - a DFT point of view  
(2015) Electrochimica Acta, 176, art. no. 25407, pp. 1092-1099.

<https://doi.org/10.1016/j.electacta.2015.07.125>

ABSTRACT: Abstract In line with a growing interest in the use of graphene-based materials for energy storage applications and active research in the field of rechargeable metal-ion batteries we have performed a DFT based computational study of alkali metal atoms (Li, Na and K) interaction with an oxidized graphene. The presence of oxygen surface groups (epoxy and hydroxyl) alters the chemisorption properties of graphene. In particular, we observe that the epoxy groups are redox active and enhance the alkali metal adsorption energies by a factor of 2 or more. When an alkali metal atom interacts with hydroxyl-graphene the formation of metal-hydroxide is observed. In addition to a potential boost of metal ion storage capability, oxygen functional groups also prevent the precipitation of the metal phase. By simulating

lithiation/de-lithiation process on epoxy-graphenes, it was concluded that the oxidized graphene can undergo structural changes during battery operation. Our results suggest that the content and the type of oxygen surface groups should be carefully tailored to maximize the performance of metal-ion batteries. This is mainly related to the control of the oxidation level in order to provide enough active centers for metal ion storage while preserving sufficient electrical conductivity. © 2015 Elsevier Ltd.

Ekmešćić, B.M., Maksin, D.D., Marković, J.P., Vuković, Z.M., Hercigonja, R.V., Nastasović, A.B., Onjia, A.E.  
Recovery of molybdenum oxyanions using macroporous copolymer grafted with diethylenetriamine  
(2015) Arabian Journal of Chemistry, . Article in Press.

<https://doi.org/10.1016/j.arabjc.2015.11.010>

ABSTRACT: The presented study describes macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) [PGME] functionalized with diethylenetriamine [PGME-deta] as a potential recovery agent for Mo(VI) oxyanions from aqueous solutions. Sorption studies were carried out by varying experimental conditions (pH, time, concentration, temperature). Kinetics of Mo(VI) sorption was investigated in batch (static) experiments, in the temperature range 298-343K. Sorption dynamics data were fitted to seven chemical-reaction and particle-diffusion models. The kinetics studies showed that Mo(VI) sorption adhered to the pseudo-second-order model under all investigated operating conditions. The sorption kinetics was determined to be governed by both the intraparticle diffusion and the external film diffusion to a lesser extent. The temperature rise promotes the molybdate species removal, with the maximum experimental uptake capacity of 4.02mmolg<sup>-1</sup> at 298K, at the selected pH which is consistent with the predominance range of hydrolyzed polynuclear Mo(VI) forms and optimum electrostatic attraction. © 2015 The Authors.

Dimić, D., Mercader, A.G., Castro, E.A.  
Chalcone derivative cytotoxicity activity against MCF-7 human breast cancer cell QSAR study  
(2015) Chemometrics and Intelligent Laboratory Systems, 146, pp. 378-384.

<https://doi.org/10.1016/j.chemolab.2015.06.011>

ABSTRACT: Chalcones and their derivatives possess a wide range of significant pharmacological activities; among the most important ones is their anticancer activity. For this reason we performed a Quantitative Structure-Activity Relationships (QSAR) study of their anticancer activity against MCF-7 human breast cancer cell lines. In this work, several descriptor options were tested on the dataset containing 93 molecular structures, using ERM (Enhanced Replacement Method). The best models were found using merely two dimensional descriptors. The two dimensional descriptor pool was further expanded using several nonlinear transformations, which resulted in an optimal five molecular descriptor model that showed very good predictive ability. Thus, ERM was capable of finding a simple to interpret and understand model that nonetheless addresses nonlinearities between the descriptors and the activity. Furthermore, the acquired model is very

straightforward to use since it does not require the optimization of chemical structures for the calculation of three dimensional descriptors. © 2015 Elsevier B.V.

Rakić, A.A., Vukomanović, M., Trifunović, S., Travas-Sejdic, J., Chaudhary, O.J., Horský, J., Ćirić-Marjanović, G.  
Solvent effects on dopant-free pH-falling polymerization of aniline (2015) *Synthetic Metals*, 209, art. no. 15042, pp. 279-296.

<https://doi.org/10.1016/j.synthmet.2015.07.031>

ABSTRACT: Polymerizations of aniline were conducted in the mixtures of water and polar organic solvents (50 vol.%): acetone, acetonitrile, dimethylsulfoxide and ethanol, by using ammonium peroxydisulphate as an oxidant, without added acid. Course of reactions was followed by recording the temperature and pH changes of the reaction systems. The influence of the organic co-solvents and the reaction time on the molecular structure, molecular weights, morphology and properties of synthesized polyaniline (PANI) samples was studied by elemental analysis, laser desorption ionization mass spectrometry (LDI-MS), gel-permeation chromatography (GPC), FTIR, Raman and UV-vis spectroscopies, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrical conductivity measurements. The results were compared with those obtained for PANI prepared under the same reaction conditions in water without a co-solvent. © 2015 Elsevier B.V.

Gurnani, C., Orević, N., Muthaiah, S., Dimić, D., Ganguly, R., Petković, M., Vidović, D.  
Extending the chemistry of carbones: P-N bond cleavage via an SN2'-like mechanism (2015) *Chemical Communications*, 51 (53), pp. 10762-10764.

<https://doi.org/10.1039/c5cc03194j>

ABSTRACT: The reactivity of nucleophilic carbodiphosphorane (C(PPh<sub>3</sub>)<sub>2</sub>, 1) and carbodicarbene (C(C(NMe)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>, 2) towards various dichlorophosphines has been explored. In most cases the expected carbene-for-chloride ligand exchange was observed. However, the use of MeN(PCl<sub>2</sub>)<sub>2</sub> resulted in a unique P-N bond cleavage that, according to computational studies, occurred via an SN2'-like mechanism. This journal is © The Royal Society of Chemistry 2015.

Maćešić, S., Čupić, Ž., Anić, S., Kolar-Anić, L.  
Autocatalator as the source of instability in the complex non-linear neuroendocrine model (2015) *International Journal of Non-Linear Mechanics*, 73, pp. 25-30.

<https://doi.org/10.1016/j.ijnonlinmec.2014.11.008>

ABSTRACT: The mathematical analogy between properties of simple and complex models of non-linear reactions was used to determine reaction steps in the complex model, necessary to generate instability region and appropriate type of bifurcations on the border between stable and unstable non-equilibrium stationary state. The autocatalator was recognized as the simple prototype two-variable non-linear model practical for examination of the complex four-variable non-linear

neuroendocrine system known as the Hypothalamic-Pituitary-Adrenal (HPA) axis. In both cases, we derived the instability criteria by stoichiometric network analysis (SNA), determine conditions under which dynamic transitions, i.e. bifurcations occur, and identify the type of bifurcation. The supercritical Andronov-Hopf bifurcation was found in both cases whereas saddle-node bifurcation was detected only in the model for HPA axis. Thus, by stoichiometric network analysis, the mathematical analogy is found between two different models with same autocatalytic steps, that is, between two models with easily recognizable qualitative analogy. © 2014 Elsevier Ltd. All rights reserved.

Puač, N., Miletić, M., Mojović, M., Popović-Bijelić, A., Vuković, D., Miličić, B., Maletić, D., Lazović, S., Malović, G., Petrović, Z.Lj. Sterilization of bacteria suspensions and identification of radicals deposited during plasma treatment (2015) *Open Chemistry*, 13 (1), pp. 332-338.

<https://doi.org/10.1515/chem-2015-0041>

**ABSTRACT:** In this paper we will present results for plasma sterilization of planktonic samples of two reference strains of bacteria, *Pseudomonas aeruginosa* ATCC 27853 and *Enterococcus faecalis* ATCC 29212. We have used a plasma needle as a source of non-equilibrium atmospheric plasma in all treatments. This device is already well characterized by OES, derivative probes and mass spectrometry. It was shown that power delivered to the plasma is below 2 W and that it produces the main radical oxygen and nitrogen species believed to be responsible for the sterilization process. Here we will only present results obtained by electron paramagnetic resonance which was used to detect the OH, H and NO species. Treatment time and power delivered to the plasma were found to have the strongest influence on sterilization. In all cases we have observed a reduction of several orders of magnitude in the concentration of bacteria and for the longest treatment time complete eradication. A more efficient sterilization was achieved in the case of gram negative bacteria. © 2015 Nevena Puač et al., licensee De Gruyter Open.

Radosavljevic-Mihajlovic, A.S., Kremenovic, A.S., Dosen, A.M., Andrejic, J.Z., Dondur, V.T. Thermally induced phase transformation of Pb-exchanged LTA and FAU-framework zeolite to feldspar phases (2015) *Microporous and Mesoporous Materials*, 201 (C), pp. 210-218.

<https://doi.org/10.1016/j.micromeso.2014.08.059>

**ABSTRACT:** Thermally induced phase transformations of Pb-exchange LTA and FAU zeolites were from ambient temperature to 1300 °C. Both frameworks collapse into amorphous intermediate products after heating between 600 and 650 °C. Prolonged heating of the intermediate product over 1100 °C results in the formation of disordered Pb-feldsparLTA [a = 8.414 (4) Å, b = 13.048 (4) Å, c = 7.169 (4) Å,  $\beta$  = 115.35° (3)] and Pb-feldsparFAU [a = 8.422 (4) Å, b = 13.054 (4) Å, c = 7.173 (4) Å,  $\beta$  = 115.37° (3)] phases. The phase conversions within the investigated temperature range were followed by thermal (DTA, TGA, and DSC), XRPD, and Raman methods. © 2014 Elsevier Inc.

Vasić, M.M., Blagojević, V.A., Begović, N.N., Žák, T., Pavlović, V.B., Minić, D.M.

Thermally induced crystallization of amorphous Fe<sub>40</sub>Ni<sub>40</sub>P<sub>14</sub>B<sub>6</sub> alloy (2015) *Thermochimica Acta*, 614, pp. 129-136.

