

# BOOK OF ABSTRACTS



3RD INTERNATIONAL CONFERENCE  
ON REACTION KINETICS, MECHANISMS  
AND CATALYSIS

22-25 MAY 2024  
MERCURE BUDAPEST CASTLE HILL • BUDAPEST • HUNGARY

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**RKMC**  
**3rd International Conference on Reaction Kinetics,  
Mechanisms and Catalysis**

**22–25 May 2024**  
**Budapest, Hungary**

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ISBN 978-963-664-038-5

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# Keynote

## Perturbation techniques in experimental and numerical investigations of the Belousov Zhabotinsky oscillatory reaction

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**Keywords:** oscillatory reactions, nonlinear dynamics, Belousov-Zhabotinsky reaction

The Belousov-Zhabotinsky (BZ) reaction is a classic example of a chemical oscillator, displaying oscillatory behavior in both, time, and space. [1] This reaction is a widely studied system in the field of nonlinear chemical dynamics and has particular importance in understanding pattern formation within reaction-diffusion systems, as well as, in developing various technological applications. BZ has attracted scientists from both experimental and theoretical point of view. In fact, this is the most investigated oscillatory chemical reaction in a closed and open reactor; the reaction where the complex dynamic states including oscillatory, mixed mode and chaotic ones are found in the narrow region of reactant concentrations. This reaction is very sensitive to external perturbation and due to its sensitivity, it is often used to examination of various analytes.

Over the years, numerous models of the BZ reaction network have been proposed with the aim to achieve better agreement with the experimental results. Modeling the influence of malonic acid based on the model [2], the experimentally determined kinetics of the overall malonic acid decomposition process was theoretically explained. Obtained results were important for understanding the mechanism and dynamic of the BZ oscillatory reaction in CSTR. Reaction model was characterized by formal kinetics approach under varying reactant concentrations and temperature. The same approach was used in other oscillatory reactions perturbed by different analyte. Therefore, we also examine BZ reaction perturbed by glycerine in both CSTR and Petry dish. Obtained results showed that glycerine modulates time, period, and amplitude of BZ oscillatory reaction and these effects are glycerine quantity dependent.

### Acknowledgments

We are grateful to the financial support from Ministry of Science, Technological Development, and Innovation of Republic of Serbia through University of Belgrade - Institute of Chemistry, Technology and Metallurgy – National Institute of the Republic of Serbia, Faculty of Physical chemistry, Faculty of Pharmacy (Contract numbers 451-03-47/2023-01/200026, 451-03-66/2024-03/200146 and 451-03-65/2024-03/ 200161) and through Mathematical Institute of Serbian Academy of Sciences and Arts.

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## Electrocatalytic refinery for production of fuels and chemicals

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**Keywords:** electrocatalysis, refinery, energy conversion, hydrogen production, CO<sub>2</sub> reduction reaction

Compared to modern fossil fuel-based industrial refineries, the emerging electrocatalytic refinery (e-refinery) is a more sustainable and environmentally benign strategy to convert renewable feedstocks and energy sources to transportable fuels and value-added chemicals. E-refinery promisingly leads to defossilization, decarbonization, and decentralization of chemical industry. Specifically, powered by renewable electricity (e.g., solar, wind and hydro power), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) can efficiently split water into green hydrogen and CO<sub>2</sub> reduction reaction (CRR) can convert CO<sub>2</sub> emissions to transportable fuels and commodity chemicals.

A crucial step in realizing this prospect is the knowledge-guided design of appropriate reactions and optimal electrocatalysts with high activity and selectivity for anticipated reaction pathways, which dominantly involve cleavage and formation of chemical bonds between H, O and C. In this presentation, I will talk about our recent progress in mechanism understanding and material innovation for some crucial electrocatalytic reactions (OER, HER, CRR, etc.), which are achieved by combining atomic-level material engineering, electrochemical evaluation, theoretical computations, and advanced *in situ* characterizations. A special emphasis is placed on the rational exploration of novel single-atom catalysts.

## Chemical dynamics in single particle catalysis: in situ microscopy and microkinetic modelling

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**Keywords:** operando, hydrogen oxidation, field emission microscopy, single particle catalysis, modelling

Operando spectroscopy of catalytic reactions has been very successful in mechanistic studies.<sup>1</sup> However, as spectroscopy typically examines large areas/volumes, this averaging “smoothens out” local variations that may be critical to understand how a reaction proceeds. Dynamics in catalyst structure, composition and adsorbate coverage may also go unnoticed by averaged spectral data. A way overcoming these limitations is to use correlative surface microscopy to directly “watch” ongoing catalytic reactions, i.e. to apply several microscopic and spectro-microscopic techniques to the same catalysts locations under identical reaction conditions.<sup>2</sup> Most of the methods herein not only image catalyst structure or composition, but also the adsorbed reactants, so that active and inactive states can be discerned (*kinetics by imaging*), active regions identified and mechanisms elucidated.<sup>3</sup>

Examples of real-time *in situ* imaging of H<sub>2</sub> oxidation include meso-scale polycrystalline Rh surfaces and Rh nanotips (as small as 30 nm, enabling *single particle catalysis*). For planar catalysts, UV- and X-ray photoemission electron microscopy (UV- and X-PEEM), low energy electron microscopy (LEEM) and scanning photoelectron microscopy (SPEM) were used with resolution up to 3 nm. For nanotips, field emission microscopy (FEM) and field ion microscopy (FIM) were applied with up to atomic resolution.

The direct, real-time and locally-resolved observation of H<sub>2</sub> oxidation on Rh-based catalysts revealed:

(i) the transition from inactive to active states via catalytic ignition and spreading of chemical waves,<sup>4</sup>

(ii) the mechanism of oscillatory H<sub>2</sub> oxidation involving subsurface oxygen,<sup>4</sup>

(iii) how particle size, support and surface composition (decoration, SMSI) affect the local activity,<sup>5</sup>

(iv) whether different facets on a single Rh nanoparticle communicate via hydrogen diffusion or not (coupled monofrequential vs. (uncloupled) multifrequential oscillations),<sup>6</sup>

(v) detecting active sites on a single particle via imaging water molecules,<sup>6</sup>

(vi) that chaos even exists at the nanoscale,<sup>7</sup> and

(vii) how La modifies the reaction dynamics on a Rh nanotip.<sup>8</sup>

The novel nanoscale insights in the dynamics of reactants and surfaces were corroborated and rationalized by microkinetic modelling and density functional theory (DFT).

### Acknowledgments

Research funded by the Austrian Science Fund (FWF). Contributions by P. Winkler, M. Raab, J. Zeininger, Y. Suchorski, A. Genest, M. Stöger-Pollach and L. Gregoratti are gratefully acknowledged.

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## Reaction-diffusion modelling and applications of autocatalytic systems: recent developments

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The on-off switches and sharp fronts observed in autocatalytic reactions play a key role in natural phenomena, such as sensing in biological cells, as well as technologies including frontal polymerization and pulsatile drug delivery. In this talk, I will discuss three different systems and the development of models combining reaction and diffusion to aid in the control of autocatalysis for applications:

1. Oxygen-driven dynamics. Diffusion of oxygen from the air can result in different chemical pathways and 3D patterns in some autocatalytic clock reactions that have been used for the spatiotemporal control of material formation.
2. Hydrogel fronts. Autocatalytic reactions involving pH changes can be coupled with gelation to form spatially patterned gel states and coatings in aqueous environments.
3. pH oscillations in enzyme-compartments. Fast diffusion of protons or hydroxide ions into cell-like compartments containing autocatalytic enzyme reactions can lead to pH oscillations, however the influence of membrane potential was not taken into account in early models. Here we discuss the incorporation of the Goldman-Hodgkin-Katz equation to better understand the influence of membrane potential on the complex dynamics and potential applications in drug delivery with synthetic vesicles.

# Oral Presentations

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## T1: Catalysts in sustainable and green chemistry

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### Deactivating effects in the co-conversion of lauric acid and anisol over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst

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**Keywords:** co-conversion, lauric acid, anisol, NiMo catalyst, hydrodeoxygenation

The involvement of bio-derived mixtures, for example bio-oil, in the production of valuable products, including components of transportation fuels, is an urgent task of modern society. The most common method for upgrading bio-oil to hydrocarbons is the complete hydrodeoxygenation (HDO) of the constituent components. Carboxylic acids with different carbon chain lengths and substituted phenols are the main compounds present in bio-oil. Much research has already been carried out on the hydroconversion of both acids and phenols over different metal-containing catalysts, including NiMo/Al<sub>2</sub>O<sub>3</sub>, and corresponding reaction routes have already been established. Nevertheless, there is a lack of information on the coprocessing of these compounds over the same catalyst under the same HDO conditions. In this work, the performance of a reduced NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst in the HDO of lauric acid and anisole mixture was studied. The NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was characterized by XRD, XRF and H<sub>2</sub>-TPR, and catalytic experiments were carried out in a batch stirred reactor (Parr Instruments) at T=260 °C and p<sub>H<sub>2</sub></sub>=40 bar. Under these reaction conditions, lauric acid taken as a reactant was completely converted within 3 hours of the reaction, and C11 and C12 alkanes were the main products, which were formed from lauric aldehyde and lauryl alcohol as intermediates, correspondingly, via decarbonylation and dehydration/hydrogenation reaction routes. Anisole conversion was also 100% under these reaction conditions, and cyclohexane was a final product formed from methoxycyclohexane and cyclohexanol as reaction intermediates. If mixed with anisole, lauric acid was successfully converted to C11 and C12 alkanes over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, suggesting that the phenolic did not introduced any deactivating effect on the hydroconversion of the acid. Nevertheless, in contrast to the experiment with anisole alone that produced mainly cyclohexane, methoxycyclohexane was the main reaction product formed from anisole if it was mixed with lauric acid. The formation of cyclohexane occurred only after the complete conversion of lauric acid, which indicated the inhibitory effect of the acid on the cleavage of C-O bonds in methoxycyclohexane and cyclohexanol molecules. The performance of NiMo/Al<sub>2</sub>O<sub>3</sub> in the co-conversion of the lauric acid-anisol mixture was explained by additional experiments using Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> catalysts as well as methoxycyclohexane and cyclohexanol as reactants. The obtained results showed that a perspective catalyst for the efficient conversion of the lauric acid-anisol mixture has to provide a fast conversion of the acid in order to promote the further conversion of intermediate methoxycyclohexane and cyclohexanol to cyclohexane.

## Polymorph selection of zeolitic imidazolate frameworks via kinetic and thermodynamic control

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**Keywords:** metal-organic framework, precipitation, kinetic control, polymorph selection

Exploring the kinetics of metal-organic framework crystallization is crucial in order to design novel synthesis methods benefiting from far-from-equilibrium conditions, such as flow, microfluidic or gel-phase reactors. Herein we focus on zeolitic imidazolate frameworks (ZIFs) obtained in the reaction of 2-methylimidazolate and zinc ions as a model system. The room temperature synthesis carried out in pure water solvent without the addition of any alkaline chemical yields the highly crystalline product with good conversion within minutes. The short-term kinetic characteristics are determined by a high-speed camera the result of which is complemented by a UV-vis photometer based long-term investigation. At low concentrations and moderate linker excess, which facilitate sluggish coordination and precipitation, the fast colloid formation is followed by a delayed and remarkable recrystallization which leads to the formation of dense dia(Zn) polymorph of ZIF. Although this is the thermodynamically favored route, it is to be avoided due to its non-porous structure. The same stoichiometric excess of the linker ions together with higher concentrations gives rise to the production of the thermodynamically less stable polymorph of ZIF, i.e., ZIF-8 with sodalite-like structure is obtained via kinetic control. Similar conclusions are drawn in the case of cobalt(II) containing imidazolate frameworks which highlights that kinetic control based polymorph selection might be achieved for other MOFs as well. Our kinetic results are supported by scanning electron microscopy, powder X-ray diffraction, nitrogen gas adsorption, and Fourier transformed infrared and Raman spectroscopy.

## T3: Combustion kinetics and catalysis

### Towards improving the accuracy of the combustion kinetic mechanism for butanol isomers

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**Keywords:** butanol isomers, mechanism reduction, data reduction, parameter optimization

Bioalcohols are considered potential candidates to decrease our dependence on fossil fuels. Bioethanol, for example, is already widely used as a petrol additive and alternative. However, its physical and chemical properties limit its use in petrol engines. Much more promising candidates are the longer chain alcohols such as biobutanol, which can be used even in neat form in present vehicles. This work aims to optimize the rate parameters of the Sarathy2014 [1] butanol combustion mechanism, which was shown to have the best overall performance for all four isomers against a large collection of combustion data. [2]

We collected large amounts of indirect experimental data from the literature: ignition delay times (IDT, 0D, 574 data points from 574 experiments), concentrations measured in jet-stirred reactors (JSR, 0D, 2634 data points from 208 experiments), and laminar burning velocities (LBV, 1D, 433 data points from 433 experiments), which served as reference for model validation. Due to the large size of the data collection (3641 data points) and the mechanism (687 species, 3435 reactions), direct optimization is not possible within a reasonable time. Therefore, we applied a reaction rate ranking-based model reduction scheme and a novel data collection reduction method to obtain a largely simplified, thereby feasible optimization problem. As a first step, the size of the mechanism was reduced. The systematically reduced mechanism (285 species, 1535 reactions) accurately reproduced the simulation results obtained with the full mechanism, while allowing more than 10 times faster zero-dimensional (0D) simulations and convergence issue-free flame simulations. The reduction of the data collection to a representative subset (100, 995, and 45 experiments for IDT, JSR, and LBV, respectively) resulted in an additional three times speed-up. The important parameters of the reduced mechanism were identified [3] via the principal component analysis of the local sensitivity matrix that had been scaled with the uncertainties of the parameters and the experimental data. The correlated parameter groups identified this way are being optimized in a hierarchical manner using the Optima++ code [4]. The obtained optimized parameters will be inserted back into the full mechanism, which will be tested on the whole data collection. Based on our previous, similar work on n-pentanol [5], a significant reduction in the prediction error of the reduced mechanism can be achieved. Using these optimized rate parameters will also improve the prediction accuracy of the original full mechanism.

