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Plenary

Network structure and dynamics for biochemical reaction networks

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Models of cellular processes are often represented with networks that describe the interactions between the constituent molecules. The mathematical study of how dynamical properties of a system relate to graphical properties of its associated network often goes by the name "reaction network theory". In this talk, I will connect some of the classical results of reaction network theory, including the Deficiency Zero Theorem and its analog in the stochastic setting, with some current results at the interface of synthetic biology and mathematics.

From snapshots of working catalysts to mechanisms: Opportunities and limitations of operando spectroscopy

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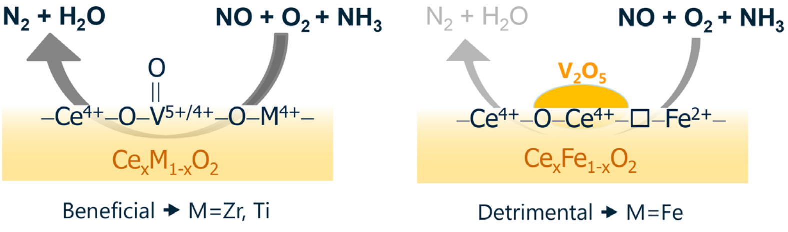
Keywords: H_2 production, photocatalysis, deNO$_x$ catalysis, structure-reactivity relationships

Rational catalyst design beyond empirical trial-and-error approaches is the ultimate goal of research in catalysis which, however, requires detailed knowledge on the role of distinct catalyst building blocks in the different steps of catalytic reactions. This can be obtained best when catalysts are monitored in their active working state by a dedicated combination of spectroscopic methods, each of which contributes a particular facet of information to the global view of the system under study. This will be illustrated by examples comprising global challenges, namely sustainable energy supply and environmental protection.

Sustainable production of hydrogen as a major energy carrier is a future challenge that might be solved by photocatalytic water splitting with sun light when sufficiently active catalysts were available. Their effective design requires rational improvement of charge separation, stabilization and transport, which can only be understood in detail by monitoring such processes with suitable spectroscopic in situ methods. In this example the potential of *in-situ* EPR, *in-situ* XANES and *in-situ* UV-vis spectroscopy for analyzing structure-reactivity relationships in plasmonic M/TiO_2 (M = Au and/or Cu) water reduction catalysts is demonstrated. EPR evidenced that the SPR effect promotes transfer of electrons from the Au conduction band to the TiO_2 support surface where they are trapped and provided in vacancies close to the Au-TiO_2 interphase for proton reduction. XANES and UV-vis spectroscopy revealed that the formation of metal particles by in-situ photoreduction of the precursors depends crucially on the catalyst synthesis route.



While selective catalytic reduction of nitrogen oxides by ammonia (NH_3-SCR of NO_x) is an established technique for cleaning exhaust gases from stationary sources, problems exist with vehicles, since the used zeolite-based catalysts are not active enough at low exhaust temperature. This came to light by the notorious diesel scandal and might boost research activities for low-temperature NH_3-SCR. Promising catalysts for this purpose are based on ceria. *Operando* EPR, *in situ* UV-vis, and *in situ* XANES spectroscopy have been used to explore structure-reactivity relationships in V/$Ce_xM_{1-x}O_2$ catalysts (M = Zr, Ti, Fe) during low-temperature NH_3-SCR of NO. Special –O–Ce–O–V(=O)–O–M–O– surface moieties have been identified in which redox shuttles of V, Ce and/or M ions are related to catalytic activity.

Oscillatory carbonylation of poly(ethylene glycol)methyl ether acetylene. Improved model of reaction mechanism

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Keywords: oscillatory reactions, catalytic carbonylation, poly(ethylene glycol)methyl ether acetylene, palladium catalyst

The reaction mechanism of palladium-catalysed oscillatory carbonylation of poly(ethylene glycol)methyl ether acetylene (PEGA) [1], [2] was examined previously by stoichiometric network analysis (SNA). [3] Reaction network was proposed to account for the experimentally observed results in the investigated process. In the proposed reaction network, instead of the direct autocatalytic steps, autocatalytic loops were used. In the published model of reaction network, the expressions for reaction rates correspond formally to their stoichiometry in accordance to mass action kinetics. The SNA identified the instability condition which was further tested and confirmed by numerical simulation. The role of conservation conditions in stability analysis of proposed model was explored, too. [4]

Previous model used to simulate nonlinear dynamics of catalytic carbonyllation included several reaction steps with several intermediary species were one of them is not confirmed in experiments. Further improvement is achieved now by simplification which successfully excluded species for which there are no proofs of existence. Moreover, two equilibria were removed from the model in order to achieve maximal simplification, although, their existence in the reaction system is beyond any doubt. Even after so rigor simplification, adjustment of rate constants allowed numerical simulations of pH oscillations in the system.