<https://doi.org/10.1016/j.tca.2015.06.015>

**ABSTRACT:** The crystallization mechanism and kinetics of Fe<sub>40</sub>Ni<sub>40</sub>P<sub>14</sub>B<sub>6</sub> amorphous alloy were studied under non-isothermal conditions. Thermal stabilization of this alloy manifests in DSC through two complex peaks, corresponding to crystallization and recrystallization, respectively. The complex crystallization DSC peak was deconvoluted into individual steps corresponding to crystallization of individual phases, where the results using both Gaussian-Lorentzian cross-product and Fraser-Suzuki function were compared. It was determined that the values of kinetic triplets of the individual steps did not exhibit any significant difference, depending on the deconvolution function. Anisotropic growth was indicated to be the prevailing type of impingement for all crystallization steps. Using the calculated values of the respective kinetic triplets and the mechanisms determined from the value of Avrami exponent, distinct values of activation energies for nucleation and crystal growth for crystallization of each individual phase were calculated, showing significantly higher values for nucleation than those for crystal growth. Alloy samples treated non-isothermally in the DSC cell exhibit inhomogeneous surface morphology with highly granulated structure dependent on heating rate. © 2015 Elsevier B.V. All rights reserved.

Popa, A., Sasca, V., Verdes, O., Holclajtner-Antunović, I.

Adsorption-desorption and catalytic properties of SBA-15 supported cesium salts of 12-molybdophosphoric acid for the dehydration of ethanol

(2015) *Reaction Kinetics, Mechanisms and Catalysis*, 115 (1), pp. 355-375.

<https://doi.org/10.1007/s11144-015-0832-5>

**ABSTRACT:** Cesium salts of molybdophosphoric acid with varying amounts of the cations Cs<sub>1</sub>H<sub>2</sub>PMo<sub>12</sub>O<sub>40</sub> and Cs<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> have been prepared as pure or supported on SBA-15. The adsorption of ethanol and its temperature programmed desorption-TPD using thermogravimetry were studied for SBA-15 supported and unsupported Cs salts. The evolved gases during the adsorption-desorption of ethanol on CsHPM/SBA-15 composites were identified by online mass spectrometry coupled with thermogravimetry. The main products observed in the evolved gases during the desorption of ethanol were C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and unreacted ethanol. The amount of acidic sites of the composites was estimated by ammonia adsorption-desorption. The dehydration of ethanol was used to test the catalytic properties of the CsHPM samples incorporated on the silica matrix. SBA15 - supported catalysts, appeared to be more active than bulk catalysts in vapor phase dehydration and dehydrogenation of ethanol reactions. The effect of the support leads to higher values of dehydration rates of ethanol as well as higher values of ethylene and acetaldehyde formation rates. © 2015 Akadémiai Kiadó.

Pašti, I.A., Skorodumova, N.V., Mentus, S.V.  
Theoretical studies in catalysis and electrocatalysis: From fundamental knowledge to catalyst design  
(2015) Reaction Kinetics, Mechanisms and Catalysis, 115 (1), pp. 5-32.

<https://doi.org/10.1007/s11144-014-0808-x>

ABSTRACT: Catalytic processes are an indispensable part of a large number of contemporary technologies that stimulate a constant research and development effort in the field. Computational methods represent a valuable tool to investigate crucial steps of catalytic cycles able to reveal the main characteristics of a catalyst and provide a basis for the design of materials with superior catalytic activity. This review is focused on the recent advances in density functional theory studies of the interactions of reactive species and intermediates with solid surfaces. As examples, we discuss the catalysts for the CO oxidation and electrocatalysis of H<sub>2</sub> and O<sub>2</sub> electrode reactions. We demonstrate how the theoretical modelling can contribute to the understanding of catalytic processes and help to design new catalysts and electrocatalysts. © 2014 Akadémiai Kiadó.

Jovanović, D.J., Dugandžić, I.M., Ćirić-Marjanović, G., Radetić, T., Ahrenkiel, S.P., Milošević, O.B., Nedeljković, J.M., Šaponjić, Z.V., Mancic, L.T.  
Spherical assemblies of titania nanotubes generated through aerosol processing  
(2015) Ceramics International, 41, .

<https://doi.org/10.1016/j.ceramint.2015.07.205>

ABSTRACT: We report on the possibility to build hierarchically organized three-dimensional (3D) titania spherical particles having high surface-to-volume-ratio, by aerosol processing of nanotubular building blocks. Morphology and crystal structure of titania based spherical assemblies, obtained in the temperature range from 150 to 650°C, were characterized by means of scanning and transmission electron microscopy, x-ray powder diffraction and Raman spectroscopy. Initial shape of 1D building units, nanotubes, was well preserved in the spherical assemblies processed at 150 and 450°C. Processing at 650°C resulted in a collapse of the nanotubular building blocks and formation of the assemblies of irregularly shaped TiO<sub>2</sub> nanoparticles. Structural analysis revealed several phase transitions in titania spherical assemblies in course with the temperature increase indicating possibility of in-situ phase composition adjustment during aerosol processing. © 2015 Elsevier Ltd and Techna Group S.r.l.

Janković, B.  
Devolatilization kinetics of swine manure solid pyrolysis using deconvolution procedure. Determination of the bio-oil/liquid yields and char gasification  
(2015) Fuel Processing Technology, 138, pp. 1-13.

<https://doi.org/10.1016/j.fuproc.2015.04.027>

ABSTRACT: In the present study, the pyrolysis process under dynamic conditions of swine manure solids collected from rearing farm was

investigated. Tested type of biomass feedstock was analyzed from the point of view of technological exploitation in order to obtain the highest possible quality and yields of bio-oil and bio-char. Furthermore, char gasification process was also examined. It was found that pyrolysis process can be described by parallel independent two-portion process model (PI-TPPM), which includes two processing state of the system (marked by processes # 1 and # 2), where process # 1 can be attributed to decomposition processes of hemicelluloses and fats/proteins, while process # 2 corresponds to pyrolyses of cellulose and lignin. Also, it was found that liquid and gas yields increase with an increase in heating rate, while approximately 40% of heavy oil yield is achieved by proposed experimental setup, which have been attained the satisfactory results for a good support in industrial extraction procedures. It was found that results associated with the presence of high reactivity at highest heating rate can be attributed to the highly porous structures formed, as we approach to the fast pyrolysis conditions. © 2015 Elsevier B.V. All rights reserved.

Begović, N.N., Stojanović, N.N., Ostojić, S.B., Radulović, A.M., Blagojević, V.A., Simonović, B., Minić, D.M.  
Thermally induced polymerization of binuclear  
[Ni<sub>2</sub>(en)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(pyr)]·4H<sub>2</sub>O complex  
(2015) *Thermochimica Acta*, 607, pp. 82-91.

<https://doi.org/10.1016/j.tca.2014.10.013>

ABSTRACT: Binuclear [Ni<sub>2</sub>(en)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(pyr)]·4H<sub>2</sub>O complex undergoes dehydration in 325-400 K temperature region, which is accompanied by polymerization. Polymerized product is characterized by chelate coordination of carboxylate group to Ni, as identified by vibrational spectroscopy. XRD and spectroscopic measurements suggest that the resulting dehydration product is two-dimensional layered polymer with weak interconnectivity between the polymer layers. A combination of experimental measurements and DFT calculations was used to identify two reaction mechanisms, as well as the factors determining the change from one mechanism to the other. Reaction mechanism changes with increase in the heating rate, due to slow diffusion of released water inhibiting the polymerization. Polymerization occurs in parallel with dehydration at lower heating rates, while it follows dehydration at higher heating rates, leading to an increase in overall enthalpy of the reaction of around 50 kJ mol<sup>-1</sup> and decrease in crystallinity of the polymeric product. Determined isokinetic temperature of the dehydration reaction corresponds to the vibrational frequency of NiOH<sub>2</sub> bond. © 2015 Dragica M. Minić.

Perić, M., Jerosimić, S., Mitić, M., Milovanović, M., Ranković, R.  
Underlying theory of a model for the Renner-Teller effect in tetra-atomic molecules: X 2Π<sup>u</sup> electronic state of C<sup>2+</sup>H<sup>2+</sup>  
(2015) *Journal of Chemical Physics*, 142 (17), art. no. 174306, .

<https://doi.org/10.1063/1.4919285>

ABSTRACT: In the present study, we prove the plausibility of a simple model for the Renner-Teller effect in tetra-atomic molecules with linear equilibrium geometry by ab initio calculations of the electronic energy surfaces and non-adiabatic matrix elements for the

X<sup>2</sup>Π<sup>u</sup> state of C<sub>2</sub>H<sub>2</sub><sup>+</sup>. This phenomenon is considered as a combination of the usual Renner-Teller effect, appearing in triatomic species, and a kind of the Jahn-Teller effect, similar to the original one arising in highly symmetric molecules. Only four parameters (plus the spin-orbit constant, if the spin effects are taken into account), which can be extracted from ab initio calculations carried out at five appropriate (planar) molecular geometries, are sufficient for building up the Hamiltonian matrix whose diagonalization results in the complete low-energy (bending) vibronic spectrum. The main result of the present study is the proof that the diabaticization scheme, hidden beneath the apparent simplicity of the model, can safely be carried out, at small-amplitude bending vibrations, without cumbersome computation of non-adiabatic matrix elements at large number of molecular geometries. © 2015 AIP Publishing LLC.

Pešić, M., Podolski-Renić, A., Stojković, S., Matović, B., Zmejkoski, D., Kojić, V., Bogdanović, G., Pavićević, A., Mojović, M., Savić, A., Milenković, I., Kalauzi, A., Radotić, K.  
Anti-cancer effects of cerium oxide nanoparticles and its intracellular redox activity  
(2015) *Chemico-Biological Interactions*, 232, art. no. 7312, pp. 85-93.