#### Acknowledgments

The authors are grateful for the funding of the NKFIH FK134332 and K147024 grants.

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5. L. Horváth, S. Dong, C. Saggese, M. Papp, H. J. Curran, W. J. Pitz, T. Turányi, T. Nagy: Mechanism reduction-assisted kinetic parameter optimization for the n-pentanol chemistry of the NUIGMech multifuel combustion mechanism (submitted)

## VOC oxidation over structured transition metal oxide catalysts prepared by plasma jet sputtering: the effect of energy delivery

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**Keywords:** volatile organic compounds, oxidation, transition metal oxides, plasma jet sputtering

Low-temperature plasma sputtering is used in industry to deposit thin films on various substrates. Recently, sputtering using a metal nozzle with a flowing gas has attracted attention [1]. Transition metal oxides are suitable for the abatement of harmful volatile organic compounds by total oxidation [2]. We decided to study a Ni-Co-Mn oxide system supported on stainless-steel meshes. The XRD showed the formation of NiO-like oxides. The XPS revealed the enrichment of the catalyst surface by Mn.

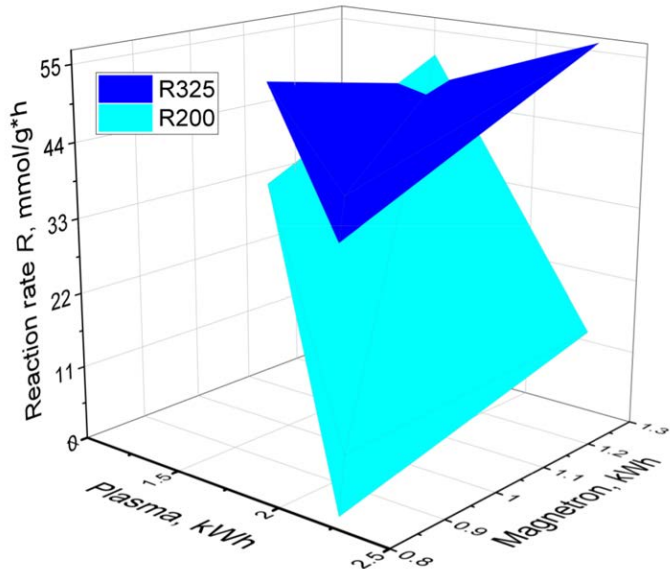


Fig. 1. Dependence of reaction rates in the gas-phase oxidation of ethanol (R200) and toluene (R325) on the delivered plasma and magnetron energy.

In ethanol oxidation (Fig. 1), the specific reaction rate at 200 °C was the highest at mild delivered plasma energy (1.6 kWh) and high magnetron sputtering energy (1.3 kWh). In toluene oxidation (Fig. 1), the specific reaction rate at 325 °C was the highest when both plasma jet and magnetron sputtering delivery of energy were high (2.3 and 1.3 kWh, respectively). Thin-film catalysts supported on meshes are promising due to high catalytic activity at low content of active phase and low pressure drop in the catalytic reactor.

### **Acknowledgments**

This work was supported by the Technology Agency of the Czech Republic (project TN02000044).

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## T4: Exploring catalytic reaction mechanisms

### Catalytic Glycerol Hydrogenolysis on bimetallic clusters of platinum and tungsten: A DFT study

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**Keywords:** DFT, glycerol hydrogenolysis, catalysis, reaction pathway

Glycerol is an inexpensive byproduct that is mostly generated during biodiesel production processes. Search for alternate products from glycerol in order to ensure the viability of the biodiesel industry is a topic of ever growing interest and discussion in the research community [1]. It is essential to develop viable technologies for the resource utilization of glycerol. Catalytic glycerol hydrogenolysis (CHG) has the potential to valorize the glut of crude glycerol issued from biodiesel production into the propanediols. Theoretical chemistry plays a crucial role in catalysis research by providing insights into the underlying mechanisms of catalytic reactions, optimizing catalyst structures, and predicting reaction pathways. The primary target of this study is to present novel reaction mechanisms of CHG in view of their possible applications using DFT calculations based micro kinetic model with the aim of modeling their kinetic behavior.

The research for an efficient reaction pathway is a primary aspect of understanding the reaction mechanism that is useful for the identification of the intermediate steps and the explanation of the formation of the byproducts. In this study, DFT calculations were performed to propose a possible reaction pathway for CHG without and with the catalyst on different platinum-tungsten clusters, Pt<sub>3-n</sub>W<sub>n</sub> (n=0-3). The adsorption of glycerol on these clusters was investigated along with the effect of cluster composition on the adsorption. The activation barriers and pre-exponential Arrhenius factor for the elementary reactions were calculated, including the adsorption energies for all surface species for the mechanism, including the catalyst. The optimized geometries, transition states, and vibrational frequencies were investigated with hybrid density functional method- B3PW91 with standard basis set 6-311+G(d,p) for the C, O, and H atoms and LanL2DZ for platinum and tungsten atoms, respectively.

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## Magnetic Field control of heterogeneous catalysis: Application to low-pressure Fischer-Tropsch

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**Keywords:** catalysis, electromagnetism, Fischer-Tropsch, catalytic enhancement

The initial step in any catalytic reaction is the adsorption of reactant molecules. The strength of the adsorption and orientation of the adsorbed molecules correlate well with the activity and selectivity of the catalyst. Most industrial catalysts are composed of various transition metals supported on relatively inert oxides. The interaction between reactant molecules and metallic active sites is governed by the electronic structure of the catalyst. This determines the adsorption strength and geometry. Modification of the electronic structure of the catalyst can alter the adsorption parameters of the reactant. This can be used to control the catalytic performance. In this study, low-pressure Fischer-Tropsch was carried out in a lab-scale fixed bed reactor system using an iron-based catalyst. The reactor was surrounded with an electromagnet and the effect of the induced electromagnetic field on the product distribution and yield was evaluated. The first prototype comprised a four-coil pair, concentric circle Helmholtz coil, providing a highly concentrated magnetic field parallel to the flow of reactants through the reactor vessel. The second was a Helmholtz cage that was able to exert three individual axes of magnetic field, and was also used to create an isolated, high intensity magnetic field system around the reaction zone, by activating all the coils in the cage at once. The magnetic field was shown to have a significant effect on methane selectivity and yield of higher alkanes.

## Small molecule activation at biological metal-macrocycle complexes: Contrasts between heme and vitamin B<sub>12</sub>

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**Keywords:** cobalamin, heme, stopped-flow, NMR, oxidative stress

In heme-containing proteins, redox-active agents such as peroxides or oxyanions of halogens/sulfur/nitrogen offer a rich chemistry involving high-valent iron, free radical reactions and small molecule activation.<sup>1</sup> By contrast, until recently our knowledge of the reactivity of cobalamin with oxidizing agents has been confined to processes where, especially with strong oxidizing agents, the corrin ring is covalently modified by oxygenation or halogenation, or where Co(I) or Co(II) are oxidized to Co(III) in an outer-sphere manner (at times in pseudocatalytic cycles where reducing agents are also present) – but no complexes of Co(III) with oxidizing agents, and no ensuing high-valent Co centers.<sup>2</sup> We have, however, recently reported that H<sub>2</sub>O<sub>2</sub> does in fact form a stable and reversible complex with cobalamin, assigned as Co(III)-hydroperoxo based on UV-vis and NMR spectra complemented by density functional (DFT) calculations.<sup>3</sup> We describe here UV-vis (including stopped-flow), NMR, DFT, resonance Raman and mass spectrometry results showing that *m*-chloroperoxybenzoic acid (MCPBA) at low concentrations yields a relatively stable complex with Co(III) cobalamin. Using the same experimental toolkit – centered mostly on <sup>1</sup>H-NMR spectroscopy and DFT calculations – we then describe a stable adduct of Co(III) cobalamin with chlorite, and rationalize the stability of this complex in contrast to the known instability of the putative heme-chlorite complex in the enzyme chlorite dismutase. With stopped-flow UV-Vis complemented by DFT, we then report on transient complexes formed by aqua and by cyano Co(III) cobalamin with hypochlorite.

A common theme of the complexes described here is the fact that the typical exploratory method for colored bioinorganic centers – UV-vis spectroscopy – appears largely blind in cases where clear differences are observed in NMR spectra (see, e.g., Figure 1). Under these conditions, the “UV-Vis-silent” area of coordination chemistry in corrin complexes may be expected to still offer surprises.[1–6]

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**T5: Homogeneous and heterogeneous photocatalysis**

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**Biochar-derived activated carbons: a comprehensive assessment of kinetic and isotherm modeling for adsorptive removal of methylene blue dye contaminants***Othman Hakami*

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The present work demonstrates a comparative study on the synthesis of “*Eucalyptus*” sawdust-derived porous carbons by two distinct methods including thermal carbonization and thermochemical activation. The representative sample-PAC demonstrate a remarkable specific surface area (SSA~2841 m<sup>2</sup> g<sup>-1</sup>), total pore volume (VT~1.2850 cm<sup>3</sup> g<sup>-1</sup>), well-developed pore-size distribution, ample amount of oxygen content (12.34 at. %), and amorphous nature with some  $\pi$ -electron-rich graphitic domains. When used for MB adsorption experiment, PAC demonstrate a remarkable MB adsorption capacity of PAC (625 mg g<sup>-1</sup> at an initial concentration of 200 mg L<sup>-1</sup>) attributed to the primary role of hierarchical micro-mesoporosity with enough population of micropores of optimum pore size (~1.5 nm) comparable to the kinetic diameter of MB (1.4 nm). Various parameters such as effect of morphology, effect of pH, regeneration/recyclability of spent adsorbent, and MB adsorption in real wastewater were comprehensively studied. Additionally, adsorption kinetics and thermodynamics studies were also explored which indicate a kind of physical endothermic mechanism existing for the biomass-derived ACs. Moreover, the distinct types of interactions including electrostatic interactions,  $\pi$ - $\pi$  interaction, and hydrogen linkage, generated between the oxygen-functionalized aromatic ring of sorbent surface and dye molecule, also facilitate the efficient MB adsorptive removal. Lastly, to demonstrate the practical application, an experiment comprising of a fixed bed of PAC on a continuous flow MB filtration unit results in a 98% removal of MB from wastewater which therefore highlights the potential of prepared material as an efficient sorbent for industrial wastewater remediation.

## Photocatalytic characteristics of (Ag,Na)-TiO<sub>2</sub>/Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu,Dy heterojunction photocatalyst synthesized by coprecipitation method

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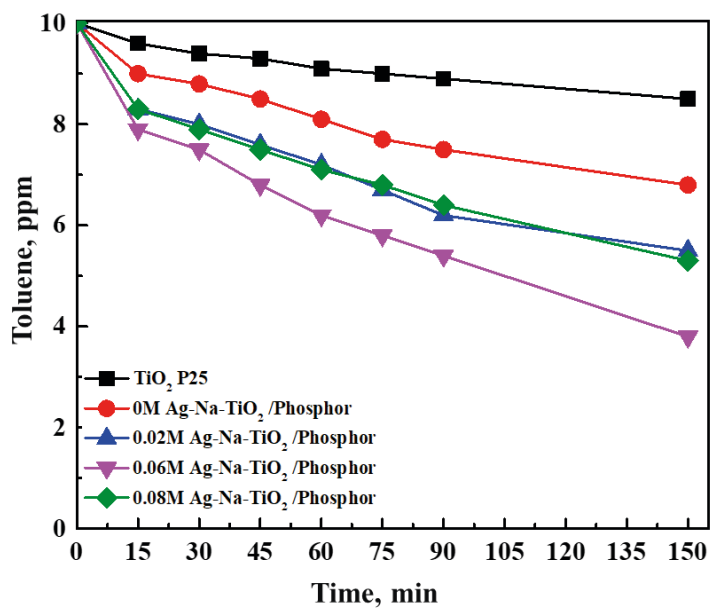
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**Keywords:** heterojunction photocatalyst, TiO<sub>2</sub>, Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>, coprecipitation

Photocatalytic materials are receiving attention as materials that can decompose harmful environmental pollutants in an eco-friendly manner through redox reactions using light energy. Among the various photocatalytic materials, TiO<sub>2</sub> is the most widely used because it is chemically stable and has a band gap of 3.2 eV, in which photo excitation reactions can occur efficiently. In this study, TiO<sub>2</sub> has been hybridized with other oxides and supported on one of long-lasting phosphors, Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>. In the hybrid photocatalysts of TiO<sub>2</sub>-coated long-lasting phosphors, the phosphor may act as an internal light source toward the acceleration or sustenance of photocatalytic reactivity even in the absence of external light irradiation.

The TiO<sub>2</sub>/Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> heterojunction photocatalyst was prepared by TiO<sub>2</sub> nanoparticles coated on the Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu,Dy phosphor substrate using a coprecipitation reaction method. To improve the generation of charge carriers in the photocatalyst, Na and Ag elements were impregnated on TiO<sub>2</sub> nanoparticles. The (Ag,Na)-impregnated TiO<sub>2</sub>/Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> hybrid photocatalyst system was synthesized under various conditions, including different Ag concentrations (0-0.08 M) and heat treatment temperatures (200-500°C). Fig. 1 shows the difference in the photocatalytic reactivity based on the amount of Ag concentration under visible light.