Acknowledgments

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Hydrogen storage and recovery with the use of chemical hydrogen batteries. Water-soluble N-heterocyclic carbene complexes of Ru(II), and Ir(I) in the forefront

Ferenc Joó[1,2*], *Henrietta Horváth*[2], *Henrietta Kovács*[1,3], *Gábor Papp*[1], *Ágnes Kathó*[1], *Mihály Purgel*[1]

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Keywords: formate, homogeneous catalysis, hydrogen storage, iridium, ruthenium

Safe and reversible storage of hydrogen is a key to building hydrogen economy. Among other approaches, chemical hydrogen storage may offer advantages over storage in high pressure tanks or sorption in alloys, etc., such as high density of stored hydrogen (by volume or weight) and the lack of need for unique storage materials. Recently, formic acid and formate salts have emerged as chemicals for viable hydrogen storage [1], and intense research efforts are devoted to the study of catalytic decomposition of HCOOH (to hydrogen and carbon dioxide), as well as to the dehydrogenation of aqueous solutions of formate salts to hydrogen and bicarbonates. Although well regulated generation of hydrogen from convenient store materials is the most important process for energy supply for e.g. vehicles with the aid of hydrogen fuel cells, one must not forget the feasibility of the storage process. Unfortunately, no efficient homogeneous catalytic processes are known for direct hydrogenation of carbon dioxide to HCCOH. In contrast, hydrogenation of bicarbonates to formates in aqueous solution proceeds with no difficulty, allowing the construction of so-called hydrogen batteries. Ru(II)- [2-4] and Ir(I)-complexes [5-8] were found outstandingly active catalysts for such processes, and the lecture gives an overview of the most prominent results achieved in our laboratory together with remarkable achievements of other research groups.

Acknowledgments

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Biodynamics of phosphorylation networks

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Keywords: reaction networks, phosphorylation networks, multistationarity, oscillations.

Understanding the organization and properties of phosphorylation networks is related to the proper functioning of most signal transduction pathways. Mathematical models of phosphorylation networks, which are composed of protein kinases, protein phosphotases and substrates, have versatile dynamics.

We will review some well-established results on multistationarity, bistability and oscillations in phosphorylation networks. Some new directions of research applicable to other reaction network models will also be presented.

Motifs of multistationarity in reaction networks

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Keywords: multistationarity, network motifs, mass-action

The idea of studying "network motifs" in biological systems, namely simple, frequently occurring substructures from which properties of larger systems may be inferred, is at the heart of systems biology, which studies how these substructures fit together to produce large-scale behaviors. In this talk we consider a bottom-up approach to the question of multistationarity (i.e. existence of multiple positive steady states) in biochemical reaction networks. Specifically, we discuss a procedure to infer multistationarity of a network from the multistationarity of its subnetworks. The procedure contains three distinct elements: (1) developing theory that "lifts" steady states of a subnetwork to steady states of the full network (inheritance of multistationarity); (2) identifying classes of small networks that are multistationary (multistationary motifs); and (3) developing graph-theoretical algorithms to find multistationary motifs in a large network. We discuss recent results on questions (1) and (2), and possible approaches to (3).

How can metal-support interactions affect the catalytic performance?

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Keywords: ammonia decomposition, dehydrogenation, catalytic oxidation, palladium, rhodium, platinum, silver, copper, alumina, zeolites, carbon support

Each year catalysts and catalytic technologies penetrate more and more our everyday life. It is hard to imagine any modern industrial process without using a catalyst. Various catalytic systems help improve the process efficiency, thus providing the highest yield of the target product, controlling the selectivity and minimizing the side by-products and wastes formation, and neutralizing the possible emissions, thus solving the environmental aspects.

In heterogeneous catalysis, supported catalysts are the most commonly used ones. In this case, an active component is deposited on some support with a specified porous structure. Depending on the nature of both the active component and support, their interaction can be varied from negligibly weak to significantly strong. In the present overview, few examples of the effect of metal-support interaction (MSI) on the catalytic performance of supported heterogeneous catalysts will be demonstrated.

Carbonaceous materials are often used as support due to their inertness, developed surface area, and optimal porosity. For the purpose of ammonia decomposition, precious metals (Pt, Pd, Ru) are deposited on these supports. Elevated temperatures along with hydrogen-rich reaction medium facilitate strong negative SMI resulting in carbon gasification with the methane formation and leading to the destruction of the catalyst [1,2]. The opposite situation takes place in the case of dehydrogenation of alcohols when strong SMI stabilizes high dispersion of the active component and thus improves the process characteristics [3,4]. For catalysts based on oxides supports, effects can be as negative as positive. Depending on the character of MSI, metal particles can be anchored on the surface in an active state or can diffuse into the bulk of the support, causing an irreversible deactivation.