<https://doi.org/10.1016/j.cbi.2015.03.013>

**ABSTRACT:** Abstract Data on medical applications of cerium oxide nanoparticles CeO<sub>2</sub> (CONP) are promising, yet information regarding their action in cells is incomplete and there are conflicting reports about in vitro toxicity. Herein, we have studied cytotoxic effect of CONP in several cancer and normal cell lines and their potential to change intracellular redox status. The IC<sub>50</sub> was achieved only in two of eight tested cell lines, melanoma 518A2 and colorectal adenocarcinoma HT-29. Self-propagating room temperature method was applied to produce CONP with an average crystalline size of 4 nm. The results confirmed presence of Ce<sup>3+</sup> and O<sup>2-</sup> vacancies. The induction of cell death by CONP and the production of reactive oxygen species (ROS) were analyzed by flow-cytometry. Free radicals related antioxidant capacity of the cells was studied by the reduction of stable free radical TEMPONE using electron spin resonance spectroscopy. CONP showed low or moderate cytotoxicity in cancer cell lines: adenocarcinoma DLD1 and multi-drug resistant DLD1-TxR, non-small cell lung carcinoma NCI-H460 and multi-drug resistant NCI-H460/R, while normal cell lines (keratinocytes HaCaT, lung fetal fibroblasts MRC-5) were insensitive. The most sensitive were 518A2 melanoma and HT-29 colorectal adenocarcinoma cell lines, with the IC<sub>50</sub> values being between 100 and 200 μM. Decreased rate of TEMPONE reduction and increased production of certain ROS species (peroxynitrite and hydrogen peroxide anion) indicates that free radical metabolism, thus redox status was changed, and antioxidant capacity damaged in the CONP treated 518A2 and HT-29 cells. In conclusion, changes in intracellular redox status induced by CONP are partly attributed to the prooxidant activity of the nanoparticles. Further, ROS induced cell damages might eventually lead to the cell death. However, low inhibitory potential of CONP in the other human cell lines tested indicates that CONP may be safe for human usage in industry and medicine. © 2015 Elsevier Ireland Ltd. All rights reserved.

Dordević, N., Tay, M.Q.Y., Muthaiah, S., Ganguly, R., Dimić, D., Vidović, D.

C-F bond activation by transient phosphonium dications  
(2015) *Inorganic Chemistry*, 54 (9), pp. 4180-4182.

<https://doi.org/10.1021/ic5031125>

ABSTRACT: C-F bond cleavage by transient phosphorus(III)-based dications  $[\text{RP}(\text{C}(\text{PPh})_3)_2]^{2+}$  ( $4a^{2+}$ , R = Ph;  $4b^{2+}$ , R = 4-F-Ph) is reported. These dications were generated by reaction of the corresponding monocationic precursors with excess  $\text{Na}[\text{BARCl}]_4$ . Evidence for the existence of transient dicationic species was obtained by trapping the dication  $4a^{2+}$  with  $\text{PMe}_3$ . According to theoretical analysis, the low-lying lowest unoccupied molecular orbitals of these species were responsible for the observed activation of C-F bonds. © 2015 American Chemical Society.

Filipović, M., Marković, Z., Dorović, J., Marković, J.D., Lučić, B., Amić, D.

QSAR of the free radical scavenging potency of selected hydroxybenzoic acids and simple phenolics  
(2015) *Comptes Rendus Chimie*, 18 (5), art. no. 3978, pp. 492-498.

<https://doi.org/10.1016/j.crci.2014.09.001>

ABSTRACT: Abstract The quantitative structure-activity relationship (QSAR) of the free radical scavenging potency of 21 selected hydroxybenzoic acids and simple phenolics was examined. We found that descriptors related to the energetics and structural aspects of free radical scavenging processes enable the development of reliable QSAR models that possess better statistical characteristics than the models developed using more than thousand molecular descriptors from the large Dragon set. The lack of standardized antioxidant assays makes the successful use of the QSAR procedure doubtful. However, we showed that by taking into account some driving forces of free radical scavenging and the associated descriptors (bond dissociation enthalpy BDE, proton affinity PA, electron-transfer enthalpy ETE, and the number of vicinal phenolic OH groups,  $n_{\text{OHvic}}$ ), it is possible to generate fair antiradical QSAR models. © 2014 Académie des sciences.

Pašti, I.A., Baljzović, M.R., Granda-Marulanda, L.P., Skorodumova, N.V.

Bimetallic dimers adsorbed on a defect-free MgO(001) surface: Bonding, structure and reactivity  
(2015) *Physical Chemistry Chemical Physics*, 17 (15), pp. 9666-9679.

<https://doi.org/10.1039/c4cp05723f>

ABSTRACT: A large number of computational studies have been devoted to the investigation of monometallic clusters supported by MgO. However, in practice, catalysis shows that multicomponent catalytic systems often win in catalytic performance over single component systems. In this study, the geometrical and electronic structure, stability and chemisorption properties of M1M2 metal dimers (M1, M2 = Ru, Rh, Pd, Ir, Pt) supported by defect free MgO(001) have been investigated in the

framework of density functional theory. The oxygen sites of MgO(001) are the preferred adsorption sites for all the studied clusters, the majority of them adsorbing parallel to the surface with metal atoms attached to two surface oxygen atoms. The energetics of  $M_1M_2 + MgO(001)$  formation shows that the adsorption complexes are stable and benefit from metal-oxygen and metal-metal interaction. The chemisorption properties of Pd and Pt atoms in PdM<sub>2</sub> and PtM<sub>2</sub> dimers are studied using CO as a probe molecule. A linear relationship between the CO chemisorption and the d-band center position of the reacting atom in the dimer is observed, extending the d-band center model to the case of highly under-coordinated metal atoms supported by a non-conductive material. This journal is © the Owner Societies.

Đukić, A.B., Kumrić, K.R., Vukelić, N.S., Stojanović, Z.S., Stojmenović, M.D., Milošević, S.S., Matović, L.L.  
Influence of ageing of milled clay and its composite with TiO<sub>2</sub> on the heavy metal adsorption characteristics  
(2015) *Ceramics International*, 41 (3), pp. 5129-5137.

<https://doi.org/10.1016/j.ceramint.2014.12.085>

ABSTRACT: The aim of the present study was to investigate the effect of ageing of mechanochemically synthesized clay and its TiO<sub>2</sub> composite on the simultaneous removal of Pb(II), Cd(II), Cu(II) and Zn(II) ions from acidic aqueous solutions. The effect of different ageing times on sorption behavior of 1, 2, 10 and 19 h milled clays, as well as the clay composite with 20 wt% of amorphous TiO<sub>2</sub> (TiO<sub>2</sub>,a), was investigated. Ageing of the milled clays has stronger influence on the removal of Zn(II) and Cd(II) than on the removal of Pb(II) and Cu(II) ions. Ageing is particularly pronounced for the samples milled for 1, 2 and 10 h (which lost enhanced sorption properties after 3 months of ageing), and less pronounced for the samples milled longer period of time, 19 h (which retained sorption properties until 6 months). After these periods of time sorption capacities became nearly the same as the sorption capacities of the raw (unmilled) clay. The different responses on the ageing process of milled clays and composite are a consequence of microstructural changes such as recrystallization of montmorillonite phase and decrease in particle sizes. Slower ageing of composite compare to the milled clays can be related to the stabilization effect of TiO<sub>2</sub> particles which are dispersed in the clay matrix thus preventing recrystallization of the sample particles. Only a slight tendency towards the formation of agglomerations was noticed after 12 months of ageing. © 2014 Elsevier Ltd and Techna Group S.r.l.

Stojmenović, M., Bošković, S., Žunić, M., Babić, B., Matović, B., Bajuk-Bogdanović, D., Mentus, S.  
Studies on structural, morphological and electrical properties of Ce<sub>1-x</sub>Er<sub>x</sub>O<sub>2-δ</sub> (x = 0.05-0.20) as solid electrolyte for IT - SOFC  
(2015) *Materials Chemistry and Physics*, 153, pp. 422-431.

<https://doi.org/10.1016/j.matchemphys.2015.01.036>

ABSTRACT: A series of four different powders ceria doped Ce<sub>1-x</sub>Er<sub>x</sub>O<sub>2-δ</sub> (0.05 ≤ x ≤ 0.20) were synthesized by applying self-propagating reaction at room temperature (SPRT method). SPRT procedure is based on the self-propagating room temperature reaction between metal nitrates and sodium hydroxide, wherein the reaction is spontaneous and

terminates extremely fast. The method is known to assure very precise stoichiometry of the final product in comparison with a tailored composition. XRPD, Raman spectroscopy, TEM and BET measurements were used to characterize the nanopowders at room temperature. It was shown that all obtained powders were single phase solid solutions with a fluorite-type crystal structure and all powder particles have nanometric size (about 3-4 nm). Densification was performed at 1550 °C, in an air atmosphere for 2 h. XRPD, SEM and complex impedance method measurements were carried out on sintered samples. Single - phase form was evidenced for each sintered materials. The best value of conductivity at 700 °C amounted to  $1.10 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$  for Ce<sub>0.85</sub>Er<sub>0.15</sub>O<sub>2- $\delta$</sub>  sample. Corresponding activation energies of conductivity amounted to 0.28 eV in the temperature range 500-700 °C. © 2015 Elsevier B.V. All rights reserved.

Mentus, S.

The evidence of limitation of oxygen reduction reaction by proton diffusion in low-concentration acid solutions  
(2015) Journal of Electroanalytical Chemistry, 738, pp. 47-50.

<https://doi.org/10.1016/j.jelechem.2014.11.022>

ABSTRACT: By voltammetry with polycrystalline platinum rotating disc electrode in either nitrogen purged or oxygen saturated  $1 \times 10^{-3} \text{ mol dm}^{-3}$  and  $2 \times 10^{-3} \text{ mol dm}^{-3}$  HClO<sub>4</sub> solutions with  $0.1 \text{ mol dm}^{-3}$  KClO<sub>4</sub> supporting electrolyte, the transition was observed from the proton diffusion limited to the oxygen diffusion limited rate of oxygen reduction reaction. The experiments confirmed roughly the calculation based on the Levich equation, that the limitation in the diffusion kinetics of oxygen reduction reaction by proton diffusion terminates for acid concentration higher than  $1.69 \times 10^{-3} \text{ mol dm}^{-3}$ . © 2014 Elsevier B.V. All rights reserved.