The impregnation of Na and Ag resulted in a decrease of the energy band gap of TiO<sub>2</sub> nanoparticles absorbing a visible light, and improving the separation of electron-hole pairs and charge transfer due to the plasmon resonance effect (SPR). Particularly, the 0.06 M Ag-(Na-TiO<sub>2</sub>)/Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> hybrid photocatalyst exhibited superior photocatalytic performance under visible light irradiation by decomposing toluene gas over 65% at 150 min.. The photocatalytic reactivity of (Ag,Na)-TiO<sub>2</sub>/Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> hybrid photocatalyst surpassed that of TiO<sub>2</sub>/Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> without impregnation, and increased with increasing Ag content. This superior performance can be primarily ascribed to the synergistic interaction between (Ag,Na) and TiO<sub>2</sub>.



**Figure 1.** Photo-decomposition of toluene gas for (Ag,Na)-TiO<sub>2</sub>/Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> hybrid photocatalysts under visible light irradiation.

## PNC-Doped TiO<sub>2</sub> nanoparticles for highly stable self-cleaning paints: A sustainable path to industrial development

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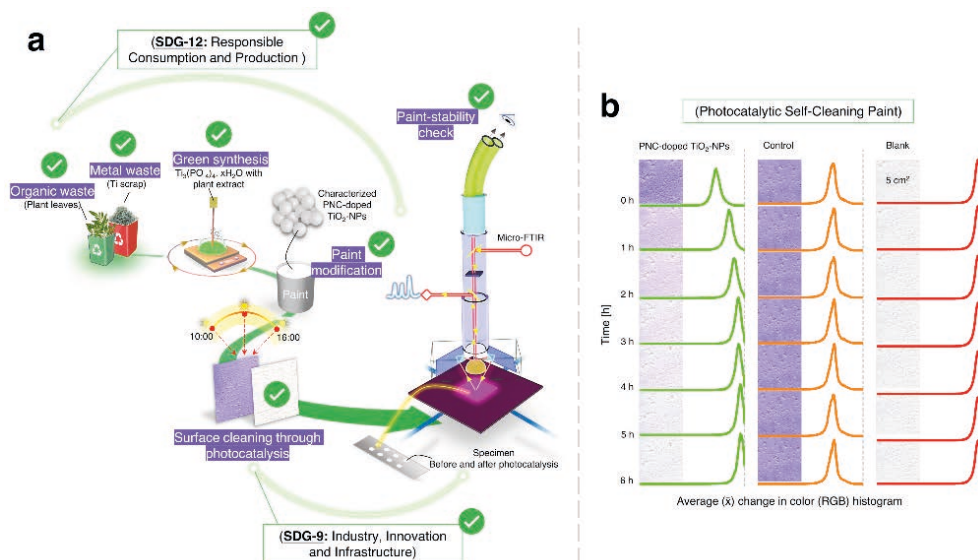
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**Keywords:** green synthesis, waste upcycling, photocatalysis, self-cleaning paints, Doped TiO<sub>2</sub> nanoparticles

In times of environmental pollution, the significance of eliminating harmful chemicals, even within our homes, becomes increasingly important. Self-cleaning photocatalytically active wall paints that operate in natural light are particularly promising. Given that a majority of both interior and exterior surfaces of buildings are coated with paint, there is substantial interest in improving paint properties by modifying polymeric paints with photocatalysts such as TiO<sub>2</sub> nanoparticles (NPs) <sup>1-3</sup> <sup>4</sup>. Adding photocatalytically active TiO<sub>2</sub> NPs to polymeric paints is a feasible route toward self-cleaning coatings. While paint modification by TiO<sub>2</sub> NPs can improve photoactivity, it may also cause paint-polymer photodegradation and release of toxic volatile organic compounds (VOCs), which can cause serious health issues <sup>4,5</sup>. This requires a targeted modification of TiO<sub>2</sub>-NPs, which so far rarely resulted in stable TiO<sub>2</sub>-NPs based paint formulations <sup>4</sup>.

To counterbalance adverse effects, a green synthesis method for non-metal (P, N and C) doped-TiO<sub>2</sub>-NPs is introduced, based purely on waste-valorization. PNC-doped-TiO<sub>2</sub>-NPs characterization by vibrational and photoelectron spectroscopy, electron microscopy, diffraction and thermal analysis suggest that TiO<sub>2</sub>-NPs were modified with phosphate (P=O), imine species (R=N-R) and carbon, which also hindered the anatase/rutile phase transformation, even after 700 °C calcination. When added to water-based paint, PNC-doped TiO<sub>2</sub>-NPs achieved 96% removal of surface adsorbed pollutants under natural sunlight or UV, paralleled by stability of paint formulation, as confirmed by micro-FTIR surface analysis. The origin of the photoinduced self-cleaning properties was rationalized by 3D and synchronous photoluminescence spectroscopy, indicating that the dopants led to 7.3-times stronger inhibition of photoinduced e<sup>-</sup>/h<sup>+</sup> recombination when compared to a benchmark P25 photocatalyst. The results are summarized in figure 1.



**Figure 1.** (a) End-to-end methodology, describing sustainable nanosynthesis (SNS), preparation/performance of photocatalytic paints and effect of NPs on paint stability. (b) Photocatalytic removal of surface adsorbed methyl violet by paint with 2.5% PNC-doped  $\text{TiO}_2$ -NPs, showing best performance.

## Acknowledgments

This research was funded in part by the Austrian Science Fund (FWF) [10.55776/F81 and 10.55776/14434] (SFB TACO, P08 and Single Atom Catalysis).

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## **Rooibos tea waste binary oxide composite: An adsorbent for the removal of nickel ions and an efficient photocatalyst for the degradation of ciprofloxacin**

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**Keywords:** rooibos tea waste, binary oxide, adsorption, nickel, photocatalyst

In this study, rooibos tea waste (RTW) incorporated with a binary oxide (BO;  $\text{Fe}_2\text{O}_3\text{-SnO}_2$ ) has been reported for the first time as a highly efficient adsorbent material for the elimination of Ni(II) ions. The as-synthesised rooibos tea waste-binary oxide (RWBO) composite adsorbent was characterised using miscellaneous techniques such as FTIR, XRD, SEM, EDX, TGA, BET, and XPS. The RWBO was then tested for the removal of Ni(II) in a batch adsorption experiment. The composite adsorbent showed a great removal efficiency of about 97% for Ni(II) ions at 45 °C, 180 min agitation time, pH 7, and dosage of 250 mg. The adsorption process was found to be endothermic and spontaneous. Also, the spent adsorbent [RWBO-Ni(II)] was found to be solar light active with a narrow band gap of 1.4 eV. It was further used as a photocatalyst for the photocatalytic abatement of 10 mg/L ciprofloxacin with an extent of degradation of 83% obtained after 150 min. In addition, the extent of mineralisation of the ciprofloxacin by the spent adsorbent as obtained from the TOC data was found to be 64%. Overall, the RWBO composite adsorbent lends itself as an efficient, eco-friendly and promising material for environmental remediation.



## Plasmon-enhanced ammonia photoelectrosynthesis

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**Keywords:** plasmon, ammonia synthesis, photoelectrocatalysis

The Haber-Bosch process for ammonia synthesis is one of the leading scientific breakthroughs of the 20th century and is vital to sustaining our society's population growth. However, the Haber-Bosch process is energy-intensive, highly polluting, and intrinsically very centralized in its application. Therefore, the study of complementary ways to produce ammonia is one of the main challenges of modern science, which has been reflected in the exponential growth in publications in recent years. While electrification is probably the best answer to this challenge, this process also carries significant challenges. The reduction of nitrogen to ammonia is a highly complex process due to the inert characteristic of nitrogen gas and the high cleavage energy of the N≡N triple bond. This leads to low yields due to kinetically favorable side reactions, such as hydrogen evolution. As an alternative, interest in nitrate reduction has recently grown. Although nitrates contain more reduced nitrogen atoms, their reduction is kinetically more favorable, improving the yields of ammonia production.<sup>1</sup> Additionally, nitrates are a common water pollutant due to using nitrogen-based fertilizers.

In this work, we demonstrated that the electrochemical nitrate reduction to ammonia can significantly benefit from the effect of surface plasmon resonance (SPR). Here, we use a hybrid material comprised of gold nanoparticles, an  $h_+$ -acceptor (NiO), and an  $e_-$ -acceptor/catalyst (TiO<sub>2</sub>) semiconductor to reduce nitrates to ammonia at neutral pH and room temperature. It is essential to highlight that the way SPR contributes to catalytic activity has been debated extensively over the years. Our system shows electrochemical indications that most of the activity comes from hot electrons injection, as corroborated by using ultrafast spectroscopy. This boosts catalytic performance, increasing the conversion to ammonia and suppressing the hydrogen evolution side-reaction.<sup>2</sup> We also investigated the mechanism by which that occurs. Our results point to a step-wise process in which NO<sub>2</sub><sup>-</sup> is accumulated in the first moment (rate-limiting step) before the complete reduction to ammonia. We hypothesize that combining hot electrons and heating generated by surface plasmon resonance offers additional driven force to the catalysis. In a subsequent step, we studied the introduction of different alcohols as PCET agents in our system. These alcohols act as proton shuttles, increasing catalytic activity, with benzyl alcohol and short aliphatic alcohols providing the best performance. Finally, we investigated the catalytic active site by studying the effect of the TiO<sub>2</sub> structure on the conversion and selectivity of our system. In that sense, the amorphous TiO<sub>2</sub> structure shows increased nitrate reduction.

### Acknowledgments

This project was possible thanks to the support of the Swedish Research Council (VR) (grant no. 2019-03597).

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## T6: Catalysts in biomass utilization

### Heterogeneous catalyst development and reaction kinetics for biodiesel production from biomass-based sources

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**Keywords:** biodiesel, waste cooking oil, biobased feed, heterogeneous catalyst

Biodiesel, a carbon neutral energy source, can provide an alternative for petro-diesel towards minimizing carbon emissions. In this work, heterogeneous catalysts were prepared to mimic biobased catalysts and optimized for waste cooking oil transesterification to biodiesel. The biocatalysts were synthesized from banana peels (BP) which contained high K<sub>2</sub>O content. In terms of preparation, banana peels were washed, dried and calcined at three temperatures (600, 800 and 900°C yielding catalysts BP600, BP800 and BP900, respectively) for transesterification of waste cooking oil. It was observed that an increase in calcination temperature resulted in an increase in fatty acid conversion, with BP900 providing the highest conversion, as shown in Table 1. Reaction conditions were then optimized for BP900 which yielded a 91.1% maximum conversion in 2 hr at 60°C. However, due to low calcination yield of BP900 (10.2%) and low availability of banana peels for commercial scale application, a replica was synthesized from inorganic precursors of the ingredients seen in BP. Three different inorganic catalyst recipes were prepared: by coimpregnation (BPIn1), coprecipitation followed by coimpregnation (BPIn2), and coimpregnation (BPIn3). Specifically, BPIn1 was prepared via coimpregnation of SiO<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> and nitrates of K, Ca and Mg precursors. In BPIn2, the nitrates were precipitated with NaHCO<sub>3</sub> followed by impregnation of non nitrates. In BPIn3 co impregnation was used with the inclusion of Fe, Mn, Al, Cu and Zn precursors in relatively small amounts. BPIn2 had the best performance of 85.7% free fatty acid conversion as shown in Table 2. Results for BPIn2 further showed that an increase in reaction temperature up to 70°C increased fatty acid conversion (Figure 1). Also, an increase in reaction time (Figure 2) and ethanol/oil ratio (Figure 3) increased fatty acid conversion.

#### Reaction Kinetics

A reaction kinetics model was developed for the transesterification of waste cooking oil over BPIn2 catalyst following the power law model as shown in Eqn 1.

$$-r = dX/Wdt = k_{oe}^{-E_a/RT} \cdot C_{oil}^n \cdot C_{ethanol}^m \dots \dots \dots \text{eqn 1}$$

Four equations were set up using the varied ethanol to oil ratios with their corresponding fatty acid conversion, and solved simultaneously to obtain the orders of reaction for oil (n) and ethanol (m) as well as the rate constant (k).