Acknowledgments

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Catalysis tailoring: From the nanostructures and molecular level understanding to the industrial applications

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Keywords: Pt nanoparticles, controlled size, mesoporous oxide, hard template – replica method, heterogeneous catalysis

Billions of dollars are investigated into information industry. Its less known, that similar budget is used for planning catalysis and industrial catalytic processes. The increasing demand for high activity and selectivity products needs new technologies and understanding of heterogeneous catalysis. The former trial-and-error method can be exchange with new techniques using in-situ methods for molecular level understanding under reaction conditions as well as controlled nanotechnology. These techniques may be exploited in CO_2 activation as well as other green methods.

In our research, mono and bimetallic nanoparticles with controlled average sizes were synthesized and anchored onto different 3D mesoporous oxide materials (SiO_2 – MCF-17, SBA-15, Co_3O_4, MnO_2, Fe_2O_3, NiO, CeO_2) prepared by the soft and hard template (replica) method. Tuning the size of the particles as well as the oxide/metal interfaces high activity and selectivity processes are favorable. NAP-XPS as well as DRIFTS techniques helped for molecular level understanding of the processes for future catalysts designs.

Beside the atomic level understanding, cheap, noble metal-free catalysts pressed into proper forms used for pilot-scale exhaust system upgrading of fuel engines or wooden-heated ovens.

The role of spectroscopy in understanding the nature of the active sites in heterogeneous catalysts: The case of TS-1

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Keywords: spectroscopy, heterogeneous catalysts, active site, TS-1

Spectroscopies are experimental techniques that investigate the interaction between matter and a particle beam (photons, neutrons, electrons, or ions), by monitoring the sample response as a function of the energy of the incoming or outcoming beam(s) [1]. Due to the complexity of heterogeneous catalysts, light-based spectroscopies gained relevance in the understanding of structural and functional properties, exploiting the full range of the electromagnetic spectrum, from radiowaves to the hard x-ray. In fact, the study of a heterogeneous catalyst requires a multi-technique approach to fully describe the system, disclosing the structure and the number of the active sites and their evolution along the reaction. Moreover, the possibility to perform experiment in controlled atmosphere in the presence of both reactants and probe molecules, at different temperature and pressure conditions, increases the possibilities to really understand the nature of heterogeneous catalysts active sites. In addition, molecular modeling is often adopted in combination with spectroscopic techniques. In order to better elucidate this complex approach, the case of TS-1 (Titanium Silicalte-1) [2,3], a well-known catalyst in partial oxidation reactions, will be reported.

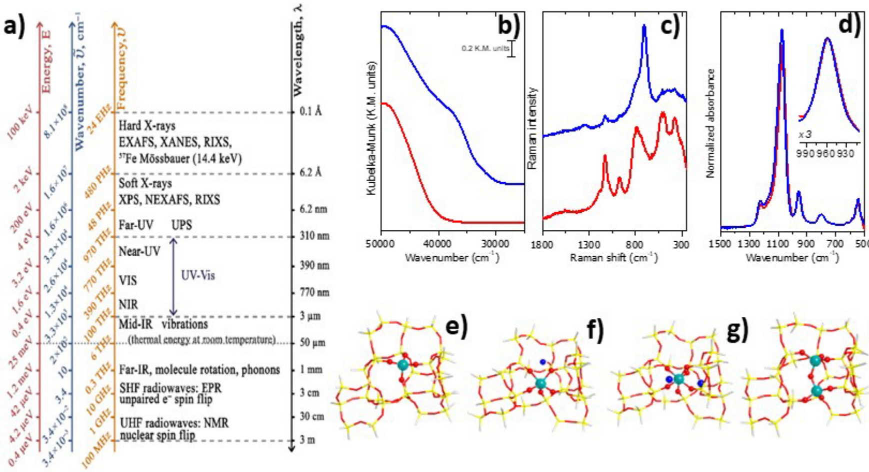

Figure 1. a) Schematic representation of the main spectroscopies used in the characterization of heterogenous catalysts; b) DR-UV-Vis, c) UV-Raman (λ = 266 nm), d) ATR-FTIR spectra of a perfect (red lines) and a defective (blue lines) TS-1; TS-1 models with Ti in different coordination environments: e) 4-folded (tetrahedral) Ti model; f) 5-folded Ti model; g) 6-folded (pseudo-octahedral) Ti model and h) dimeric 4-folded (tetrahedral) Ti model.