Ćirić-Marjanovic, G., Pašti, I., Mentus, S.

One-dimensional nitrogen-containing carbon nanostructures  
(2015) Progress in Materials Science, 69, pp. 61-182.

<https://doi.org/10.1016/j.pmatsci.2014.08.002>

ABSTRACT: One-dimensional nitrogen-containing carbon nanostructures (1-D NCNSs) have emerged in the past two decades as exceptionally promising nanomaterials due to their unique physical and chemical properties which enable a broad range of applications in various fields of modern technology. Recent investigations revealed that the 1-D NCNS-based materials can have a profound impact on energy conversion and storage, catalysis and electrocatalysis, sensors, electronic nanodevices, environmental protection, and biology-related applications. The aim of the present review article was to provide a comprehensive overview of scientific progress in 1-D NCNSs such as N-containing carbon nanotubes (NCNTs, e.g., single-walled (SWNCNTs), double-walled (DWNCNTs), and multi-walled NCNTs (MWNCNTs)), nanofibers (NCNFs), nanowires (NCNWs), nanorods (NCNRs), and nanohorns (NCNHs), and evaluate their future perspective. Various methods of preparation of 1-D NCNSs and their composites are summarized and discussed. The structure-properties relations of 1-D NCNSs, based on the theoretical approach and numerous relevant physico-chemical methods of characterization, were outlined. The emphasis is given to the

properties of 1-D NCNSs rendered by nitrogen incorporation into the carbon matrix in order to provide deeper insight into the specific characteristics which determine materials' performances within the specific fields of applications. © 2014 Elsevier Ltd.

Vujković, M.

Comparison of lithium and sodium intercalation materials

(2015) Journal of the Serbian Chemical Society, 80 (6), pp. 801-804.

<https://doi.org/10.2298/JSC141119127V>

**ABSTRACT:** The low abundance of lithium in the Earth's crust and its high participation in overall cost of lithium-ion batteries incited intensive investigation of sodium-ion batteries, in the hope that they may become similar in their basic characteristics: specific energy and specific power. Furthermore, over the last years, research has been focused on the replacement of the organic electrolytes of Li- and Na-ion batteries by aqueous electrolytes, in order to simplify the production and improve safety of use. In this lecture, some recent results on selected intercalation materials are presented: layered structure vanadium oxides, olivine and nasicon phosphates, potentially usable in both Li and Na aqueous rechargeable batteries. After their characterization by X-ray diffraction and electron microscopy, the electrochemical behavior was studied by both cyclic voltammetry and chronopotentiometry. By comparing the intercalation kinetics and coulombic capacity of these materials in  $\text{LiNO}_3$  and  $\text{NaNO}_3$  solutions, it was shown that the following ones:  $\text{Na}_{1.2}\text{V}_3\text{O}_8$ ,  $\text{Na}_2\text{V}_6\text{O}_{16}/\text{C}$ ,  $\text{NaFePO}_4/\text{C}$  and  $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$  may be used as electrode materials in aqueous alkali-ion batteries. © 2015 SCS. All rights reserved.

Bajuk-Bogdanović, D., Uskoković-Marković, S., Holclajtner-Antunović, I. Vibration Spectroscopy Stability Investigation of 12-Tungstosilicic Acid Solution

(2015) Journal of the Iranian Chemical Society, 12 (1), pp. 137-145.

<https://doi.org/10.1007/s13738-014-0466-y>

**ABSTRACT:** Heteropoly acids (HPA) attract the attention of large variety of scientists, due to HPA's extraordinary interesting properties and possible application fields. 12-tungstosilicic acid (WSiA), the Keggin type HPA, has some promising characteristic to be used in catalytic processes, but with not well-defined stability. Raman spectroscopy was used for in situ analysis of WSiA hydrolysis in detail in a wide pH range of 1-12. Raman spectroscopy is able to give an almost immediate response/spectrum as a representation of the exact profile/composition of the solution. This method and FTIR spectroscopy, as a complementary technique, enabled recording of the solid and liquid phases of the same sample under different conditions. Our results confirm that the decomposition pathways of WSiA in solution proceed via the formation of the lacunary monovacant anion at  $\text{pH} > 6.4$ . This anion is a major constituent in pH range up to 9.5. With further increases in pH this species convert to the trivacant lacunary anion. The total decomposition of the Keggin anion to silicate and tungstate occurs at  $\text{pH} > 11.0$ . The results of the performed study contribute to understand

the behavior of WSiA in the water-methanol solution, as the model system of aqueous-organic system. It is concluded that addition of methanol in aqueous solution of WSiA leads to expansion of the pH region where Keggin anion is stable up to 8.1 and above this pH value, precipitation occurs. The obtained data clarify the stability range of WSiA in both water and water-methanol solutions, as well. © 2014 Iranian Chemical Society.

Stojadinović, S., Vasilić, R., Radić-Perić, J., Perić, M.  
Characterization of plasma electrolytic oxidation of magnesium alloy AZ31 in alkaline solution containing fluoride  
(2015) Surface and Coatings Technology, 273 (1), pp. 1-11.

<https://doi.org/10.1016/j.surfcoat.2015.03.032>

ABSTRACT: Plasma electrolytic oxidation (PEO) of magnesium alloy AZ31 in water solution containing 4g/L Na<sub>2</sub>SiO<sub>3</sub> · 5H<sub>2</sub>O+4g/L KOH+0.5g/L NaF was investigated. Scanning electron microscopy was used to characterize morphology of the formed surface coatings, while the crystallinity of the samples was analyzed by X-ray diffraction. Spectral luminescence measurements during PEO of magnesium were taken. The spectra consisted of atomic/ionic lines originating from the elements present both in the substrate and the electrolyte. Besides, the  $v'=v''$  sequence of the B<sub>1</sub>Σ<sup>+</sup> - X<sub>1</sub>Σ<sup>+</sup> emission transition of MgO, and two broad peaks assigned to the unresolved  $v'=v''$  and  $v'=v''+1$  sequences of the A<sub>2</sub>Π - X<sub>2</sub>Σ<sup>+</sup> band system of MgF were identified. The measured intensity distributions within these band sequences were utilized for determination of the plasma temperature, found to be (8500±1000) K. The composition of plasmas containing Mg, O, H, and F was calculated in the temperature range up to 12000K. The results of these calculations explain the appearance of observed spectral features and support the assumption of high-pressure conditions in the microplasmas built during the PEO process. © 2015 Elsevier B.V.

Ostojić, B.D., Stanković, B., Dordević, D.S.  
Aromaticity and conformational deformability of some environmental pollutants - Methylated anthracenes  
(2015) Fresenius Environmental Bulletin, 23 (12), pp. 3036-3040.

ABSTRACT: There is little information on methylated anthracenes which are constituents of diesel fuel. In this paper, a theoretical investigation of some molecular properties of methyl-anthracenes (MAs), 1-MA and 2-MA, and all dimethylan-thracene isomers (DMAs), 1,2-DMA, 1,3-DMA, 1,4-DMA, 1,5-DMA, 1,6-DMA, 1,7-DMA, 1,8-DMA, 1,9-DMA, 1,10-DMA, 2,3-DMA, 2,6-DMA, 2,7-DMA, 2,9-DMA, 2,10-DMA, and 9,10-DMA, are presented. The aromaticity indices, based on nucleus-independent chemical shifts (NICS), indicate the aromatic character of methylated anthracenes. The lowest frequencies associated with the out-of-plane deformations of the anthracene (ANTH) aromatic system decrease in the order ANTH > MAs > DMAs. They are related to an increase in conformational non-rigidity of the aromatic system in these molecules, and indicate that they can change their conformation easily through intermolecular interactions, such as interactions with the enzymes of bacteria that catalyze the dioxygenation of these molecules.

Momcilovic, M., Kuzmanovic, M., Rankovic, D., Ciganovic, J., Stoiljkovic, M., Savovic, J., Trtica, M.

Optical emission studies of copper plasma induced using infrared transversely excited atmospheric (IR TEA) carbon dioxide laser pulses (2015) Applied Spectroscopy, 69 (4), pp. 419-429.

<https://doi.org/10.1366/14-07584>

ABSTRACT: Spatially resolved, time-integrated optical emission spectroscopy was applied for investigation of copper plasma produced by a nanosecond infrared (IR) transversely excited atmospheric (TEA) CO<sub>2</sub> laser, operating at 10.6 μm. The effect of surrounding air pressure, in the pressure range 0.1 to 1013 mbar, on plasma formation and its characteristics was investigated. A linear dependence of intensity threshold for plasma formation on logarithm of air pressure was found. Lowering of the air pressure reduces the extent of gas breakdown, enabling better laser-target coupling and thus increases ablation. Optimum air pressure for target plasma formation was 0.1 mbar. Under that pressure, the induced plasma consisted of two clearly distinguished and spatially separated regions. The maximum intensity of emission, with sharp and well-resolved spectral lines and negligibly low background emission, was obtained from a plasma zone 8 mm from the target surface. The estimated excitation temperature in this zone was around 7000 K. The favorable signal to background ratio obtained in this plasma region indicates possible analytical application of TEA CO<sub>2</sub> laser produced copper plasma. Detection limits of trace elements present in the Cu sample were on the order of 10 ppm (parts per million). Time-resolved measurements of spatially selected plasma zones were used to find a correlation between the observed spatial position and time delay. © 2015 Society for Applied Spectroscopy.

Trtica, M.S., Savovic, J., Stoiljkovic, M., Kuzmanovic, M., Momcilovic, M., Ciganovic, J., Zivkovic, S.

Laser-Induced Breakdown Spectroscopy (LIBS): Specific applications (2015) Proceedings of SPIE - The International Society for Optical Engineering, 9810, art. no. 981010, .