Eqn 1 was then evaluated at different temperatures to determine their corresponding (ks). Lnk was plotted against 1/T in as shown in **Figure 4** to obtain the frequency factor (ko) and activation energy (Ea) as tabulated in **Table 3**.

$$k = k_{oe}^{-E/RT} \dots \dots \dots \text{eqn 2}$$

**Table 1:** Effect of calcination temperature on the fatty acid conversion of banana peel catalyst

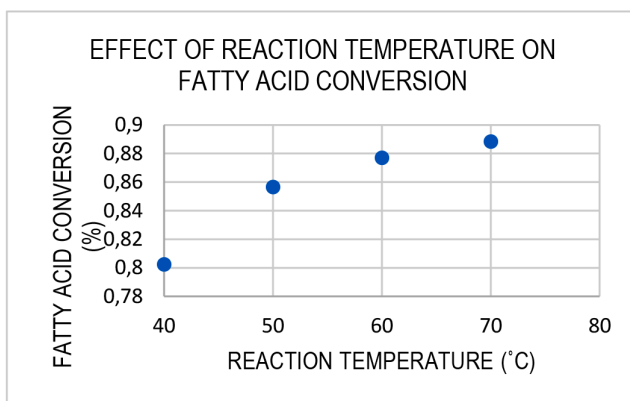
Reaction time: 6hrs, catalyst wt%: 2wt% reaction temperature: 60°C, Ethanol to oil ratio: 15:1, stirring rate: 600rpm		
Banana peel catalyst	Calcination Temperature (°C)	Fatty acid conversion (%)
BP600	600	77.52
BP800	800	79.74
BP900	900	89.01

**Table 2:** Fatty acid conversion of inorganic banana peel catalysts

Inorganic replica catalysts	Preparation method	Fatty acid conversion (%)
BPIIn1	Coimpregnation	80.81
BPIIn2	Coprecipitation followed by coimpregnation	85.74
BPIIn3	Coimpregnation	72.51

**Table 3:** Activation energy and collision factor

Ko	0.002045 ± 0.00003	
Ea	2,973.34 ± 36.572	J/mol



**Figure 1:** Reaction temperature optimization

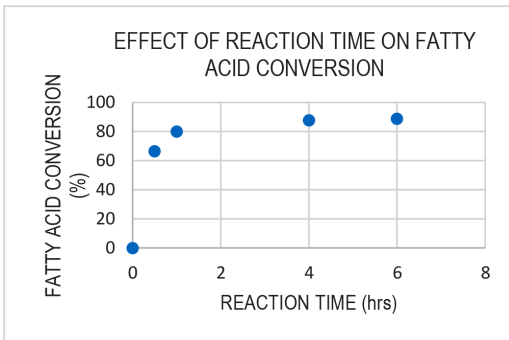


Figure 2: Reaction time optimization

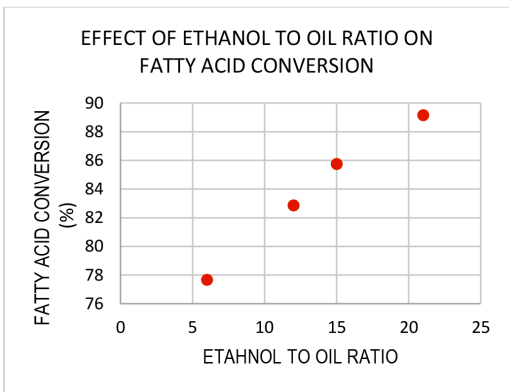


Figure 3: Ethanol to oil ratio optimization

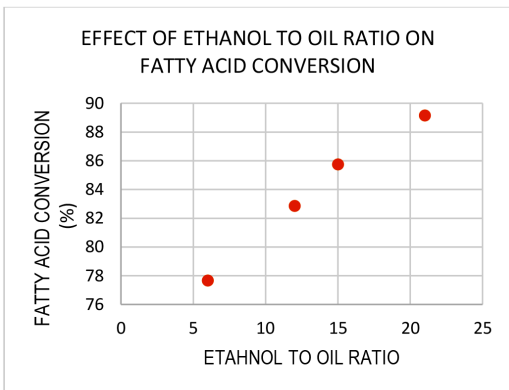


Figure 4: lnk vs. 1/T

## Hydroconversion of $\gamma$ -valerolactone on alumina- and Beta zeolite-supported Co catalysts: The role of catalyst acidity in the reaction pathways

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**Keywords:** Gamma-valerolactone hydroconversion; solid acid supported Co catalysts; 2-Methyl-tetrahydrofuran; pentanoic acid; quasi-operando DRIFT spectroscopy

Dependence on fossil carbon resources can be reduced by converting non-crop lignocellulosic biomass into fuels and chemicals. Levulinic acid (LA) can be produced from biomass using acid catalyzed dehydration and hydration [1]. From LA,  $\gamma$ -valerolactone (GVL) can be produced by consecutive hydrogenation and dehydrogenation steps [2]. Hydroconversion of GVL results in mainly 2-methyl-tetrahydrofuran (2-MTHF) gasoline blending compound and/or pentanoic acid (PA). The esters of PA are also useful fuel blending compounds.

In this study, hydroconversion of GVL was studied over a Co/Al<sub>2</sub>O<sub>3</sub> and Co/H-Beta catalyst in the temperature range of 200 to 275 °C, at 30 bar, and space time varied between 0.1–1 g<sub>cat</sub>·g<sub>GVL</sub><sup>-1</sup> h. Conversion of GVL on the neat  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or H-Beta support gave pentanoic acid product indicating that both Lewis acid and Brønsted acid sites can catalyze the cleavage of the GVL ring on the methyl side. The bifunctional Co/H-Beta catalyst yielded PA with high selectivity suggesting the hydrogenation of pentanoic acid intermediate to PA. However, the Co/Al<sub>2</sub>O<sub>3</sub> catalyst unexpectedly showed high selectivity towards 2-MTHF and thus the dominance of a reaction pathway starting with the hydrogenation of the carbonyl group under the applied reaction conditions. The quasi-operando Diffuse Reflectance Infrared Fourier-Transform spectroscopic (DRIFTS) results implied that the strength of interaction between the reaction intermediates and the catalyst strongly affects the reaction kinetics and thus the observed product distribution. The carboxylic acid intermediate reversibly poisons the Lewis acid sites of Co/Al<sub>2</sub>O<sub>3</sub> up to about 250 °C by forming strongly bonded monodentate carboxylate species thereby effectively hindering the ring opening reaction and acid formation. In contrast, the Brønsted acid sites in Co/H-Beta are not poisoned by carboxylic acid intermediate and thus the acceleration of the acid catalyzed ring opening reaction prevails over the hydrogenation reaction pathway.

### Acknowledgments

The authors thank the financial support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, under the 2019-2.1.13-TÉT\_IN funding scheme (Project No. 2019-2.1.13-TÉT\_IN-2020-00043). The support from the European Regional Development Fund and the National Research, Development and Innovation Office, under the Interreg V-A Slovakia - Hungary Cooperation Program, SKHU/1902, (Project No: SKHU/1902/4.1/001) is also acknowledged.

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## Triglyceride hydroconversion over alumina-supported and phosphatized-alumina-supported Pd catalysts

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**Keywords:** hydrodeoxygenation, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd/phosphatized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, tricaprylin, valeric acid

Production of biodiesel by transesterification of edible or non-edible fats and vegetable oils (triglycerides) by a lower alcohol is a conventional technology used to get fuel for replacing crude oil based diesel fuel. Hydrodeoxygenation (HDO) was considered as a favorable alternative of transesterification for producing diesel range hydrocarbons (C16–C18) directly from vegetable oil. The fuel derived is oxygen and sulfur free, and completely compatible with the conventional diesel fuel [1].

In the present work the mechanism of catalytic HDO of triglycerides was studied using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and phosphatized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported Pd catalysts and tricaprylin as model reactants in a high pressure fixed-bed flow-through microreactor system. To understand the relationships between structural properties of the catalysts and their HDO activity, catalysts were characterized by XRPD, <sup>31</sup>P and <sup>27</sup>Al MAS NMR, specific surface area measurements, temperature-programmed desorption (TPD) of adsorbed NH<sub>3</sub>- and CO<sub>2</sub>. FT-IR spectroscopy was used to study the interaction of the catalyst surface with adsorbed pyridine and CO. Quasi-operando DRIFT spectroscopy of the adsorption and reaction of valeric acid was carried out to gain deeper understanding of intermediate carboxylic acid/catalyst interactions.

The first step of the hydroconversion of triglycerides is the hydrogenolysis of the ester bonds producing carboxylic acids and propane. Later, the carboxylic acids are deoxygenated to paraffins. The Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed good activity in the hydrogenolysis reaction of the ester bonds to convert tricaprylin to caprylic acid, but poor activity in the consecutive HDO of the acid. The surface modification of the alumina support by phosphate groups significantly increased the HDO activity of the Pd catalyst and, consequently, the paraffin yield. The activity change was accounted partly for the partial replacement of the weak base Al–OH groups by weak acid P–OH groups but mainly for the partial elimination of Lewis acid (Al<sup>⊕</sup>) – Lewis base (O<sup>⊖</sup>) pair sites on the surface of the support. Carboxylates of less basic surface sites were found to be more prone to HDO reaction than those of strong base sites. Monodentate carboxylates, formed on Al<sup>⊕</sup> O<sup>⊖</sup> pair sites were of low reactivity. Phosphatizing eliminated most of the Lewis type acid-base pair sites, therefore, reactive bidentate carboxylates represented the most abundant surface intermediate during the HDO reaction of triglyceride. Our recent results show that similarly good activity and paraffin selectivity can be obtained when noble metal Pd is replaced by Ni<sub>2</sub>P active phase.



### Acknowledgments

The authors thank the financial support provided by the Ministry of Innovation and Technology of Hungary from National Research, Development and Innovation Fund, under the 2019-2.1.13-TÉT\_IN funding scheme (Project No. 2019-2.1.13-TÉT\_IN-2020-00043), and acknowledge the support from the European Regional Development Fund and the National Research, Development and Innovation Office, under the Interreg V-A Slovakia – Hungary Cooperation Programme SKHU/1902, (Project No: /1902/4.1/001.).

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## T7: Mathematical aspects of reaction kinetics

### Structure of the slow manifold as a tool for parametrisation of the reaction mechanism for oscillatory reactions

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**Keywords:** oscillatory reactions, nonlinear dynamics, slow manifold, Bray-Liebhafsky reaction

Any reaction system starting from some arbitrary initial conditions tends to reach its final steady (equilibrium) state that plays the role of an attractor, passing through distinct regions of the phase space as result of different chemical species interacting through the reaction network. A reaction network may consist of several reaction routes. The competition between them sometimes results in oscillatory evolution, for example: the Bray-Liebhafsky oscillatory reaction (first reported homogeneous oscillatory chemical reaction) [1], [2]

Since, almost all complex high dimensional dynamical systems are characterized by multiple-time-scales, various forms of attractors and transitions between different dynamical states are present in such systems. In systems, where concentrations of crucial species differ significantly, the relaxation oscillations are common. There, fast variables always quickly adjust to any change in slow variables, which act as the parameters for the fast subsystem. Thus, in a phase space of two slow and several fast variables, the stationary values of fast variables are positioned on the two-dimensional surface in multi-dimensional space. In the domain where relaxation oscillations are present this surface is folded having at least two stable and one unstable branch. Such surface is known as slow manifold. Fast variables in that case often alternate between two stable branches resulting in relaxation oscillatory evolution of considered dynamical system.

The shape of the stable manifold and relative position of the steady state determine the form of mozda oscillatory dynamics. [3] Therefore, comparison between experimental recorded oscillations and theoretically calculated slow manifold structures may be used to evaluate or refine rate constants in the model of the reaction mechanism. Procedure for model parametrisation based on slow manifold structure, will be described in more details.

#### Acknowledgments

We are grateful to the financial support from Ministry of Science, Technological Development and Innovation of Republic of Serbia through University of Belgrade - Institute of Chemistry, Technology and Metallurgy – National Institute of the Republic of Serbia, (Contract numbers 451-03-47/2023-01/200026 and 451-03-66/2024-03/200146). This research was also supported by Science Fund of Republic of Serbia #Grant Number. 7743504, NES.

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## Computational profiling of fast, base-free synthesis of quinolin-2-(1H)-one

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**Keywords:** DFT, reaction profile, QTAIM, FMO

Quinolinones are heterocyclic aromatic compounds with various pharmacological activities. Their importance has brought about the need for green synthetic methods. Exploring greener pathways using an experimental trial and error approach is costly and hazardous, hence computational investigations of the existing mechanistic pathways are an alternative. This study focuses on the computational study of a fast, base-free aqueous synthesis of quinolin-2-(1H)-one. Molecular simulations were done using density functional theory (DFT), MP2 and CCSD(T) together with the M062X functional to obtain reaction energy profiles of quinoline-2-(1H)-one in gas phase, water and dichloromethane. The profiles for the two-step reaction helped to elucidate the energy barriers for the chemical reaction. The barrier for the reaction in water and dichloromethane for the first step was 22.44 and 20.58 kcal/mol, respectively, while for the second step 27.24 and 28.35 kcal/mol were obtained, respectively. Frontier molecular orbitals analysis and quantum theory of atoms in molecules simulations were also performed in order to obtain further insight into the reaction and it was discovered that the final product produced an energy gap of 0.24942 eV as well as an average rho and Laplacian of 0.253169 and -0.55821, respectively, indicating that the final product formed can itself participate in further reactions.

### Acknowledgments

We would like to extend our gratitude to the Center for High Performance Computing (CHPC), Cape Town, South Africa, for providing access to the resources that were used to successfully complete this work.

## T9: Carbon dioxide as a resource in chemical processes

### Femtosecond laser generation of defect-rich CuZn nanoalloys for model catalysis

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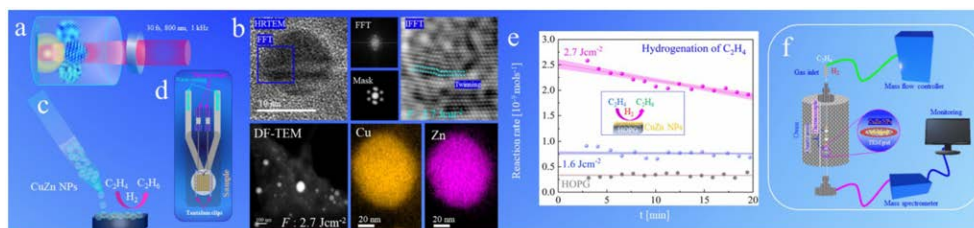
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**Keywords:** ultrashort pulses, CuZn nanoalloys, stacking fault, twinning, ethylene hydrogenation

Heterogeneous catalysis contributes to at least 80% of all produced chemicals. Thus, developing and improving methods to synthesize highly efficient catalysts is important. In heterogeneous catalysis, a chemical reaction occurs at an interface (e.g., solid/gas) and several processes including adsorption/desorption, diffusion and reaction take place. These processes are governed by the physicochemical properties of the catalyst, which, in turn, are determined by its atomic structure and composition.<sup>1</sup> Accordingly, to produce defect-rich CuZn nanoparticles, which cannot be easily achieved by conventional chemical methods, femtosecond laser ablation<sup>2</sup> was applied herein. Ultrashort interaction with (thermally conductive) metals<sup>3</sup> results in higher nanoparticle productivity; thus, laser energy is not wasted as heat.