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Oral Presentations

T01: Catalysts in sustainable and green chemistry

Preparation of Pt electrocatalyst supported by novel, graphite oxide derived $Ti_{(1-x)}Mo_xO_2$-C type of composites

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Keywords: graphite oxide, solvothermal treatment, XRD, TEM, ATR-IR, ^{13}C NMR, XPS

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) convert chemical energy of hydrogen-rich fuels into electricity without emission of greenhouse gases. A significant part of the price of PEMFCs belongs to the electrocatalysts that require high amounts of Pt as the active element. Therefore, it is very important to increase the utilization of Pt and to decrease the corrosion of the catalysts.

We have developed novel, $Pt/Ti_{(1-x)}Mo_xO_2$-C (C= active carbon) type of electrocatalysts which showed better stability and increased CO tolerance compared to the commercial Pt/C one [1]. The concept of Mo-doped TiO_2 – active carbon composite supports is based on the idea of bringing together the excellent stability and nanoparticle-stabilizing ability of TiO_2 with the good co-catalytic properties of Mo and with the good conductivity and large surface area of active carbon in a unique material system. A key ingredient of the stability of catalysts is the incorporation of the Mo-dopant into substitutional sites of the TiO_2 lattice, which protects the Mo from dissolution, but can still provide CO tolerance.

The aim of this work was the adaptation of the multistep sol-gel-based synthesis method for the use of a new types carbonaceous material, *i.e*. exfoliated graphite-oxide (GO) obtained by the modified Hummers method. $Ti_{0.8}Mo_{0.2}O_2$-C composites with 25 wt.% GO and rutile-TiO2 structure were prepared by a slightly altered synthesis procedure. As GO is known to be thermally unstable, we studied the changes of the carbonaceous component during the preparation of the composite. Based on literature data we supposed that the destruction of the GO plates could be reduced by solvothermal treatment. Therefore, a new solvothermal treatment in *i*-PrOH was involved into the procedure prior to high-temperature treatment (Ar, 600 °C, 8 h). As demonstrated by XRD, using the optimized synthesis route, despite the very different structural and surface chemistry of the carbon materials comparing to the samples obtained without solvothermal treatment, the rutile structure of the mixed oxide was maintained and almost complete Mo incorporation was achieved. GO-derived composites with

S_{BET} = 100–300 m^2/g were loaded with 20 wt.% of Pt by a $NaBH_4$-assisted ethylene glycol reduction-precipitation method. The effect of an additional solvothermal treatment on the structure, catalytic activity and stability of Pt electrocatalysts was demonstrated.

Acknowledgments

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Hydrolysis-oxidation of starch in the presence of solid and soluble heteropoly acid catalysts for the production of formic acid

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Keywords: starch, formic acid, hydrolysis-oxidation, heteropoly acid

Formic acid (FA) is applied for the production of medicaments, solvents, fragrances, and fibers, for conservation of forage, and also used in pulp and leather industries. Nowadays, FA is payed attention as a promising hydrogen precursor (53 g H_2 per liter of formic acid) [1]. The main advantage of formic acid over molecular hydrogen is the simplicity and safety of its storage and transportation. Nowaday, new methods have already been proposed for replacing molecular hydrogen with formic acid in biofuel production processes. Thus, biogenic formic acid is one of the most perspective compounds which can be derived from biomass and involved into energy industry [2, 3]. Starch which is commercially produced during processing of cereal (mainly corn) and tuber (potato) crops may be considered as a promising feedstock for FA production.

Hydrolysis-oxidation of starch with air can be effectively made in the presence of bifunctional heteropolyacid catalysts (HPA) [2, 3]. Traditionally, homogeneous HPA catalysts are applied for the transformation of biomass into formic acid. In our experiments, starch hydrolysis-oxidation was investigated in the resence of Mo-V-P HPA which had different acidity and vanadium content. Optimal process conditions such as reaction temperature, catalyst concentration, air oxygen pressure and the optimal catalyst composition were revealed. The highest yield of formic acid equal to 65% was achieved in the presence of a bifunctional catalyst of composition $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ at 120 °C under air pressure of 2 MPa.

An essential disadvantage of soluble HPA is the difficult separation of the catalyst from the reaction mixture and/or the main product. The problem may be solved using heterogeneous catalysts based on vanadium-containing cesium salts of HPA (CsHPA). In this work, the activity of W(Mo)–V–P(Si) CsHPA catalysts was investigated. The optimum reaction temperature (150 °C) was revealed. Catalyst composition was found to significantely influence on FA yield and selectivity. The most promising catalyst composition was $Cs_{3.5}H_{0.5}PMo_{11}VO_{40}$. 51 % formic acid yield can be reached from starch over this catalyst. High efficiency of heterogeneous HPA catalysts was shown in nine cycles of the reaction [2].