<https://doi.org/10.1117/12.2228621>

ABSTRACT: A short overview of Laser Induced Breakdown Spectroscopy (LIBS) with emphasis on the new trends is presented. Nowadays, due to unique features of this technique, LIBS has found applications in a great variety of fields. Achievements in the application of LIBS in nuclear area, for hazardous materials detection and in geology were considered. Also, some results recently obtained at VINCA Institute, with LIBS system based on transversely excited atmospheric (TEA) CO<sub>2</sub> laser, are presented. Future investigations of LIBS will be oriented toward further improvement of the analytical performance of this technique, as well as on finding new application fields. © 2015 SPIE.

Momcilovic, M., Ciganovic, J., Rankovic, D., Jovanovic, U., Stoiljkovic, M., Savovic, J., Trtica, M.

Analytical capability of the plasma induced by IR TEA CO<sub>2</sub> laser pulses on copper-based alloys (2015) Journal of the Serbian Chemical Society, 80 (12), pp. 1505-1513.

<https://doi.org/10.2298/JSC150416061M>

ABSTRACT: The applicability of a nanosecond infrared (IR) transversely excited atmospheric (TEA) CO<sub>2</sub> laser, operating at 10.6 μm and 100 ns pulse length (initial spike), induced plasma under reduced air pressure for spectrochemical analysis of bronze and brass samples was investigated. The plasma consisted of two clearly distinguished and spatially separated regions and expanded to a distance of about 10 mm from the surface. The elemental composition of the samples was determined using a time-integrated space-resolved laser-induced plasma spectroscopic (TISR-LIPS) technique. Sharp and well-resolved spectral lines mostly atomic, and negligibly low background emission, were obtained from a plasma region 7 mm from the target surface. Good signal to background and signal to noise ratios were obtained. The estimated detection limits for the trace elements Mg, Fe, Al and Ca were in the order of 10 ppm in bronze and around 50 ppm in brass. Damage on the investigated samples induced by TEA CO<sub>2</sub> laser radiation was negligible. © 2015 SCS.

Vasić Aničijević, D.D., Nikolić, V.M., Marčeta Kaninski, M.P., Pašti, I.A.

Structure, chemisorption properties and electrocatalysis by Pd<sub>3</sub> Au overlayers on tungsten carbide - A DFT study  
(2015) International Journal of Hydrogen Energy, 40 (18), pp. 6085-6096.

<https://doi.org/10.1016/j.ijhydene.2015.03.083>

ABSTRACT: Tungsten carbide (WC) is in the focus of current research as a suitable electrocatalyst support. Typically, supported monometallic system are investigated, in spite the fact that practice in catalysis shows that multimetallic systems can have significantly better performance compared to monometallic counterparts. In this work, WC-supported Pd<sub>3</sub>Au overlayers were studied theoretically using periodic Density Functional Theory calculations and compared to bulk-like Pd<sub>3</sub>Au and pure Pd. Stability of studied surfaces and the electronic structures were analyzed. Chemisorption properties were probed using atomic H and CO molecule. Electrocatalytic activities of studied surfaces were estimated using hydrogen binding energy as catalytic activity descriptor for hydrogen electrode reactions. The connection between H binding energy and CO adsorption energy enabled us to establish the link between catalytic activity and CO tolerance of studied surfaces. It is considered that formation of bimetallic layers on WC opens a new perspective in designing new core-shell electrocatalysts with high performance and significantly reduced content of noble metals. Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Marković, Z.M., Prekodravac, J.R., Tošić, D.D., Holclajtner-Antunović, I.D., Milosavljević, M.S., Dramićanin, M.D., Todorović-Marković, B.M. Facile synthesis of water-soluble curcumin nanocrystals  
(2015) Journal of the Serbian Chemical Society, 80 (1), pp. 63-72.

<https://doi.org/10.2298/JSC140819117M>

ABSTRACT: In this paper, a facile synthesis of water-soluble curcumin nanocrystals is reported. Solvent exchange method was applied to synthesize curcumin nanocrystals. Different techniques were used to characterize the structural and photophysical properties of the

curcumin nanocrystals. It was found that the nanocurcumin prepared by this method had good chemical and physical stability, could be stored in the powder form at room temperature, and was freely dispersible in water. It was established that the size of curcumin nanocrystals varied in the range of 20-500 nm. Fourier transform infrared spectroscopy and UV-Vis analyses showed the presence of tetrahydrofuran inside the curcumin nanocrystals. Furthermore, it was found that the nanocurcumin emitted photoluminescence with a yellow-green color. © 2015 SCS. All rights reserved.

Damjanović, L., Marjanović, O., Stojanović, M.M., Andrić, V., Mioč, U.B.

Spectroscopic investigation of two Serbian icons painted on canvas (2015) *Journal of the Serbian Chemical Society*, 80 (6), pp. 805-817.

<https://doi.org/10.2298/JSC140722099D>

ABSTRACT: A multianalytical study of two Serbian icons, "The Virgin and Child" and "St. Petka", painted on canvas by unknown authors was performed in order to identify the materials used as pigments, binders and the ground layer. The investigated icons belong to the Museum of the Serbian Orthodox Church in Belgrade. Samples, collected from different parts of the icons, were analysed by: optical microscopy (OM), energy dispersive X-Ray fluorescence (EDXRF), Fourier transform infrared (FTIR) and micro-Raman spectroscopy. The obtained results revealed the presence of the following pigments: Prussian Blue, ultramarine, Green Earth, iron oxides, Lead White and Zinc White. Linseed oil was used as the binder. The materials used for the ground layers were gypsum, calcite, baryte and Lead White. The gilded surface of the icon "The Virgin and Child" was made of gold. The gilded surface on the frame of this icon was made of imitation of gold, i.e., Schlagmetal, since EDXRF spectroscopy showed the presence of copper and zinc, while gold was not detected. Based on the style and the consideration of an art historian, as well as on the obtained results for the corresponding pigments and binder, both icons were most probably made at the end of 19th or the beginning of the 20th century. © 2015, Serbian Chemical Society. All rights reserved.

Holclajtner-Antunović, I., Bajuk-Bogdanović, D., Popa, A., Sasca, V., Nedić Vasiljević, B., Rakić, A., Uskoković-Marković, S.

Preparation, characterization and catalytic activity of mesoporous Ag<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>/SBA-15 and Ag<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>/TiO<sub>2</sub> composites (2015) *Materials Chemistry and Physics*, 160, pp. 359-368.

<https://doi.org/10.1016/j.matchemphys.2015.04.052>

ABSTRACT: The current study reports the synthesis and characterization of tungstophosphoric acid and its acid silver salt supported on mesoporous molecular sieve SBA-15 and TiO<sub>2</sub>. Because silver salts are partially insoluble, the SBA-15 and TiO<sub>2</sub> supported silver acid salts were prepared by two step sequential impregnations. The synthesized catalysts were characterized by various physicochemical methods such as Fourier transform infrared and Raman spectroscopy, differential thermal analysis, thermogravimetric analysis, X-ray diffraction, scanning electron microscopy and nitrogen physisorption at

-196 °C. It is observed that both active phases keep their Keggin-type structure after being supported on the supports while their specific surface area is considerably increased by deposition on mesoporous substrates. The results also indicated that the synthesized catalysts retained the morphology specific for each of the supports, while their thermal stability is increased in comparison with their active phases. The catalytic activity of the prepared catalysts was probed for the vapor phase dehydration of ethanol at 300 °C. Results revealed that all the catalysts show considerably improved catalytic activity in comparison to the bulk active phases. © 2015 Elsevier B.V.

Holclajtner-Antunović, I., Bajuk-Bogdanović, D., Popa, A., Nedić Vasiljević, B., Krstić, J., Mentus, S., Uskoković-Marković, S. Structural, morphological and catalytic characterization of neutral Ag salt of 12-tungstophosphoric acid: Influence of preparation conditions (2015) *Applied Surface Science*, 328, pp. 466-474.

<https://doi.org/10.1016/j.apsusc.2014.12.062>

ABSTRACT: The objective of this study is the structural and morphological characterization of the Ag<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> salts (AgWPA) of 12-tungstophosphoric acid (WPA) obtained under different preparation conditions and testing of their acid catalytic activity in dehydration of ethanol. The structure, morphology and physicochemical characteristics were determined by Fourier transform infrared (FT-IR) and Raman spectroscopy, X-ray diffraction (XRD), nitrogen physisorption at -196°C, scanning electron microscopy (SEM) and differential thermal (DTA) and thermogravimetric analysis (TGA). It is shown that the preparation process has a significant influence on the morphological properties of the obtained materials which may be explained by the supposed mechanism of the formation of nanocrystallite's aggregates with more or less epitaxial connection. Neutral AgWPA obtained by filtration from supernatant forms porous aggregates of a symmetric dodecahedral shape, having average sizes about 2 μm. This sample shows higher specific area in comparison with the salt obtained by evaporation due to the higher micropore volume, while mesopore volumes are the same for both salts. Thus conversion of ethanol and selectivities of the main products, ethylene and diethyl ether, are almost the same and constant for both prepared salts, while their values are changed over the reaction time for the parent WPA acid. © 2014 Elsevier B.V. All rights reserved.

Dragišić Maksimović, J., Poledica, M., Mutavdžić, D., Mojović, M., Radivojević, D., Milivojević, J. Variation in Nutritional Quality and Chemical Composition of Fresh Strawberry Fruit: Combined Effect of Cultivar and Storage (2015) *Plant Foods for Human Nutrition*, 70 (1), pp. 77-84.

<https://doi.org/10.1007/s11130-014-0464-3>

ABSTRACT: Bioclimatic air ionisation system (BI) works by neutralising air pollutants and microorganisms by means of oxidation with "activated oxygen". We investigated the effects of storage on changes in weight loss, chemical and sensory fruit properties in eight cultivars of strawberries (*Fragaria x ananassa* Duch.). All cultivars were evaluated for their standard parameters of quality (soluble solids content, total acidity, vitamin C content, total antioxidant activity - TAC, total

phenolic and anthocyanins content) at different store conditions: fresh fruits–control, cold stored (at 4 °C) fruits without controlled atmospheres and cold stored (at 4 °C) fruits in BI. The present study outlines that anthocyanins of the strawberries stored in BI were subjected to significant degradation. These strawberries have prolonged shelf-life accompanied by weight loss reduction, TAC increment, and sensory properties improvement in tested cultivars, retaining other nutritional fruit qualities. © 2015, Springer Science+Business Media New York.