Femtosecond laser ablation of  $\text{Cu}_{0.70}\text{Zn}_{0.30}$  targets in ethanol led to the formation of crystalline CuZn alloy nanoparticles with defects, low-coordinated surface sites and, controlled by the applied laser fluence, different size and elemental composition. Increasing the fluence yielded larger particle sizes and more stacking fault defects and multiple twinning, as evident from high-resolution transmission electron microscopy, aided by (inverse) Fast Fourier Transform analysis. This is due to the higher plasma temperature, leading to increased random collisions/diffusion of small-sized primary nanoparticles and their incomplete ordering due to immediate solidification typical of ultrashort pulses. The fs laser-synthesized defective CuZn nanoparticles were supported on highly oriented pyrolytic graphite and applied for ethylene hydrogenation, demonstrating their promising potential as model catalysts.



**Figure 1.** Schematic of CuZn nanoparticle production and catalysis. (a) Laser ablation of CuZn alloy in ethanol (30 fs, 1kHz, 800 nm); (b) HRTEM of CuZn nanoalloys, FFT with spot masks, inverse FFT clearly showing twinning; dark field imaging and with EDX mapping analysis (c) CuZn nanoparticle deposition on highly oriented pyrolytic graphite; (d) Schematic of the flow reactor cell used for ethylene hydrogenation; (e) Reaction rate vs time of catalytic tests of CuZn nanoalloys and HOPG; (f) Simulation of catalytic reaction on CuZn deposited on lacy carbon TEM grids for post-reaction analysis of their size and defect nature.

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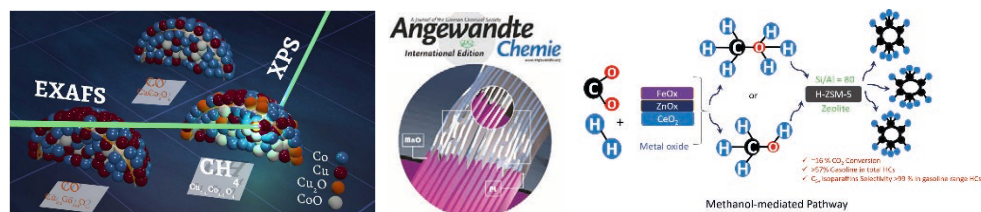
## Tuning Quality of C<sub>1</sub> and C<sub>5+</sub> green fuels by CO<sub>2</sub> hydrogenation over Structured Catalysts

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**Keywords:** CCS/CCU, nanocatalysts, surface science, in situ analysis

In our research, we are focusing on direct hydrogenation of carbon-dioxide with high activity and controlled selectivity of C<sub>1</sub> as well as C<sub>5+</sub> products using of designed nanoparticles and supports as well as interfaces followed by molecular level understanding of the reactions. In this talk, I will discuss our research on the field from the last 5 years evidenced by >20 scientific publications show plenty of results on the field of nanocatalysis and CO<sub>2</sub> activation reactions towards a new sight into green catalysis<sup>1,2,3</sup>. Beside regular characterization techniques NAP-XPS, in-situ RAMAN, XRF as well as DRIFTS techniques helped for molecular level understanding of the processes for future catalysts design. I will show plenty of results on CO<sub>2</sub> activation towards CO and CH<sub>4</sub> with high activity and >99% selectivity (Figure 1 - left) beside showing novel catalysts of production of C<sub>5+</sub> liquid fuels with tunable selectivity of catalyst moderation, e.g demonstrated FeZnCeOx catalyst with >99% of C<sub>5+</sub> iso-paraffins (Figure 1 - right) or tunable jet-fuel catalyst from designed Fe-based systems. Under the umbrella of RRF-2.3.1-21-2022-00009 we are scaling up Fe-catalyst based C<sub>5+</sub> production to 5-10 kg liquid product/day based on solar power-motored H<sub>2</sub> generation. Also, I will speak about cheap ceramic supports for flue gas and C<sub>5+</sub> production invented with collaboration of HK-Ceram Ltd. ceramic factory<sup>4</sup>.



**Figure 1.** Tuned Co/Cu ratio in mixed oxides resulted in 100 % CH<sub>4</sub> selectivity (left); Cover Pt/MnOx resulted in highly active defect sites resulted from the mismatch structure of interface (middle); Fe/Zn/CeOx system for > 99% C<sub>5+</sub> isoparaffin selectivity.

### Acknowledgments

Authors are grateful for the support of FK 143583 and Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

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# Poster Presentations

## T1: Catalysts in sustainable and green chemistry

### Palladium-catalysed hydroaminocarbonylation of olefins with aliphatic amines without additives

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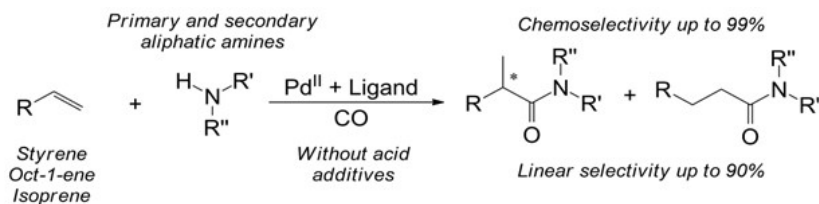
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**Keywords:** homogeneous catalysis, palladium catalyst, hydroaminocarbonylation

A new palladium-catalyzed hydroaminocarbonylation protocol of olefins, using aliphatic amines under carbon-monoxide atmosphere is disclosed. Previously reported protocols have revealed, that the strong basicity of the nucleophiles requires the addition of acid in order to facilitate the reaction. This work represents an additive-free approach of the synthesis of hydroaminocarbonylated compounds in moderate to good isolated yields. Styrene, oct-1-ene and isoprene were transformed under optimized reaction conditions in the presence of various aliphatic amines to get the corresponding amide isomers. The effect of chiral diphosphine ligands on product distribution, and enantiomeric excess was investigated and a mechanism for the additive-free hydroaminocarbonylation reaction was proposed.

#### Figures



Hydroaminocarbonylation of aliphatic olefins without additives

## Catalytic-like effect of alternating electric field on the growth and germination of wheat seeds

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**Keywords:** alternating electric field catalytic-like effect, wheat seed treatment

The biological effect of electric, magnetic or electromagnetic fields on eukaryote and prokaryote has awakened strong interests of biologists since mentioned physical fields could act as stress factors and thus affect the metabolism, behaviour and survival of cells [1]. Moreover increasing interest can be noted in a search of production technologies based on physical treatments of seeds which could substitute or improve conventional methods, mostly including usage of harmful fertilizers. Our previous experimental results performed on yeast cells indicated statistically significant effects on the metabolism of yeast cells by application of microwave irradiation [2] and low-frequency magnetic fields [3], but because both techniques are not easily scalable to larger volumes, we wanted to develop a more economy and user-friendly experiments in order to study effects of alternating electric field (AEF). In comparison to our previous studies performed on yeast cells, in the present research the influence of AEF was examined on one of the most important cereals used in human nutrition that is wheat.

In this preliminary experimental study wheat seed samples were treated with AEF (in the frequency range up to 1 MHz). Obtained results suggest that AEF used in this research may enhance seed germination and its growth. Besides this catalytic-like effect, statistically significant differences were observed in important photosynthetic pigments such as chlorophyll a and b as well as in total chlorophyll content in wheat leaves, while carotenoid pigments showed statistically insignificant differences between control and AEF treated samples. Also some of the most commonly used vegetation indices used to monitor plant health, such as Normalized Difference Vegetation Index and Greenness Index also showed statistical significant differences between control and seeds treated with AEF. Even though future experimental research is needed to optimize the experimental conditions as well as to confirm observed effects, we believe that AEF effects in pre-sowing seed treatment may have a great potential for agricultural production in future or even to potentially improve phytoremediation processes.

### Acknowledgments

This research was supported by the Science Fund of the Republic of Serbia, Grant No 6684, *Phytoremediation for in situ treatment of agricultural soil and surface waters polluted with per- and polyfluoroalkyl substances - research on PFOS and PFOA as model compounds* - PhytoPFAS.

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## Hydrogen sulfide removal using Copper (II) nitrate-impregnated ZSM-5 derived from sugarcane bagasse ash

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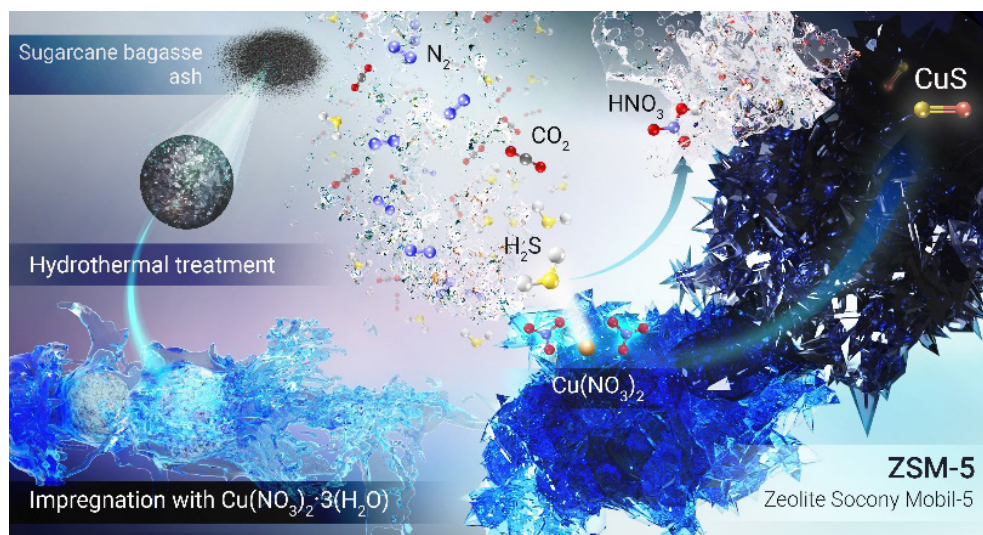
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**Keywords:** hydrogen sulfide, ZSM-5, sugarcane bagasse ash, copper (II) nitrate, adsorbent

Sugarcane bagasse ash (SC) was used as an alternative silica source to synthesize ZSM-5 support (SC-ZSM-5), which was then used to impregnate with copper (II) nitrate (CuN) to produce an alternative adsorbent for hydrogen sulfide (H<sub>2</sub>S) removal. Different advanced instrument techniques were used to characterize the samples' structural, morphological, and surface chemical features. We then investigated the effects of different CuN loading levels, inlet gas components (CO<sub>2</sub> and moisture), and H<sub>2</sub>S adsorption temperatures on adsorption capacity. We have found that copper (II) nitrate and copper (II) hydroxy nitrate are the typical main phases of the CuN/SC-ZSM-5 samples. After H<sub>2</sub>S removal, the CuN/SC-ZSM-5 sample was governed into copper (II) sulfide and copper (II) sulfate phases, and NO<sub>x</sub> was released as a by-product. High adsorption temperatures could increase the H<sub>2</sub>S breakthrough capacity and NO<sub>x</sub> emission, which could affect biogas quality. The CO<sub>2</sub> and moisture had a great effect on H<sub>2</sub>S removal performance. Additionally, the ambient conditions were found to be the best for the H<sub>2</sub>S removal using an optimized 5CuN/SC-ZSM-5.

### Figures



**Acknowledgments**

This work was financially supported by: the National Research Council of Thailand through the Fundamental Fund under the Kasetsart University Research and Development Institute (KURDI), Bangkok, Thailand through Grant No. FF(KU)2.65; and the National Research Council of Thailand through the Research Team Promotion Grant/Senior Research Scholar (Grant No. N42A640324). G.R. acknowledges support by the Austrian Science Fund (FWF; SFB TACO F81-P08).

## Effect of calcination temperature on the activity of K-Co/Al<sub>2</sub>O<sub>3</sub> catalyst for oxidative coupling of methane

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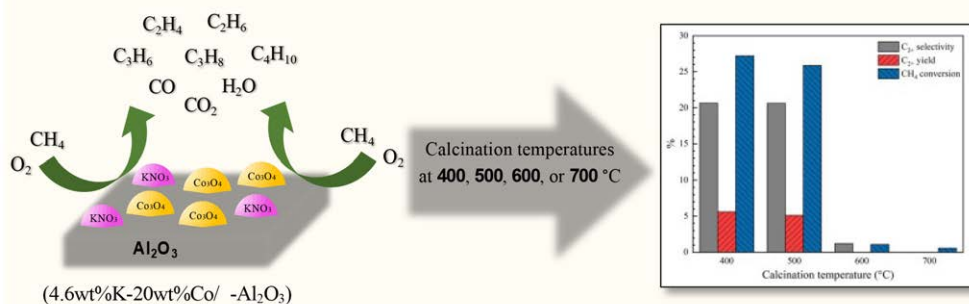
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**Keywords:** alumina support, calcination temperature, cobalt catalyst, methane conversion, oxidative coupling of methane

The oxidative coupling of methane (OCM) involves the direct converting methane to C<sub>2+</sub> hydrocarbons (such as ethylene and ethane) via a reaction with oxygen. This study elucidated the effect of the calcination temperature on the structure and catalytic performance of potassium-doped-cobalt oxide supported on an alumina (K-Co/Al<sub>2</sub>O<sub>3</sub>) catalyst for the OCM reaction. The catalyst was highly active at relatively low reactor temperatures (500–640 °C). Four calcination temperatures (400, 500, 600, and 700 °C) were investigated, with the results showing that the calcination temperature strongly affected catalytic properties, such as the crystalline phases, elemental distribution, physical properties, and catalytic basicity, leading to a wide range in catalytic performances. The catalyst calcined at 400 °C was superior among the catalysts, with 8.3% C<sub>2+</sub> yield, 24.8% C<sub>2+</sub> selectivity, and 33.6% CH<sub>4</sub> conversion at 640 °C. Furthermore, the catalyst was robust over 24 h of testing.