Acknowledgments

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Effect of hydrodynamic cavitation on oxidation of sulfide solutions with oxygen

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Keywords: hydrogen sulfide catalytic oxidation, cobalt tetrasulfophthalocyanine, hydrodynamic cavitation

The development of new methods for the fine purification of gases and liquid effluents from hydrogen sulfide, which promotes to reduce the impact on the environment and to increase environmental sustainability, is an important environmental and technological task. This is due to the high toxicity and corrosive activity of hydrogen sulfide. Effective removal of H_2S from waste solutions is possible due to its aerobic liquid-phase oxidation in the presence of catalysts based on cobalt pthalocyanine sulfonates. The mechanism of the oxidation reaction depends on the pH of the solution. In neutral and weakly alkaline media (pH 7-9), the reaction proceeds according to the polysulfide mechanism associated with the Red-Ox transition Co (II) ↔ Co (I), and with the participation of intermediates with high reactivity – polysulfide ions S_n^{2-}. In strongly alkaline media (pH $\geq$ 11), the destruction of the S_n^{2-} chain occurs, and a slow mechanism of direct oxidation of HS - ions associated with the Red-Ox transitions Co (II) ↔ Co (III) has been occured. In the transition region (pH 10-11), the reaction route depends on the concentration of the catalyst, the presence of additives in the solution that stimulate the formation of polysulfide ions and inhibit its destruction. Mechanochemical activation of the components of the reaction solution under conditions of hydrodynamic cavitation can promote the formation of Red-Ox radicals with high reactivity and be an effective way to achieve a stable mode of catalytic oxidation of a sulfide solution with oxygen according to the polysulfide mechanism in a wide range of solution pH.

Here, we demonstrated results of sulfide solutions oxidation with air oxygen in the presence of cobalt tetrasulfonated phthalocyanine ($CoPc(SO_3Na)_4$) under high mass transfer and cavitation impact. The oxidation of 0.05-0,15M Na_2S solution was carried out at atmospheric pressure, temperature 25-40°C and a solution pH of 10,5 and 12,5 in the range of catalyst concentrations $5\cdot10^{-6}$-10^{-5} mol/l. Reaction was investigated in devices with high mass transfer coefficients and cavitation effect: the shake-reactor with frequency of 360 shakes/min in which mixing of gas and liquid is occurred (mode of foam formation); the reactor with rotor generator of hydrodynamic cavitation (mode of foam formation + cavitation effect).

It was found that the cavitation effect promotes the formation of active intermediates - polysulfides in alkaline media (pH = 10-12.5).

It was found that cavitation impact leads to increasing the reaction rate in in alkaline media (pH = 10-12.5). (Fig.). It was shown that the acceleration of the chemical reaction occurs due to the generation of active intermediates – polysulfide ions S_n^{2-}.

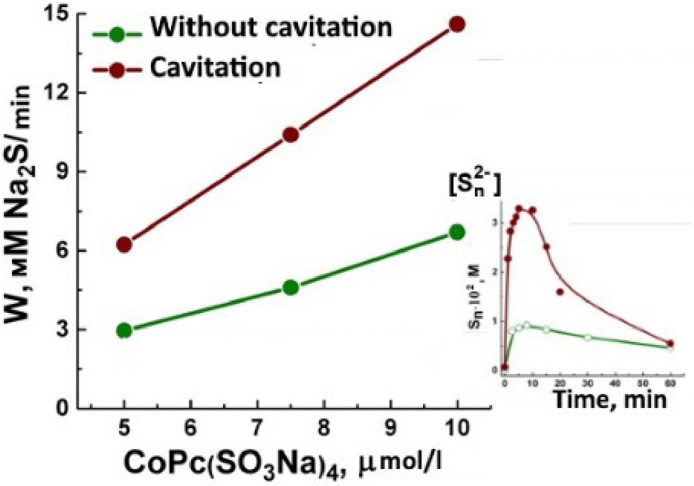

Fig. Dependence of the reaction rate on the catalyst concentration

0,05 M Na_2S; 25^oC; pH= 10,5; Catalyst $CoPc(SO_3)Na$ dependence of the reaction rate on the catalyst concentration.