Radoičić, M.B., Milošević, M.V., Miličević, D.S., Suljovrujić, E.H., Ćirić-Marjanović, G.N., Radetić, M.M., Šaponjić, Z.V.

Influence of TiO<sub>2</sub> nanoparticles on formation mechanism of PANI/TiO<sub>2</sub> nanocomposite coating on PET fabric and its structural and electrical properties  
(2015) *Surface and Coatings Technology*, 278, pp. 38-47.

<https://doi.org/10.1016/j.surfcoat.2015.07.070>

ABSTRACT: Polyester fibers gained significant share from all other man-made fibers, but despite numerous advantages a characteristic static electricity generation is still seeking innovative solutions. In order to improve electrical properties of poly(ethyleneterephthalate) (PET) fabric, coating consisting of polyaniline/TiO<sub>2</sub> (PANI/TiO<sub>2</sub>) nanocomposite was deposited on its surface. Coating was synthesized in acidic medium by the chemical oxidative polymerization of aniline with ammonium peroxydisulfate (APS) in the presence of colloidal TiO<sub>2</sub> nanoparticles (d~4.5nm) and PET fabric. The morphology, molecular structure and dielectric properties of PANI/TiO<sub>2</sub> nanocomposites were studied by scanning electron microscopy (SEM), Raman and dielectric spectroscopies. SEM analysis revealed the formation of non-uniform PANI coating on the reference PET sample. In contrast, uniform PANI/TiO<sub>2</sub> coating on the surface of PET fabric was generated when TiO<sub>2</sub> nanoparticles were engaged. The existence of conductive emeraldine salt form of PANI and phenazine units was confirmed by Raman spectroscopy. Formation mechanisms of PANI and PANI/TiO<sub>2</sub> coatings on PET fabrics were proposed. The presence of TiO<sub>2</sub> nanoparticles significantly affected the dielectric properties (permittivity and loss tangent) and AC conductivity of PANI/TiO<sub>2</sub> coated PET fabrics. PET fabrics coated by PANI/TiO<sub>2</sub> nanocomposite showed up to two orders of magnitude higher conductivity in the measured frequency region compared to PANI coated PET fabric. © 2015 Elsevier B.V.

Milošević, S., Stojković, I., Mitrić, M., Cvjetičanin, N.

High performance of solvothermally prepared VO<sub>2</sub>(B) as an anode for aqueous rechargeable lithium batteries  
(2015) *Journal of the Serbian Chemical Society*, 80 (5), pp. 685-694.

<https://doi.org/10.2298/JSC140922128M>

ABSTRACT: The VO<sub>2</sub>(B) was synthesized via a simple solvothermal route at 160 °C in ethanol. The initial discharge capacity of the VO<sub>2</sub>(B) anode, in saturated aqueous solution of LiNO<sub>3</sub>, was 177 mAh g<sup>-1</sup> at a current rate of 50 mA g<sup>-1</sup>. After 50 cycles, the capacity fade was 4%, but from 20th-50th cycle, no

capacity drop was observed. The VO<sub>2</sub>(B) showed very good cyclability at a current rate of even 1000 mA g<sup>-1</sup> with initial discharge capacity of 92 mAh g<sup>-1</sup>. The excellent electrochemical performance of VO<sub>2</sub>(B) was attributed to the stability of micro-nano structures to a repeated intercalation/deintercalation process, very good electronic conductivity as well as the very low charge transfer resistance in an aqueous electrolyte. © 2015 SCS. All rights reserved.

Potkonjak, B., Jovanović, J., Stanković, B., Ostojić, S., Adnadjević, B.

Comparative analyses on isothermal kinetics of water evaporation and hydrogel dehydration by a novel nucleation kinetics model (2015) Chemical Engineering Research and Design, 100, pp. 323-330.

<https://doi.org/10.1016/j.cherd.2015.05.032>

ABSTRACT: A comparative analysis of the isothermal kinetics of water evaporation and equilibrium swollen poly(acrylic-g-gelatin) hydrogel (PAAG) dehydration was performed. The isothermal thermogravimetric (TG) curves of water evaporation and PAAG hydrogel dehydration were obtained in temperature range from 313K to 353K, at the same conditions. We found that the kinetics of water evaporation could be mathematically described by the model of zero order chemical reaction. The values of the kinetic parameters:  $E_{a,0} = 29 \text{ kJ/mol}$  and  $\ln(A_{e,0}/\min) = 12.1$  for water evaporation were calculated. By the application of the isoconversional method it was found that water evaporation was a kinetically complex process. It was shown that the kinetics of hydrogel dehydration could be described by a linear combination of logistic functions. A novel model, called the nucleation model, able to describe the kinetics of hydrogel dehydration and water evaporation was presented. The rate constants values for nucleation and the multiplication of the nuclei centers (bubbles) at different temperatures were calculated. The values of activation energy of the multiplication of the nuclei centers were calculated. The difference found between the kinetics of water evaporation and hydrogel dehydration was explained by different values for the constant rates of nucleation and multiplication of the nuclei centers during the water evaporation and hydrogel dehydration. © 2015 The Institution of Chemical Engineers.

Djajic, T., Jovanovic, J., Potkonjak, B., Adnadjevic, B.

The kinetics of isothermal nicotinamide release from poly(acrylic-co-methacrylic acid) loaded xerogel (2015) Polymer Engineering and Science, 55 (1), pp. 60-69.

<https://doi.org/10.1002/pen.23870>

ABSTRACT: The isothermal kinetics of in vitro nicotinamide release from poly(acrylic-co-methacrylic acid) loaded xerogel into water was evaluated. The isothermal kinetics curves of nicotinamide release from poly(acrylic-co-methacrylic acid) xerogel were measured at different temperatures ranging from 296 K to 315 K. It was proven that the kinetics of nicotinamide release from poly(acrylic-co-methacrylic acid) xerogel was a kinetically complex process which was neither controlled by the processes of drug diffusion nor with the relaxation of the xerogel. The kinetic of nicotinamide release from poly(acrylic-co-

methacrylic acid) may be described by the kinetics model of reversible first order chemical reaction and the apparent activation energy have value of  $E_{a,M5}=14.1 \text{ kJ mol}^{-1}$  and preexponential factor  $\ln(AM \text{ min}^{-1})=2.3$ . The rate constants of nicotinamide release ( $k_R$ ) and the rate constants of its reversible absorption reaction ( $k_A$ ) were calculated and found to fall within the range  $0.019 \text{ min}^{-1}$ - $0.033 \text{ min}^{-1}$  for  $k_R$  and  $0.014 \text{ min}^{-1}$ - $0.016 \text{ min}^{-1}$  for  $k_A$ . The value of activation energy for the nicotinamide release,  $E_{a,R}=21.25 \text{ kJ mol}^{-1}$ , is significantly higher than the value for the process of nicotinamide absorption ( $E_{a,A}=2.6 \text{ kJ mol}^{-1}$ ). The rate of nicotinamide release was predetermined with the rate of nicotinamide molecules distribution between the hydrogel and surrounding solution. © 2014 Society of Plastics Engineers.

Janković, B.

Isothermal thermo-analytical study and decomposition kinetics of non-activated and mechanically activated indium tin oxide (ITO) scrap powders treated by alkaline solution  
(2015) Transactions of Nonferrous Metals Society of China (English Edition), 25 (5), pp. 1657-1676.

[https://doi.org/10.1016/S1003-6326\(15\)63771-2](https://doi.org/10.1016/S1003-6326(15)63771-2)

ABSTRACT: Isothermal decomposition process of chemically transforming indium tin oxide (ITO) powders into indium (III) hydroxide powders was investigated. Two types of powders were analyzed, i.e., non-activated and mechanically activated. It has been found that in the case of activated sample, shorter induction periods appear, which permits growth of smaller crystals, while in the case of non-activated sample, long induction periods appear, characterized by the growth of larger crystals. DAEM approach has shown that decomposition processes of non-activated and mechanically activated samples can be described by contracting volume model with a linear combination of two different density distribution functions of apparent activation energies ( $E_{a,i}$ ), and with first-order model, with a single symmetrical density distribution function of  $E_{a,i}$ , respectively. It was established that specific characteristics of particles not only affect the mechanism of decomposition processes, but also have the significant impact on thermodynamic properties. © 2015 The Nonferrous Metals Society of China.

Dukić, A.B., Kumrić, K.R., Vukelić, N.S., Dimitrijević, M.S., Bašcarević, Z.D., Kurko, S.V., Matović, L.L.  
Simultaneous removal of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  from highly acidic solutions using mechanochemically synthesized montmorillonite-kaolinite/ $\text{TiO}_2$  composite  
(2015) Applied Clay Science, 103, pp. 20-27.

<https://doi.org/10.1016/j.clay.2014.10.021>

ABSTRACT: The aim of the present study was to synthesize a composite of raw interstratified montmorillonite-kaolinite clay (Mt-K) with  $\text{TiO}_2$  as an additive by mechanochemical activation and investigate its usability as low-cost adsorbent for simultaneous removal of heavy metals from acidic aqueous solutions. The composite synthesized with amorphous  $\text{TiO}_2$  ( $\text{TiO}_2,a$ ) showed a significantly better removal ability of heavy metals

from highly acidic solutions (pH=2.0-4.0) compared with the Mt-K milled for an optimum period of time of 19h (Mt-K,m) and composite synthesized with crystalline TiO<sub>2</sub> (TiO<sub>2</sub>,c). As both of the composites showed the same morphologies, the same distribution of TiO<sub>2</sub> particles on the clay matrix, the same particle size distribution (PSD) dependencies and point of zero charge (pHPZC) values, it has to be noticed that the difference in the adsorption behavior lies only in the different crystalline forms of the additive, i.e. TiO<sub>2</sub> that was used for the composite preparation. It has been shown that 20% of TiO<sub>2</sub>,a was the optimal amount of an additive in the composite to achieve improved adsorption ability. © 2014 Elsevier B.V.