### Figure



### Acknowledgments

This work was financially supported by: the National Research Council of Thailand through the Fundamental Fund under the Kasetsart University Research and Development Institute (KURDI), Bangkok, Thailand through Grant No. FF(KU)38.67; the Center of Excellence on Petrochemical and Materials Technology; and the National Research Council of Thailand through the Research Team Promotion Grant/Senior Research Scholar (Grant No. N42A640324). G.R. acknowledges support by the Austrian Science Fund (FWF; SFB TACO F81-P08).

## T2: Catalytic solutions for energy-related challenges

### Development of catalysts for the catalytic hydrogenation of aromatic nitro compounds for industry

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**Keywords:** hydrogenation catalyst, 2,4-dinitrotoluene, nitrobenzene, catalyst metal, catalyst support

The research and development project "Complex, integrated technological development of aromatic isocyanate feedstock production", funded by the NKFI Fund and launched in October 2021 in cooperation with BorsodChem Zrt. and the University of Miskolc, aims to develop a tuneable, intelligent hydrogenation catalyst system adapted to market conditions and environmental regulations, which will increase the efficiency of the catalytic process.

BorsodChem Zrt. has initiated an applied research process for the development of a catalyst system for the hydrogenation of aromatic nitro compounds, including 2,4-dinitrotoluene and nitrobenzene, within the framework of the project "ARIZO". The primary aim of the research is to develop, in close collaboration between the two consortium members, an industrially applicable catalyst with the right selectivity and activity. On the other hand, it is important that it not only performs excellently in the catalytic process, but also has favourable properties in the technological process.

The paper prepared for the conference aims to present the research progress of the catalyst development process, highlighting the catalyst production process under laboratory conditions and the catalyst composition study. In industrially important hydrogenation processes, we have investigated the activity of the catalyst metals and their interactions, as well as the catalyst and catalyst support system.

The project 2020-1.1.2-PIACI-KFI-2020-00121 is funded by the Ministry of Innovation and Technology through the National Research, Development and Innovation Fund.

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## Synthesis, characterization and application of Fe-SBA-15 catalyst

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**Keywords:** esterification, acid catalyst, kinetic model

Acid catalysis is one of the most important catalyzed processes in the chemical industry. Important organic transformations are esterifications, transesterifications, etherifications, dehydrogenations, oxidations, acetylations, silylations and biodiesel synthesis. Solid acid catalysts are an alternative to hazardous and corrosive homogeneous acid catalysts. They contain less environmentally harmful components, but at the same time have a higher activity and selectivity compared to homogeneous catalysts. [1–3].

One type of solid acid catalyst is mesoporous silica, a solid inorganic support with a large surface area and relatively large pores. It is suitable for the immobilization of chemical and biochemical catalysts mainly due to its high thermal and physical stability and its controlled pore size. Depending on the pore size, diffusion of various substrates to the active sites is possible. Silica-based catalysts are inexpensive, insoluble in most organic solvents, easy to synthesize and easy to recycle. One type is the modified mesoporous silica SBA-15, which can be used for a variety of organic reactions. Its catalytic activity depends on the type and amount of functional groups attached. [4]

The aim of our work was to synthesize a functionalized SBA-15 catalyst. We used the wet impregnation method using  $\text{FeSO}_4$  solution. Nitrogen adsorption-desorption (BET), Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS) and thermogravimetric analysis (TGA) were used for characterization. The efficiency of the synthesized solid acid catalyst was tested on a well-known reaction of myristic acid esterification with methanol. All reactions were carried out in an automated laboratory batch reactor at different temperatures (50, 55, 60 and 64.5 °C) and different masses of Fe-SBA-15 catalyst (0.05, 0.075, 0.1 and 0.125 g). The esterification of myristic acid catalyzed by the functionalized catalyst SBA-15 was described by the Langmuir-Hinshelwood-Hougen-Watson kinetic model.

### Acknowledgments

We would like to thank the Slovenian Research Agency (ARIS) for co-financing the research program "Process systems engineering and sustainable development" with the code P2-0414.

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## Extrusion of optimized catalysts with smart extrusion technology from ECT-KEMA

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**Keywords:** extrusion systems, catalysts, pelletizing

In recent years, ECT-KEMA GmbH has widened its range of auger and piston extruders for the extrusion of catalysts with different geometries in a goal-oriented process and developed a set of tools that can be used to optimize the extrusion of catalysts. Global champions in the manufacture of catalytic converters use our technology.

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- Seamless online monitoring and logging of all relevant machine related parameters with state-of-the-art sensor and control systems.
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- Permanent optimization of wear technology based on the latest findings in coating systems for monolithic augers made of ceramic or carbide.
- Supply of dies and pressure heads made of different materials – if wanted as well support to optimize the die geometry based on material specific simulations of the extruded masses of the customer.
- Selective temperature control of all components that come into contact with the ceramic body like auger, barrel, pressure head and die – essential for temperature-sensitive bodies.
- With sensor systems applied for ECT-KEMA in combination with newly developed cutting technology, we have succeeded in extruding catalysts with near-constant L/D ratio and if wanted to round off the extruded pellets into granulates.
- Development of integrated solutions from preparation, optimization of the formulation in our laboratory, cutting and handling of the green extrudates.

We are looking forward to the talks and contacts at the annual German Catalysis Meeting.

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The poster features a dark teal background with a white and orange color scheme. At the bottom, there is a photograph of various catalyst pellets and granules in different colors (white, yellow, brown) and shapes (spheres, cylinders, irregular granules).

## T5: Homogeneous and heterogeneous photocatalysis

### Photochemical processes in aqueous benzoquinone and anthraquinone solutions

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**Keywords:** quinone, photokinetics, PhotoCube™ photoreactor, matrix rank analysis

Quinone derivatives play an important role in biological systems. They are good model compounds in solar energy utilization experiments, in which the photosensitivity and redox properties of quinones are used (e.g. in flow batteries). [1]

1,4-Benzoquinone and anthraquinone derivatives dissolved in water were examined in a PhotoCube™ photoreactor under illumination with 365, 365, 395, 457, 500, 523, 595, 623 nm, or white light. Derivatives with different electron-withdrawing and electron-donating substituents were studied. The photosensitivity of 1,4-benzoquinone solutions is known. However, a different kind of product was formed during the standing than under illumination.

Using classical matrix rank analysis and the Peintler method, [2] the number of light-absorbing particles in each photochemical reaction was determined. In general, one of the colored particles is the quinone, and the other is a constant ratio mixture of hydroquinone and hydroxyquinone formed as a product, which are weak acids, so their protonation/deprotonation also occurs as the pH of the solution changes, thereby increasing the number of colored particles. This effect was previously avoided by using buffers or pH-stat technique. [3]

In the case of the 2,6-dichloro-1,4-dichlorobenzoquinone derivative, photochemical kinetic measurements at various temperatures were carried out in a diode array spectrophotometer with polychromatic light source. [4] The reaction was only slightly accelerated by increasing the temperature from room temperature to 45 °C.

#### Acknowledgments

The research was funded by project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, which has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

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## Photochemical study of the reaction between 2,3-dimethoxy-5-methyl-p-benzoquinone and water

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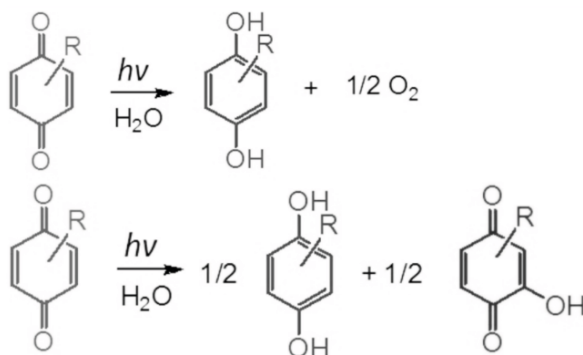
**Keywords:** quinone, photokinetics, diode array spectrophotometer, matrix rank analysis, HPLC

Quinone derivatives are used by nature in energy transfer or storage processes. The reactions of 1,4-benzoquinones are well-known in an aqueous environment, where they are exposed to polychromatic light to form hydroquinone, hydroxyquinone and oxygen. A new research area has emerged based on the quinone/hydroquinone conversion flow battery, [1] where in addition to storing electrical energy, illumination may increase the energy content because of the photochemical reactions.

The solution of 2,3-dimethoxy-5-methyl-p-benzoquinone in water was examined in a diode array spectrophotometer. As light passes through the sample, a photosensitive substance (the quinone in this case) is transformed by light and a photochemical reaction is induced. At the same time, the changes in the mixture are detected through absorbance measurements. [2] The resulting quinone derivatives are readily detected by high performance liquid chromatography (HPLC) [3] or other analytical techniques as well.

Matrix rank analysis was used to determine the number of coloured particles in a solution.

### Figure



Reaction scheme of the photochemical decomposition of 1,4-benzoquinones

### Acknowledgments

The research was funded by project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, which has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

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## Photochemical decomposition of sodium anthraquinone-sulfonate in aqueous solution

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**Keywords:** anthraquinone, photokinetics, actinometry, diode array spectrophotometer

The development of flow batteries offers a promising way to convert sunlight into chemical energy. In such systems, quinone and anthraquinone solutions can be used as energy carriers due to their water solubility and photo-sensibility.[1]

To investigate the photochemical reactions in aqueous solutions of sodium anthraquinone-2-sulfonate, a diode array spectrophotometer with polychromatic light sources [2], as well as a high intensity lamp (emitting at 254 nm) was used. In the second apparatus, the polychromatic light of the diode array spectrophotometer was replaced with a light source emitting mainly in the UV range, so that the photoreaction could be accelerated and still be monitored spectrophotometrically. For this purpose, the high intensity UV lamp was fixed on top of the cuvette holder of the spectrophotometer.

Actinometric measurements using potassium [trioxalate-ferrate(III)]-trihydrate [3] were performed to determine the light intensities of the lamps.

The kinetic curves of the photo-decomposition reaction of sodium-anthraquinone-sulfonate in water were monitored at several different wavelengths. Aqueous solutions of the anthraquinone derivative showed a decrease in absorbance at 332 nm and an increase at 410 nm. For longer measurements, the kinetic curve measured at 332 nm showed an S-shape, while the kinetic curve determined at 410 nm was a straight line.

### Acknowledgments

The research was funded by project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, which has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

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## A kinetic study of the photooxidation of water by aqueous cerium(IV) in perchloric and nitric acids

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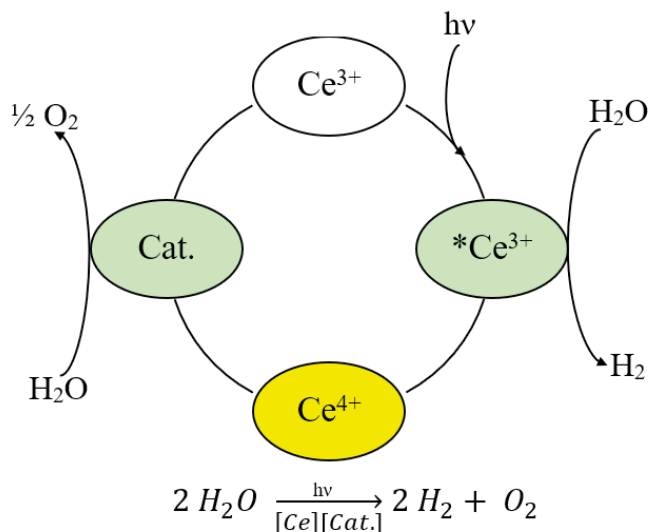
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**Keywords:** water oxidation, photocatalysis, quantum yield determination

The light sensitivity of various aqueous cerium(III) and cerium(IV) complexes has been known since the 1950s. It was found that when an acidic aqueous cerium(III) solution is illuminated by UV light, water splitting occurs to form gaseous oxygen and hydrogen [1]. The essence of the interpretation was that excited cerium(III) ions are able to reduce water to liberate hydrogen, then cerium(IV) ions formed as a product oxidize water to oxygen in a separate step. This sort of cerium-based photocatalytic cycle still considered to be one of the possibilities in storing solar power in a chemical form. [2]

The spectral and kinetic properties of cerium ions have been investigated in perchloric acid and nitric acid quantitatively using a diode array spectrophotometer as a photoreactor. The photon flux of the lamps of the spectrophotometer was determined using a modified actinometric technique. [3] Molar absorption coefficients and quantum yields have been determined under these acidic conditions. A detailed mathematical analysis of the measured absorbance time traces was carried out based on the numerical solution of the photochemical rate equation. [4]

### Figures



**Figure 1:** Photocatalytic cycle for water splitting catalyzed by Ce(III).

**Acknowledgments**

The research was funded by project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, which has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

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## T6: Catalysts in biomass utilization

### Ethanol coupling reactions over noble metal (Pt, Pd) promoted MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxide-based catalysts

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**Keywords:** ethanol coupling to butanol; MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxide-based catalysts; in situ DRIFT spectroscopy

Conversion of bioethanol to biobutanol via Guerbet coupling reaction attracted significant interest of chemical industry, because 1-butanol could be used as renewable fuel or blending component of gasoline, as well as precursor for the production of other valuable chemicals [1-3].