Hydrodeoxygenation of lignin-derived guaiacol on supported Pd and Ni catalysts using neat and phosphorus-modified γ-alumina supports

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Keywords: lignin, hydrodeoxygenation, guaiacol, Pd and Ni/γ-alumina

Conversion of lignocellulosic biomass to fuels and chemicals has recently got in the focus of research, because of the progressive increase in energy demand and the environmental concerns about the extensive use of fossil carbon sources. Lignin is polymeric component of lignocellulose, comprising of functionalized phenols as monomers. Its thermal and chemical conversion gives a number of aromatic and aliphatic products, having good market potential [1]. Ring-opening hydrogenation of the aromatics generates aliphatic compounds that are potential starting materials of the synthesis of polymers, resins, dyes, and fine chemicals. Cyclohexanones and cyclohexanols are favored target products since they are precursors of polymer intermediate caprolactone or Nylon monomer adipic acid. Cyclohexanones are rarely reported as products of catalytic conversion of lignin-derived monomers. In research studies guaiacol (2-ethoxyphenol, GUA) is often used as model compound of lignin monomers. Supported noble metals and transition metals were found to be active in the hydrogenation of GUA to cyclohexanone [2]. Disadvantage of the described process was that high yield could be obtained only in the presence of high amount of active noble metal. Hydrodeoxygenation (HDO) without hydrogenation of the aromatic ring gives catechols, phenols, and benzenes, which are valuable aromatic compounds. Hydrogenation of bio-derived phenols to aromatic and aliphatic hydrocarbons provides products of increased caloric value. In the present study, supported Pd and Ni catalysts were investigated in GUA hydrodeoxygenation (HDO). Commercial γ-Al_2O_3 and phosphorous-modified γ-Al_2O_3 were used as support.

Pd- and Ni-containing catalysts were prepared by wet impregnation of γ-Al_2O_3 (Alfa Aesar) or its P-modified form. The P content of the modified support was 5 m/m %. Catalysts were characterized by XRD, whereas the dispersion of palladium and nickel was determined by the CO and H_2-chemisorption method, respectively. The acidity of the catalysts was characterized by the FT-IR spectra of adsorbed pyridine. Catalytic experiments were carried out in a flow-through fixed-bed microreactor at 10 bar total pressure in the 250-300 °C temperature range at space time of 1.0 $g_{cat}\ g_{GUA}^{-1}$ h. The H_2/GUA molar ratio was 20. The Pd/Al_2O_3 catalyst showed high selectivity to cyclohexanones. The Ni/Al_2O_3 initiated HDO to cyclohexane. Significantly different product distribution was obtained by the catalyst having P-modified support. The catalysts were inactive in the hydrogenation of the aromatic ring. Demethylation and demethoxylation of GUA were the main reactions.

Using the right catalyst and reaction conditions, the GUA hydroconversion could be directed towards selective formation of required target compounds.

Acknowledgments

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Base-catalyzed aldol condensation of propanal with cinnamaldehyde followed by hydrogenation

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Keywords: aldol condensation, hydrogenation, 2-methyl-5-phenylpentan-1-ol, layered double hydroxides

The desired final product of aldol condensation of propanal with cinnamaldehyde followed by hydrogenation, 2-methyl-5-phenylpentan-1-ol, is the fragrance, commercially known as Rosaphen. It can be synthesized as a racemate or selectively as the (R) - and (S) - enantiomers, but their properties are only slightly different. This work is focused on the preparation of racemate with fruity, brilliant, rosy, wine-like, honey, tea-like, geranyl acetate-like, sweet grapefruit-like odour profile[1]. Because of its excellent stability and relatively low price, it is used in many perfumery fields. In this work, we have studied and optimized various conditions influencing the course of both reactions such as temperature, used solvent, the molar ratio of reactants, catalysts type, and its amount and hydrogen pressure. In an industrial scale homogeneous catalysts, hydroxides, are used almost exclusively as the aldol condensation catalysts. The most suitable conditions of aldol condensation were the molar ratio of the reactants equals 1:1, 36% NaOH solution at 0.1:1 molar ratio to cinnamaldehyde and methanol, as the solvent, in a molar ratio of cinnamaldehyde to methanol of 1:13. After 2 hrs of reaction 88% conversion with 85% selectivity to desired product was achieved. The use of hydroxides can represent a large number of disadvantages namely necessary removal of residual hydroxide from a product, use of large amount of water for washing, or the relatively high corrosion caused by hydroxide. Due to the escalating demands for cleaner, more environmentally acceptable technology, use of heterogeneous catalysts based on layered double hydroxides have been also tested. The second step, hydrogenation of 2-methyl-5-phenylpenta-2,4-dienal, can be catalyzed either by nickel or ruthenium supported catalysts. The ruthenium supported catalyst was not suitable for the mentioned hydrogenation, hydrogenolytic products have been mainly formed. The total pressure of 10-12 MPa, the temperature of 120 °C and nickel supported catalyst proved to be the most suitable hydrogenation conditions. After 3 hrs of reaction total conversion with 86% selectivity to desired Rosaphen was achieved.