Novaković, T., Rožić, L., Petrović, S., Stanisavljev, D.  
Desorption of  $\beta$ -carotene from bentonite adsorbent under microwave irradiation  
(2015) Macedonian Journal of Chemistry and Chemical Engineering, 34 (2), pp. 363-371.

ABSTRACT: The desorption behavior of  $\beta$ -carotene from a bentonite adsorbent under microwave irradiation in isopropanol was studied as a function of temperature and different initial loading concentrations. A first-order, two-component, three-parameter model described the desorption kinetics with a coefficient of determination  $R^2 > 0.9932$ , and the  $\beta$ -carotene desorption process under microwave irradiation was controlled by both rapid and slow desorption. The activation energies of  $\beta$ -carotene desorption for the rapid and slow desorption processes were 19.61 and 53.04 kJ mol<sup>-1</sup>, respectively. It was observed that the desorption equilibrium data fitted well to both the Freundlich and Langmuir isotherms. The data obtained from the desorption-isotherm model were used to determine the thermodynamic parameters. The positive value of free energy indicates the non-spontaneity of  $\beta$ -carotene desorption. The change in entropy relative to the enthalpy of desorption reveals that the reaction is physical in nature.

Maćešić, S.R., Čupić, Ž.D., Blagojević, S.M., Pejić, N.D., Anić, S.R., Kolar-Anić, L.Z.  
Current rates and reaction rates in the Stoichiometric Network Analysis (SNA)  
(2015) Open Chemistry, 13 (1), pp. 591-599.

<https://doi.org/10.1515/chem-2015-0077>

ABSTRACT: In stoichiometric network analysis (SNA) the instability condition is calculated by the current rates. Recently, we have shown that in the final result the current rates can be substituted by reaction rates, which is a more appropriate value for the examination of instability from experimental point of view. Here, we elaborate the problem of whether the current rates are necessary parameters in the calculation, with the aim of obtaining the region of instability. All calculations are performed on a model for Belousov-Zhabotinsky (BZ) reaction, which has not been examined by SNA. © 2015 Stevan R. Maćešić et al., licensee De Gruyter Open.

Mudrinić, T., Mojović, Z., Milutinović-Nikolić, A., Mojović, M., Žunić, M., Vukelić, N., Jovanović, D.

Electrochemical activity of iron in acid treated bentonite and influence of added nickel  
(2015) Applied Surface Science, 353, pp. 1037-1045.

<https://doi.org/10.1016/j.apsusc.2015.07.054>

ABSTRACT: Bentonite originated from Mečji Do, Serbia, was submitted to acid treatment at 70 °C for 30 min, while only the concentration of applied HCl varied. The obtained acid treated samples were used to modify glassy carbon (GC) electrode. The effect of applied acid treatment on the electrochemical behavior of GC electrodes modified with these materials was investigated. Furthermore, the effect of the introduction of nickel into acid treated samples was studied. The incorporation of nickel into acid treated bentonite was achieved by either ion exchange or impregnation/decomposition method. The obtained samples were characterized using the following methods: inductively coupled plasma (ICP), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and electron spin resonance (ESR) spectroscopy. The electrochemical behavior of these samples was tested by cyclic voltammetry in 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution. The ICP, FTIR and ESR results exhibited a slight decrease of iron content in the acid treated samples. XRD and FTIR results confirmed that the conditions applied for the acid treatment were mild enough for the smectite structure to be preserved. The electrocatalytic test showed that the current response of Fe<sup>2+</sup>/Fe<sup>3+</sup> oxidation/reduction process increased on the GC electrodes separately modified with each of the acid treated samples in comparison with current obtained on the GC electrode modified with untreated sample. These results indicated that applied acid treatment probably increased the accessibility of the electroactive iron within smectite. Cyclic voltammograms obtained for the GC electrodes modified with acid treated bentonite materials showed greater anodic charge ( $q_a$ ) than cathodic charge ( $q_c$ ). This difference might be due to iron detachment from smectite structure during the oxidation process. Further modification of the selected acid treated sample with nickel species resulted in decreased current response of the Fe<sup>2+</sup>/Fe<sup>3+</sup> oxidation/reduction process and improved the reversibility of this process. © 2015 Elsevier B.V. All rights reserved.

Ristić, A.J., Daković, M., Kerr, M., Kovačević, M., Parojčić, A., Sokić, D.

Cortical thickness, surface area and folding in patients with psychogenic nonepileptic seizures  
(2015) Epilepsy Research, 112, pp. 84-91.

<https://doi.org/10.1016/j.eplepsyres.2015.02.015>

ABSTRACT: Objective: To determine cortical thickness (CTh), cortical surface area (CSA), curvature and sulcal depth (SD) in patients with psychogenic nonepileptic seizures (PNES). Methods: Freesurfer software was used to identify differences between active and control group in Cth, CSA, curvature, and SD. Neuropsychological tests intending to document possible frontal lobe deficit were applied. Results: We included 37 patients with PNES (age 37.3. ±. 13.8; female/male 31/6; age of disease onset 26.1. ±. 10.6; age of disease duration 11.1. ±. 11.1), and 37 healthy controls (age 38.4; ±12.7; female/male 26/11). No difference in CSA and curvature was detected between groups. Patients

with PNES had increased CTh in the left insula, left and right medial-orbitofrontal, and left lateral-orbitofrontal, and decreased CTh in the left and right precentral, right enthorinal, and right lateral-occipital region than healthy controls. SD was increased at the level of the left and right insula, right rostral anterior cingulate, right posterior cingulate, and left cuneus, and reduced at the level of the right and left medial-orbitofrontal sulci in patients with PNES compared to healthy controls. Conclusion: Individuals with PNES display a distinct profile of changes in CTh, in association with increase in SD in both insula as compared to controls. Our results may contribute to the understanding of the neurobiological background of PNES. Further research, to include replication of the findings and directed to understand the role of insula is needed. © 2015 Elsevier B.V.

Vujković, M., Pašti, I., Simatović, I.S., Šljukić, B., Milenković, M., Mentus, S.

THE INFLUENCE of INTERCALATED IONS on CYCLIC STABILITY of V2O5/GRAPHITE COMPOSITE in AQUEOUS ELECTROLYTIC SOLUTIONS: EXPERIMENTAL and THEORETICAL APPROACH

(2015) *Electrochimica Acta*, 176, pp. 130-140.

<https://doi.org/10.1016/j.electacta.2015.07.004>

ABSTRACT: An amorphous V2O5 xerogel/graphite composite was synthesized and subjected to electrochemical characterization by cyclic voltammetry, chronopotentiometry and impedance measurements in aqueous LiNO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> solutions. The kinetics of cyclic intercalation/deintercalation reactions, and the dependence of coulombic capacity on cycle number were examined. The capacity retention depended on the type of inserted ions and decreased in the following order: Mg<sup>2+</sup> > Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup>. By ultraviolet/visible (UV/VIS) spectroscopy the concentration of dissolved vanadium oxide was determined and correlated with the capacity fade in various electrolyte solutions. By means of Density Functional Theory calculation (DFT), the bond strength between vanadium and triple coordinated oxygen in V2O5 was found to be responsible for the differences in its solubility in various aqueous solutions. © 2015 Elsevier Ltd. All rights reserved.

Begović, N.N., Blagojević, V.A., Ostojić, S.B., Radulović, A.M., Poletić, D., Minić, D.M.

Thermally activated 3D to 2D structural transformation of [Ni<sub>2</sub>(en)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(pyr)]·4H<sub>2</sub>O flexible coordination polymer (2015) *Materials Chemistry and Physics*, 149, pp. 105-112.

<https://doi.org/10.1016/j.matchemphys.2014.09.052>

ABSTRACT: Thermally activated 3D to 2D structural transformation of the binuclear [Ni<sub>2</sub>(en)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(pyr)]·4H<sub>2</sub>O complex was investigated using a combination of theoretical and experimental methods. Step-wise thermal degradation (dehydration followed by release of ethylene diamine) results in two layered flexible coordination polymer structures. Dehydration process around 365 K results in a conjugated 2D structure with weak interlayer connectivity. It was shown to be a reversible 3D to 2D framework transformation by a guest molecule, and rehydration of the dehydration product occurs at room temperature in saturated water vapor. Rehydrated complex exhibits lower dehydration temperature, due to decreased average crystalline size, with higher surface area

resulting in easier release and diffusion of water during dehydration. Thermal degradation of dehydration around 570 K, results in loss of ethylene diamine, producing a related 2D layered polymer structure, without interconnectivity between individual polymer layers. © 2014 Elsevier B.V. All rights reserved.

Kuzmanović, M., Jugović, D., Mitrić, M., Jokić, B., Cvjetičanin, N., Uskoković, D.

The use of various dicarboxylic acids as a carbon source for the preparation of LiFePO<sub>4</sub>/C composite  
(2015) *Ceramics International*, 41 (5), pp. 6753-6758.

<https://doi.org/10.1016/j.ceramint.2015.01.121>

ABSTRACT: Olivine-type LiFePO<sub>4</sub> composite powders with carbon were synthesized by freeze drying and subsequent thermal annealing. The main purpose of the research is to explore how various dicarboxylic acids as carbon sources influence the electrochemical properties of the resulting composites. Three dicarboxylic acids (oxalic, malonic, and adipic) were used as a carbon source. The synthesis was followed by X-ray powder diffraction, scanning electron microscopy, particle-size analysis, and electrochemical experiments. It is shown that the amount of the in situ formed carbon depends on the thermal behaviour of the acids in inert atmosphere rather than on their carbon content. Cyclic voltammetry experiments and galvanostatic cycling illustrate the behaviour of different powders: the powder obtained with oxalic acid yields the highest discharge capacity at small currents, while the one obtained with adipic acid shows better high-current response. Malonic acid has turned out to be a poor carbon source and it consequently yields powder with poor electrochemical performance. © 2015 Elsevier Ltd and Techna Group S.r.l.