Catalytic conversion of ethanol to 1-butanol was studied over hydrotalcite-derived MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxide-based catalysts and their noble metal (Pt, Pd) promoted derivatives. Relationships between acid-base and catalytic properties and the effect of active metal on the hydrogen transfer reaction steps were investigated. The acid-base properties were studied by temperature-programmed desorption of CO<sub>2</sub> and NH<sub>3</sub>, and by the FT-IR spectroscopic examination of adsorbed pyridine. Dispersion of the metal promoter was determined by CO pulse chemisorption. The ethanol coupling reaction was studied using a flow-through microreactor system, He or H<sub>2</sub> carrier gas, and at WHSV = 1 g<sub>EtOH</sub> · g<sub>cat.</sub><sup>-1</sup> · h<sup>-1</sup> space velocity, 21 bar total pressure, and 200 – 350 °C reaction temperature. Formation and transformation of surface species under catalytic conditions were studied by in situ DRIFT spectroscopy.

The highest butanol selectivity and yield was observed when the MgO-Al<sub>2</sub>O<sub>3</sub> catalyst contained relatively high amount of strong base and medium-strong Lewis acid sites. The presence of metal, especially Pd promoter improved the activity both in He and H<sub>2</sub>, however the butanol selectivity significantly decreased at temperatures ≥300 °C due to acceleration of undesired side reactions. DRIFT spectroscopic results showed that the active metal promoted H-transfer from H<sub>2</sub> over the narrow temperature range of 200-250 °C, where the equilibrium allowed significant concentrations of both dehydrogenated and hydrogenated products.

#### Acknowledgments

The authors thank the financial support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, under the 2019-2.1.13-TÉT\_IN funding scheme (Project No. 2019-2.1.13-TÉT\_IN-2020-00043). The support from the European Regional Development Fund and the National Research, Development and Innovation Office, under the Interreg V-A Slovakia - Hungary Cooperation Program, SKHU/1902, (Project No: SKHU/1902/4.1/001) is also acknowledged.



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## T7: Mathematical aspects of reaction kinetics

### Examples for non-autonomous pH-oscillation systems and applications

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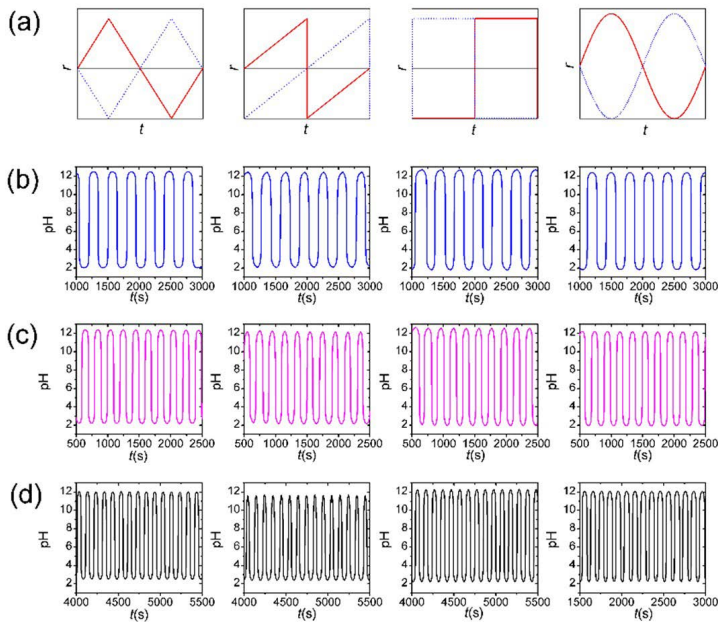
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**Keywords:** pH-oscillation, MOF synthesis, pH-controlled precipitation, pH controlled self-assembly

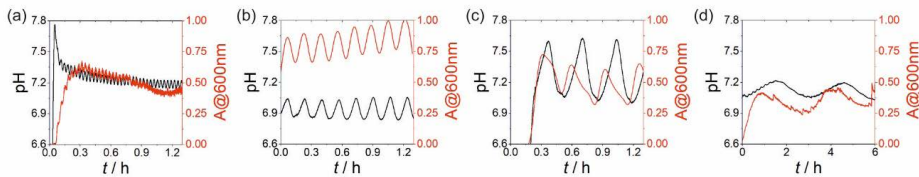
The main aim of our study was to create, design and engineer non-autonomous pH-controlled chemical oscillating systems in which the characteristics of the temporal oscillations (such as amplitude, time period) can easily, and precisely be controlled by the experimental conditions such as the flow rates and feed concentrations. The demonstrated phenomena can be exploited in practical applications: we used them to drive the reversible assembly and disassembly of pH-sensitive building blocks (oleic acid, ZIF-8 and gold nanoparticles), all of them highly relevant in nanotechnology and biomedical applications. [1] [2]

We made two types of systems: The simplest one used only hydrochloric acid and sodium hydroxide solutions. In this case we dissolved in the reaction mixture oleic acid and synthesized gold nanoparticles respectively and followed their colour-change in a wide-range of pH-change ( $\Delta\text{pH}\sim 13$ ). [1] The other one used the ZIF-8 components (zinc ion and 2-methylimidazole) solutions with acidic and base characteristics and followed ZIF-8 periodic crystallization and decomposition. [2] In all cases we used various periodic time-dependent inflow rate functions (waveforms) of the reagents with an identical time-period and the phase difference ( $\varphi$ ) of  $\pi$ .

The reaction mixture was placed in a 100 mL cuvette and stirred with magnetic stirrer, the solutions were injected anti phase with two programmable syringe pumps, pH was measured with an electrode and the turbidity change was followed by using an UV-Vis spectrophotometer at a given wavelength.



**Fig 1.** Non-autonomous pH oscillations in the acid-base neutralization reaction by using various time-dependent inflow rate functions (waveforms) of the reagents, acid and alkaline solutions, with the phase difference of  $\pi$  (a). The time periods of the various inflow rate functions (triangular, sawtooth, square and sinusoidal) were identical,  $T_{\text{acid}} = T_{\text{base}} = 300$  s (b),  $T_{\text{acid}} = T_{\text{base}} = 200$  s (c), and  $T_{\text{acid}} = T_{\text{base}} = 100$  s (d). The concentrations of HCl and NaOH solutions in the input feed were 0.1 M ( $c_{\text{H}^+}^0 = c_{\text{OH}^-}^0 = 0.1$  M), respectively.



**Fig 2.** Generated ZIF-8 oscillations in the turbidity and the monitored pH changes  $T=2$  min (a),  $T=10$  min (b),  $T=20$  min (c), and  $T=3$  h (d). The concentrations of the zinc sulfate and 2-methylimidazole solutions in the input feed were 20 mM.

## Acknowledgments

Thanks for the collaboration to Federico Rossi.

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## Modeling of thiol waves in two-channel gel reactors

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**Keywords:** autocatalysis, chemical wave, reaction-diffusion system, pattern formation

Chemical systems in biological organisms contain many components (e.g., DNA and enzymes) with thousands of interactions between them. Therefore, finding minimal motifs responsible for emergent behaviors in them (e.g. traveling waves) is very challenging. Using synthetic organic chemistry, we can design systems<sup>1</sup> exhibiting complex behaviors with a minimal number of interacting components, because reaction rates and diffusion coefficients can be controlled by altering the molecular structures of the reactants. Semenov and coworkers<sup>2</sup> have shown that cystamine-based chemical oscillations may evolve in a continuously stirred tank reactor in the presence of maleimide and acrylamide acting as slow and fast inhibitors. The flow of these reactants in a two-channel gel reactor<sup>3</sup> can give rise to wave evolution in the gel. The pattern formation has been characterized by its front speed and the time period between the subsequent waves.

In this work, we have described the reaction with an eight-step, seven-component model, besides considering diffusion in the gel as a transport process. The reactor was approximated by a two-dimensional configuration where the initial and the boundary conditions were set to match the experiments. The CVODE software package was used to solve the generated ordinary differential equations after spatial discretization. With the right choice of parameters we were able to reproduce the chemical waves observed experimentally. The characteristics of the patterns were in qualitative agreement with those of the experimental results. Furthermore, we have studied the spatiotemporal pattern formation at different inhibitor concentrations and diffusion constants. The effect of the flow rate of the reactants and the spatial separation of the fast inhibitors on the emerging patterns has also been investigated. In addition, we have determined the minimum and maximum concentration of the fast inhibitor, between which the existence of diffusion-controlled waves are possible.

Insights into the spatiotemporal behavior originating from synthetic networks may reveal new strategies to synthesize life-inspired systems and materials.

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## The kinetics of a generalized nucleation-growth type model

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**Keywords:** nucleation kinetics, nanoparticle growth, symbolic solution, Gillespie algorithm, final size distribution

A family of nucleation-growth type kinetic models describing nanoparticle formation is analyzed in this contribution based on both the deterministic and stochastic approaches to chemical kinetics. The model starts from monomer units, some of which combine in a seed formation reaction. Second-order particle growth between a particle and a monomer unit follows, the rate constant of which depends on the size of the growing nanoparticle in a way that is given in a kernel function. Four different kernels are considered: diffusion kernel (size independence), mass kernel (direct proportionality with volume or mass), surface kernel (proportionality with the surface) and the Brownian kernel (proportionality with the linear size). The two main parameters of the model are the ratio of the nucleation and the growth rate constant and the minimum size of a viable seed ( $n$ )<sup>1</sup>. The infinitely large number of concentration variables do not make it possible to handle the model by the common methods developed for the numerical integration of kinetic differential equations. To overcome this problem, several specific approximations were developed for giving final results that are comparable with experimental observations.

The approximations give closed, explicit formulas for the time dependence of the average size of the nanoparticles in each of the cases. These explicit formulas are compared with the results of simulations using the Gillespie algorithm<sup>2,3</sup> and this is applied for the four different kernel functions<sup>4</sup>, as well.

An interesting aspect of the system is that the very high number of different species guarantees that the individual concentrations or particle numbers are very low, yet the deterministic approach still gives a description that seems acceptable for interpreting experimental results, so in fact there is no need to employ the more demanding mathematics of the stochastic approach. With these approximations, there might be a chance to obtain the full size distribution in these types of models.

### Acknowledgments

The research was funded by project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, which has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

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## Stationary distribution control of a gene regulation network using compartmental discretization

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**Keywords:** stochastic kinetics, biochemical networks, mathematical modeling

Gene expression is a fundamental process in living systems where DNA information is converted to proteins. A stochastic approach in the modeling of gene regulation networks is often necessary to describe the molecular noise present in the system, particularly when the number of molecules is low. One important consequence of noise is the occurrence of random bursts in protein production which have been observed and validated experimentally. To model this behaviour, a mathematical model in the form of a partial integro-differential equation (PIDE) was proposed in [1] where the described quantity is the time dependent protein distribution. This model was extended in [2] for multiple protein species. For easier numerical treatment and analysis, a kinetic and compartmental semi-discretization scheme was constructed in [3] which results in a set of linear time-varying (LTV) ordinary differential equations. It is easy to show that this discretized model has the structure of a nonautonomous master equation. The control of stochastic gene regulation networks where the key properties of the stationary distribution are to be set, is known to be a challenging problem. In this contribution, we use the above-mentioned LTV model to design a controller which is able to track the prescribed mean value of the stationary protein distribution. The manipulable inputs of the model are inducers which can be added to the system in a time dependent manner. To explore the fundamental limitations of control, firstly we perform a reachability analysis, i.e., prepare a map which shows the set of mean values which can be attained by physically realizable inducer quantities. Then the invertibility of the mapping between inducer inputs and distribution mean values is studied numerically by setting up a multidimensional lookup table. Using these preliminary results, we propose a dynamic feedback loop to set the given mean values of the protein distribution. Using the theory of compartmental systems, conditions are given for the existence and uniqueness of the stationary distribution, and it is shown that the tracking error converges to zero while the control inputs remain within their physical bounds.

### Acknowledgments

This work was partially supported by the Hungarian National Research, Development and Innovation Office (NKFIH) through the grant 145934.

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**T8: Electrocatalysis, electrode development and fuel cells**

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**Two-dimensional electrochemical imaging of the Belousov-Zhabotinsky reaction using a microelectrode**

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**Keywords:** BZ reaction, microelectrode, scanning, redox potential

The Belousov-Zhabotinsky (BZ) oscillating reaction might not be interesting anymore from a reaction kinetics point of view, but it still presents an interesting challenge for analytical chemists. In the poster we will show a new application of a certain scanning probe microscopic technique, called the scanning electrochemical microscope (SECM) using the pattern formation in the BZ reaction as an example. The technique involves physically rastering a microelectrode in the distributed BZ reaction while measuring the redox potential, one of the parameterers that is oscillating during the reaction. The challenge was that any traditional microelectrode stirs the reaction during movement, thereby influencing the observed phenomena; an effect that is undesired in any analytical technique. The solution to this problem and the results of the SECM scanning will be shown in the poster, presenting the first spatially resolved redox map of undisturbed chemical waves in the BZ reaction.

**Acknowledgments**

The research was funded by project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, which has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

## **T10: Catalysts in the hydrogen economy**

### **Cobalt supported on a mesoporous TiO<sub>2</sub> for Fischer-Tropsch reaction**

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**Keywords:** cobalt, TiO<sub>2</sub>, mesostructured, SMSI, Fischer-Tropsch

Mesoporous titania were prepared by the surfactant templating pathway, using titanium isopropoxide, and the triblock copolymer P123 as structure-directing agent. The obtained solid was calcined at 3 different temperatures (300, 340 and 380 °C) in order to study the effect of the calcination temperature on the porous structure. The metallic phase was incorporated into the synthesized supports through the incipient wetness impregnation method. Commercial TiO<sub>2</sub> Evonik P90 has been used as reference material.