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Catalyst development for the direct synthesis of hydrogen peroxide

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Keywords: direct synthesis of hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a green chemical, because it is non-toxic and biodegradable. H_2O_2 is a strong oxidant and it has numerous applications as a bleaching agent in pulp and textile industries as well as a reactant in the formation of several chemicals such as percarboxylic acids and epoxides. However, the currently applied industrial process for the production of H_2O_2, the anthraquinone process, is based on successive hydrogenation and oxidation of quinonic components. High yields of H_2O_2 are obtained, but the process suffers from serious disadvantages such as side reactions, accumulation of impurities in the circulating working solution as well as catalyst deactivation in the hydrogenation step of anthraquinone. For both these reasons, the cost of H_2O_2 is rather high and the only large production units can be economically profitable.

However, the use of biomass as raw materials for chemicals increases the need of H_2O_2 in future and a preferable way is to produce H_2O_2 on site where it is used for further reactions. Direct synthesis of H_2O_2 from molecular hydrogen and oxygen is the evident solution: the process is principally straightforward, because direct synthesis can be conducted on a solid catalyst implemented in a fixed bed reactor, a micro- or a millireactor. Both classical catalyst particles and structured catalysts can be used. The catalytically active metal is palladium (Pd), but in order to suppress the ´hyperactivity‘ of Pd it is doped with gold. Zirconia and sulfated ceria are used as ingredients in the Pd/Au catalysts, too. The critical issue in the success of direct synthesis is the selectivity: decomposiotion and further hydrogenation of H_2O_2 to water impairs the selectivity and profitability of the process.

In the present work, potential catalysts for the direct synthesis of H_2O_2 were prepared and screened. The performance of the laboratory-prepared catalysts were compared with commercial Pd/C. The powder-form catalysts were synthesised with different support materials such as Alumina, Silica and Beta zeolite with varying acidities. The influence of the synthesis method, acidities adn structures on the catalytic properties were investigated. Furthermore mass transfer limitation investigations were conducted by variations of the catalyst particle size. The catalysts were characterized with nitrogen physisorption, Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The metal content was determined with ICP-MS.

Performance experiments were carried out in a tailored laboratory-scale trickle bed reactor and the components were analyzed with HPLC, GC and Karl-Fischer-titration. Typical reaction conditions were conduced under 15°C and 20 bar. The reactor was fed with hydrogen, oxygen, carbon dioxide and methanol was used as the solvent. The detail correlations of physico-chemical properties of Pd modified catalysts and catatyic activities will be presented during the conference.

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Effect of the reductive treatment on the state and electrocatalytic behavior of Pt in catalysts supported on $Ti_{0.8}Mo_{0.2}O_2$-C composite

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Keywords: Mo-doped mixed oxide composite, strong metal-support interaction, Pt, XPS, electrocatalysis

$Ti_{(1-x)}Mo_xO_2$-carbon composites are promising new supports for Pt-based electrocatalysis in Polymer Electrolyte Membrane fuel cells offering exciting catalytic properties and enhanced stability against electrocorrosion as a result of the interplay between the dopant, the oxide and the carbon backbone [1]. Pt and the mixed oxide form a couple liable for strong metal-support interaction (SMSI) phenomenon, generally manifesting itself in decoration of the metal particles by ultrathin layers of the support material upon annealing under reductive conditions. The aim of this work is to evaluate the SMSI phenomenon as a potential strategy [2] for tailoring the properties of the electrocatalyst in terms of stability and reactivity.

A 20 wt.% Pt/50 wt.% $Ti_{0.8}Mo_{0.2}O_2$-50 wt.% C electrocatalyst prepared on Black Pearls 2000 carbon functionalized with HNO_3 and glucose was reduced at 250 °C in H_2 in order to induce SMSI. The electrocatalytic properties and the stability of the reduced and the original catalysts were analyzed by cyclic voltammetry and CO_{ads} stripping voltammetry. X-ray photoelectron spectroscopy (XPS) measurements combined with *in situ* H_2 exposure experiments were performed on the reduced catalyst in order to obtain information about the details of the interaction between the oxide and the Pt particles.

The electrochemical experiments pointed out a small loss of the electrochemically active surface area (ECSA) of Pt with respect to the original catalyst, while XPS suggested only a minimal decrease of the Pt dispersion. At the same time, hydrogen exposure experiments combined with XPS on the reduced catalyst demonstrated the presence of a Mo species very easily reducible to the metallic state, which was interpreted as Mo directly adsorbed on the Pt surface [1]. No such behavior was observed for Ti. Accordingly, even if Mo remains support-bound in the original catalyst [1], the reductive treatment at 250 °C is enough to induce a partial encapsulation of the Pt particles with a Mo-containing overlayer, which explains the decrease of the electrochemically active surface area (ECSA). In addition, enhanced stability of the reduced catalyst was demonstrated by 10,000-cycle stability test.