Janković, B.Ž., Janković, M.M.

Pyrolysis of pine and beech wood under isothermal conditions: The conventional kinetic approach  
(2015) *Research on Chemical Intermediates*, 41 (4), pp. 2201-2219.

<https://doi.org/10.1007/s11164-013-1339-1>

ABSTRACT: Pyrolysis of pine and beech wood was investigated by isothermal thermogravimetry at five different temperatures (280, 290, 300, 310, and 320 °C) in an atmosphere of flowing nitrogen. It was found that isothermal pyrolysis of pine and beech can be described by three-dimensional diffusion mechanisms with different reaction geometry (Jander type for pine and Ginstling-Brounstein type for beech). It was established that, for both systems, values of the apparent activation energy ( $E_a$ ) calculated in an extrapolated temperature range coincide with values calculated by use of the classical Arrhenius equation. It was found that different values of the kinetic data and diffusion geometry of the volatile products probably result from slight changes of the structure and chemical composition of the wood which occur during pyrolysis. © 2013 Springer Science+Business Media Dordrecht.

Mihajlidi-Zelić, A., Dordević, D., Relić, D., Tošić, I., Ignjatović, L., Stortini, M.A., Gambaro, A.

Water-soluble inorganic ions in urban aerosols of the continental part of Balkans (Belgrade) during the summer - Autumn (2008) (2015) *Open Chemistry*, 13 (1), pp. 245-256.

<https://doi.org/10.1515/chem-2015-0010>

**ABSTRACT:** Size-segregated aerosol samples were collected using six stages High Volume Cascade Impactor. Aerosol mass and water soluble ions concentrations were determined. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to study the origin of air masses arriving to Belgrade in the investigated period. The obtained results of aerosol mass and water-soluble ion concentrations have been divided into six sub-data sets based on air mass categories. The highest average mass concentration of the fine mode ( $D_p \leq 0.49 \mu\text{m}$ ) was found for air masses coming to Belgrade from the southeast and northwest directions, and of the coarse mode ( $3.0 < D_p \leq 7.2 \mu\text{m}$ ) for air masses arriving from the northwest direction. The highest concentrations of  $\text{SO}_4^{2-}$  were found in the fine particles transported to the investigated area by air masses from southeast direction. The analysis of contribution of marine aerosol components ( $\text{Na}^+$  and  $\text{Cl}^-$ ), the Correlation and Cluster Analysis indicated the influence of marine aerosol on urban aerosol of the central Balkans coming from the Western Mediterranean and northern direction.  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  and  $\text{K}^+$  dominated in the fine mode for all air mass categories. PCA demonstrated the dominant impact of secondary aerosol formation processes on urban aerosols. © 2015 Aleksandra Mihajlidi-Zelić et al., licensee De Gruyter Open.

Žižić, M., Dučić, T., Grolimund, D., Bajuk-Bogdanović, D., Nikolic, M., Stanić, M., Križak, S., Zakrzewska, J.  
X-ray absorption near-edge structure micro-spectroscopy study of vanadium speciation in *Phycomyces blakesleeanus* mycelium (2015) *Analytical and Bioanalytical Chemistry*, 407 (24), pp. 7487-7496.

<https://doi.org/10.1007/s00216-015-8916-7>

**ABSTRACT:** Vanadium speciation in the fungus *Phycomyces blakesleeanus* was examined by X-ray absorption near-edge structure (XANES) spectroscopy, enabling assessment of oxidation states and related molecular symmetries of this transition element in the fungus. The exposure of *P. blakesleeanus* to two physiologically important vanadium species ( $\text{V}^{5+}$  and  $\text{V}^{4+}$ ) resulted in the accumulation of this metal in central compartments of 24 h old mycelia, most probably in vacuoles. Tetrahedral  $\text{V}^{5+}$ , octahedral  $\text{V}^{4+}$ , and proposed intracellular complexes of  $\text{V}^{5+}$  were detected simultaneously after addition of a physiologically relevant concentration of  $\text{V}^{5+}$  to the mycelium. A substantial fraction of the externally added  $\text{V}^{4+}$  remained mostly in its original form. However, observable variations in the pre-edge-peak intensities in the XANES spectra indicated intracellular complexation and corresponding changes in the molecular coordination symmetry. Vanadate complexation was confirmed by  $^{51}\text{V}$  NMR and Raman spectroscopy, and potential binding compounds including cell-wall constituents (chitosan and/or chitin), (poly)phosphates, DNA, and proteins are proposed. The evidenced vanadate complexation and reduction could also explain the resistance of *P. blakesleeanus* to high extracellular concentrations of vanadium. © Springer-Verlag Berlin Heidelberg 2015.

Krstić, J., Gabrovska, M., Lončarević, D., Nikolova, D., Radonjić, V., Vukelić, N., Jovanović, D.M.

Influence of Ni/SiO<sub>2</sub> activity on the reaction pathway in sunflower oil hydrogenation

(2015) Chemical Engineering Research and Design, 100, pp. 72-80.

<https://doi.org/10.1016/j.cherd.2015.05.001>

ABSTRACT: Sunflower oil hydrogenation process was studied on silica supported nickel catalysts. Three texturally different silica gel materials were used as supports for synthesis of Ni/SiO<sub>2</sub> catalyst precursors. After precursors' reduction and paraffin oil impregnation, obtained catalysts were used in sunflower oil hydrogenation reaction. For catalytic test, a new type of catalyst feeder was constructed and presented. The hydrogenation activity of catalysts was monitored through the decrease of refractive index and hydrogen consumption. A correlation between iodine value, refractive index and hydrogen consumption was established. The reaction rate constants were obtained from fatty acid composition of partially hydrogenated oil and further studied for the investigation of possible reaction pathways. Kinetics and mechanisms were evaluated and tested with the aim to reduce the number of reactions participating in the reaction scheme. A set of ordinary differential equations, corresponding to the investigated model, was solved numerically by Gear's algorithm. It was shown that a number of significant reactions in a model depend on the activity of catalysts. More active catalyst results in more reaction pathways and more side chemical reactions. © 2015 The Institution of Chemical Engineers.

Janković, B., Marinović-Cincović, M., Dramićanin, M.

Kinetic study of isothermal crystallization process of Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

precursor's powder prepared through the Pechini synthetic approach

(2015) Journal of Physics and Chemistry of Solids, 85 (1), pp. 160-172.

<https://doi.org/10.1016/j.jpcs.2015.05.009>

ABSTRACT: Crystallization process of Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> precursor's powder prepared by Pechini-type polymerized complex route has been studied under isothermal experimental conditions in an air atmosphere. It was found that the crystallization proceeds through two-parameter Šesták-Berggren (SB) autocatalytic model, in the operating temperature range of 550 °C ≤ T ≤ 750 °C. Based on the behavior of SB parameters (M, N), it was found that in the lower operating temperature range, the crystallites with relatively low compactness exist, which probably disclosed low dimensionality of crystal growth from numerous nucleation sites, where the amorphous solid is produced. In the higher operating temperature region (above 750 °C), it was established that a morphological well-defined and high-dimensional particles of the formed pyrochlore phase can be expected. It was found that at T=850 °C, there is a change in the rate-determining reaction step, from autocatalytic into the contracting volume mechanism. © 2015 Elsevier Ltd. All rights reserved.

Hercigonja, R., Rac, V., Rakic, V., Auroux, A.

Effect of transition metal cations on the commensurate freezing of n-hexane confined in micropores of ZSM-5  
(2015) Journal of the Serbian Chemical Society, 80 (10), pp. 1297-1309.

<https://doi.org/10.2298/JSC150203032H>

ABSTRACT: Besides its importance concerning fundamental studies on gas adsorption in narrow pores, investigation of the commensurate freezing of a fluid within a zeolite is of practical importance in the application of zeolites in the processes of adsorption, separation and catalysis. In this work, the adsorption of n-hexane on HZSM-5 and its transition metal ion-exchanged modified forms was studied at 303 K by means of microcalorimetry. The thermal molar entropies changes of adsorption were calculated and thereby, the freezing-like behaviour of n-hexane inside the structure of the zeolite as a confinement media was noticed. This effect is governed by the attractive interactions between n-hexane molecules and the pore walls, and is influenced by the length of the pores and the nature of the charge-balancing cations. Among the investigated zeolites, a solid-like phase of n-hexane in the pores of zeolites with Fe(II) ions was the most similar to solid bulk n-hexane, while Cu(II) ions contributed to the lowest ordering of the obtained solid-like n-hexane phase. © 2015 SCS.

Pašti, I.A., Baljzović, M., Skorodumova, N.V.  
Adsorption of nonmetallic elements on defect-free MgO(001) surface - DFT study  
(2015) Surface Science, 632, pp. 39-49.

<https://doi.org/10.1016/j.susc.2014.09.012>

ABSTRACT: Adsorption of 11 non-metals (H, B, C, N, O, F, Si, P, S, Cl and Br) on defect-free MgO(001) surface was investigate using DFT approach. Adsorption energies were found to be between - 0.56 eV (hydrogen adsorption) and - 2.63 eV (carbon adsorption). Charge transfer from substrate to adsorbate was observed to follow the periodicity in the Periodic Table of Elements, as increases from left to right and decreases from top to bottom. All investigated adsorbates prefer oxygen sites on MgO surface. The analysis of adsorbate-MgO(001) electronic structure suggested that the electronic structure of the O adsorption center and adsorbate atom is molecule-like and there is no strong interaction with MgO electronic bands. Based on the obtained dataset for adsorption energies of selected non-metallic adsorbates (X) the reactivity of MgO towards the bond cleavage in the cases of X-X, H-X and HO-X bonds was discussed. Obtained results point to weak reactivity of MgO(001) towards atomic adsorption and low activity for bond cleavage. However, these results can be used as a starting point for the functionalization of MgO, particularly in the cases where bond cleavage activity and surface-mediated stabilization of dissociation products are desired. © 2014 Elsevier B.V.