We have obtained high surface area and well-ordered mesoporous TiO<sub>2</sub> structures showing anatase crystalline phase. After cobalt impregnation, metal clusters are located inside the mesopores. As we have stated from XPS and TPR experiments, in the case of Co/TiO<sub>2</sub>-380 reduction treatment induces a significant diffusion of surface Co species toward the inner surface. In fact, by observing the HAADF-SEM images for reduced Co/TiO<sub>2</sub>-380 it seems that Co mobilization inside the pores creates more discrete clusters along the mesoporous structure (Figure 1). Moreover, the calcination at 380°C leads the higher catalytic performance, with a CO conversion of ca 55%.

While Co/P90 exhibits initial CO conversion rate higher than mesostructured Co/TiO<sub>2</sub>-380, after 30 minutes, reference catalyst shows a drastic deactivation, obtaining a final conversion of 10 %, without reaching a stationary state. Unlikely, the Co/TiO<sub>2</sub>-380 catalyst immediately reaches a stable pseudo-steady state that is maintained over time. Additionally, morphological important differences between mesoporous system and reference material have been observed after reduction and reaction. Well dispersed Co clusters are observed on spent mesoporous catalyst while important covered Co is attained for TiO<sub>2</sub> P90 due to SMSI effect.

From the obtained results, we have stated that cobalt deposition over mesoporous TiO<sub>2</sub> clearly hinders the catalyst deactivation. Such structural disposition controls and stabilize Co cluster during reduction and avoid the covering by SMSI effect.



## Figures

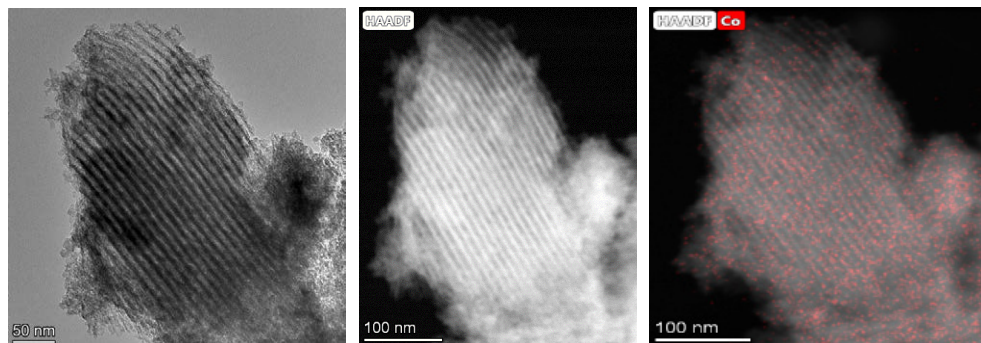


Figure 1. HAADF-STEM images for Co/TiO<sub>2</sub>-380 after reduction at 260°C

## Acknowledgments

Authors acknowledge the financial support through grant PID2020-119946RB-I00 funded by MCIN/AEI/ 10.13039/501100011033.

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## The computational screening of van der Waals heterostructures as sustainable hydrogen production materials

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**Keywords:** Type-II materials, heterostructures, hydrogen production, computational studies, sustainable energy

The fabrication of type-II vertical van der Waals (vdWs) heterostructures has much potential for hydrogen production. Using computational tools, the monolayers and heterostructures were investigated and output for the absorption capabilities, charge density distributions, band alignments and electronic properties were recorded. The stability of the heterostructures were also verified by using ab initio molecular dynamics, binding energy, and phonon calculations. The heterostructures under investigation were type-II materials, known to increase the separation of charge carriers. Moreover, the prevention of recombination of the charge carriers was successful due to the high built-in electric field attributed to the significant difference of the charge density and potential drop across the interface of MSe<sub>2</sub>/BSe. Results from the visible-light optical properties of both the heterostructures were found to be much enhanced with suitable bandgap energy for water splitting. In acidic solutions ( $0 < \text{pH} < 7$ ), the band alignment of the heterostructures is suggested to straddle water redox potentials. Our study predicted that MSe<sub>2</sub>/BSe vdW heterostructures have great potential for photolytic hydrogen production.

### Acknowledgments

The authors will like to acknowledge the financial contributions from the Faculty of Science: University of Johannesburg-South Africa, Centre for Nanomaterials and Science Research, Department of Chemical Sciences and the National Research Foundation (TTK14052167682). We acknowledge the computational support provided by the Centre for High Performance Computing (CHPC), Cape Town.

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## Analysis of safe operation characteristics of SOFC pre-reformer with integrated heat exchanger

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**Keywords:** type your, keywords here, separated, by commas

Countries around the world, especially developed countries, are making constant efforts to secure various energy sources to respond to climate change and soaring oil prices. In particular, in the case of fuel cells, which have the best energy sustainability among new and renewable energy sources, the solid oxide fuel cell (SOFC) system is closest to commercialization mainly in Korea and Japan, which have the best city gas infrastructure. It is hoped that the resulting SOFC system component price reduction technology will become a driving force in the spread of the domestic fuel cell market.

In this study, as part of research to reduce the price and increase the performance of the pre-reformer, which is the core BOP of the SOFC system, we aim to reduce the price and secure the safety of the SOFC hot BOP by evaluating the safety performance of a hybrid pre-reformer combining a heat exchanger and a pre-reformer. We conducted a safety performance evaluation of the 20kW SOFC hybrid pre-reformer system, and by sharing the evaluation results, we aim to present design directions for domestic SOFC manufacturers and confirm the safety of the SOFC hybrid pre-reformer system. In particular, we aim to promote the early revitalization of the SOFC BOP parts industry by redefining the SOFC BOP certification standards by comparing evaluation results of catalyst operation characteristics, harsh condition tests, and environmental tests such as temperature.

## In search of oxo-rhenium catalyst compositions for development of an active new formulation for one-step water-gas shift reaction

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**Keywords:** rhenium, water-gas shift reaction, hydrogen, green energy

The work is aimed at finding oxo-rhenium catalyst compositions for the purification of hydrogen suitable to realizing the water-gas shift (WGS) reaction in only one stage, thus eliminating intermediate cooling in the classical process of going from the high-temperature stage (300–450 °C) to the low-temperature stage (180–250 °C). One stage WGS reaction will simplify the overall energy system design of green energy production by fuel cells. The interest to rhenium as active component for development of active water-gas shift catalysts arouses due to its low cost compared to investigated platinum group metals catalysts such as Pt, Rh, Pd, Ru, and Au on various supports like CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, and MgO as well as its WGS ability to stabilize formate species, to increase H<sub>2</sub> formation rate, to affect water dissociation to OH species and also to impact positively CH<sub>4</sub> selectivity. The exploration was done in two directions: (i) Re as dopant in Re/NiAl and Re/CeNiAl compositions; Re as basic component in CoRe/Al<sub>2</sub>O<sub>3</sub> and K-CoRe/Al<sub>2</sub>O<sub>3</sub>. The catalysts' definitions were chosen on our findings of CeO<sub>2</sub> modified NAl layered double hydroxide (CeNiAl) as active WGS catalyst and K-CoRe/Al<sub>2</sub>O<sub>3</sub> recognized as capable sour WGS catalyst.

The results indicated that the Re-catalyst compositions showed almost equilibrium CO conversion of 93–94% in the interval of 260–350 °C (Figure 1) and activity rapidly decreased on diminishing reaction temperature. Comparative assessment of maximum catalysts' sensitivity at 50% CO conversion discovers their promising performance relative to the best activity of Au-promoted CeNiAl.

It is known that the behavior of the Re-catalyst compositions is affected by redox cycle between Re<sup>4+</sup> and Re<sup>7+</sup> oxidation states and the Re<sup>4+</sup> ↔ Re<sup>7+</sup> balance during WGS reaction is activity-determining factor. K-CoRe/Al<sub>2</sub>O<sub>3</sub> did not reach 50% CO conversion.

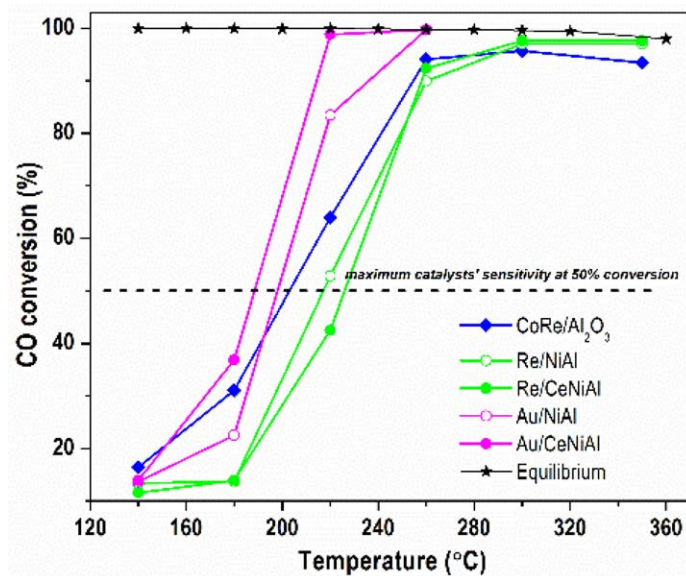


Fig.1. WGS activity of Re catalysts vs Au ones

The conclusion of the begun research is that the future oxo-rhenium catalyst compositions development for improvement of WGS activity by  $\text{Re}^{4+}/\text{Re}^{7+}$  ratio adjustment should be done by changes in composition of the corresponding formulations and activation conditions.

## Dehydrogenation of methyl cyclohexane over nickel-ceria-alumina LOHC catalysts

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**Keywords:** ceria-alumina, nickel, dehydrogenation of methyl cyclohexane, LOHC

Methyl cyclohexane (MCH)-toluene (TOL) couple is a potential industrial candidate for an economical and safe organic liquid hydrogen carrier (LOHC) system. Pt based alumina catalysts are the most active and selective for the hydrogenation-dehydrogenation cycle, as C-C bond breaking with the formation of benzene and methane can be avoided with them. Substitution of noble metals with transition metals is a cost-effective solution, however the commonly used nickel catalysts are less selective due to their high hydrogenolysis activity. The type of supporting oxide and the use of bimetallic catalysts can play a decisive role in improving selectivity.

A series of mono and bimetallic, nickel-ceria-alumina based catalysts were prepared and studied in hydrogenation-dehydrogenation cycle of TOL-MCH. CeO<sub>2</sub> is an active support compared to alumina due to its reducible oxide centers, influencing the metal-support interaction and mediating spillover of hydrogen. 20 wt.% cerium containing CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> supports were prepared by two synthesis methods. One of them was impregnation of a commercial γ-alumina, having bimodal pore size distribution, with cerium nitrate, and a subsequent thermal decomposition. The other was a sol-gel procedure, combining pseudo boehmite (AlOOH) suspension with cerium nitrate solution and ammonia. 10 wt.% Ni was loaded on both types of support by incipient wetness impregnation. Ni/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> bimodal catalyst showed better performance compared to sol-gel preparation. It was also much more active and selective in dehydrogenation reaction than Ni/Al<sub>2</sub>O<sub>3</sub>, reaching 95 % conversion with 80% selectivity to TOL at 375°C and LHSV=1 h<sup>-1</sup>. Hydrogenation of TOL proceeded with 100 % conversion and selectivity between 125-175°C, with 30 bar H<sub>2</sub> pressure. Textural investigations showed that bimodal catalyst has higher specific surface area and pore volume than sol-gel type one and that finely dispersed, crystalline ceria totally covered the surface of alumina. This impregnation method can actually produce a high surface area ceria support, which is more difficult to achieve by using pure ceria. Coverage of alumina by ceria layers modifies the surface favorably, inhibiting the strong interaction between nickel and alumina resulting in hardly reducible spinel structure. In fact, according to TPR measurements reducibility of nickel was higher on ceria catalysts. Modification of nickel phase with zinc or copper improved the selectivity by inhibiting the hydrodealkylation activity by influencing the electronic properties of nickel phase.

### Acknowledgments

Financial supports of HUN-REN Proof of Concept project, ELKH POC-2022-006, KSZF-16/2022, and National Research, Development and Innovation Fund project FK134332 are greatly acknowledged.

## Solar photocatalytic water splitting for hydrogen generation using a novel chromium-doped SrTiO<sub>3</sub> integrated MXene nanocomposite

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**Keywords:** hydrogen generation, Mxene, nanocomposites, photocatalysis, water splitting.

Photocatalytic hydrogen production is necessary for advancing sustainable energy solutions, reducing environmental impact, and addressing the challenges associated with the intermittent nature of renewable energy sources. It plays a crucial role in the transition towards a cleaner and more sustainable energy landscape.

This study focuses on the synthesis and characterization of chromium-doped SrTiO<sub>3</sub> nanocomposites, emphasizing the pursuit of high photocatalytic activity and superior light-harvesting capabilities. Hence, chromium-doped SrTiO<sub>3</sub> integrated MXene nanocomposites (Cr-SrTiO<sub>3</sub>/MXene) were generated and the synergistic effects were assessed. The synthesis involved the integration of chromium dopants into SrTiO<sub>3</sub>, ensuring effective interaction with MXene maximizing their combined catalytic potential. The fabrication process was precisely designed to tailor the nanocomposite's structural and electronic properties, with a focus on improving photocatalytic efficiency and light absorption characteristics. Solar photocatalytic water splitting performance of the novel Cr-SrTiO<sub>3</sub>/MXene nanocomposite was optimized under various operating conditions. Systematic adjustments and parameter tuning were conducted to maximize H<sub>2</sub> production efficiency, accounting for factors such as solar irradiation intensity, temperature, and catalyst concentration.

This research significantly contributes to the advancement of efficient solar-driven hydrogen production by introducing a tailored Cr-SrTiO<sub>3</sub>/MXene nanocomposite.

### Acknowledgments

The authors gratefully acknowledge ANID/FONDECYT Regular grant 1240705 for its financial support.