In conclusion, the results of this preliminary study confirmed that utilization of the SMSI phenomenon can indeed be a valuable approach for improving the stability of the mixed oxide – carbon composite supported electrocatalysts.

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Co,H-SSZ-13 zeolite catalysts prepared by solid-phase reaction for NO-SCR by methane

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Keywords: NO-SCR, cobalt SSZ-13, solid-state ion-exchange

Selective catalytic reduction of environmentally hazardous nitric oxide to nitrogen (NO-SCR) is feasible and important method for the elimination of NO_x emissions both from mobile and stationary sources. Cu-SSZ-13 zeolites were proved to be effective, selective, and hydrothermally stable catalysts of the NO-SCR reaction by reducing agent NH_3. However, replacement of expensive ammonia by cheap and abundantly available CH_4 would be advantageous especially at power plants fuelled by natural gas [1-3].

Due to the extremely high thermal and hydrothermal stability of SSZ-13 zeolite, it was expected that Co-SSZ-13 can be prospective catalysts of the CH_4/NO-SCR reaction for practical application. However, it is a challenge to introduce sufficient amount of active cobalt species in the small pore, high silica SSZ-13 zeolite. The amount of cations, exchangeable into zeolites by aqueous phase ion exchange is limited by the thermodynamic equilibrium of the exchange process. In the solid-phase reaction, often referred to as solid-state ion-exchange (SSIE), the temperature of finely homogenized mixture of zeolite and cobalt salt is increased to induce the reaction of the components. Using this method, the desired amount of cobalt can be introduced in the zeolite in a single step.

Co/SSZ-13 zeolite catalysts, having Si/Al_F and Co/Al_F ratio of 12.5 and 0.3-0.4, respectively, where Al_F means framework aluminum, were prepared by reacting NH_4–SSZ-13 zeolite and different cobalt salts at 550 ^{o}C in solid phase. The kinds and relative amounts of cobalt species, incorporated by the zeolite, were found to be strongly influenced by the type of the Co precursor salt. Upon thermal treatment, formation of Co carrying volatile species or hydrate melt was found to proceed from chloride, nitrate or acetylacetonate Co precursor salts. This phase change allows the transport of the Co species into the pores of the zeolite, and the predominant formation of Co^{2+} cations balancing negative framework charge. The obtained catalysts are of good activity and N_2 selectivity in the CH_4/NO-SCR reaction. In contrast, those catalysts prepared with acetate or formate Co precursor contain mainly Co-oxide clusters located on the outer surface of the zeolite crystallites and show enhanced activity for NO to NO_2 oxidation reaction. On these catalysts, the NO-SCR reaction becomes selective for N_2 only in the high temperature range (>600□C), where Brønsted acid sites can already catalyze the reaction between NO_2 and CH_4 at a considerable rate. In this temperature range the NO_2 formation becomes thermodynamically limited and thereby the N_2-forming reaction can consume the full amount of the NO_2 intermediate.

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Activity of $MgO-SiO_2$ catalysts in ethanol-to-butadiene reaction

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Keywords: ethanol, butadiene, $MgO-SiO_2$ catalysts, acid-base properties

The 1,3-butadiene (BD) is the most important conjugated diene. It is used as monomer for the synthesis of polybutadiene and as building block for different heteropolymers. Currently, the production of BD is based on petrochemical basis, namely more than 99% of BD is produced from petroleum, natural and shale gas. Concerns about the limited availability of fossil carbon resources, as well as, global warming and climate change encourage the use of renewable energy and carbon sources. Bioethanol, as biological product, completely fulfills these requirements. The conversion of ethanol to butadiene (ETB) dates back to the beginning of the last century. The rapidly increasing bioethanol production and the declining ethanol prices have brought the ETB process again to the forefront of interest.

The butadiene is formed in chain of consecutive reactions. To get reasonable overall yield the process requires a catalyst that has a subtle balance of acidic and basic properties as well as hydrogenation/dehydrogenation and dehydration activities. Mixed oxide $MgO-SiO_2$ is one of the most widely studied catalyst or catalyst component for the ETB reaction. Reported results show that catalytic efficiency depends remarkably on the applied method of catalyst preparation, affecting specific surface area, homogeneity/heterogeneity, crystal size/shape and pore-size distribution of the catalyst. The main methods are incipient wetness impregnation, wet-kneading and coprecipitation of magnesia and silica precursors.[1] Our previous results showed that introducing MgO in the framework or on the surface of mesoporous silica gives better performing catalyst than the corresponding catalysts based on microporous silica.[2] In this lecture we present our results on “reverse” $MgO-SiO_2$ catalysts. First mesoporous MgO was prepared and SiO_2 was added to it then by wet-kneading or template-assisted grafting. For comparison “reverse” catalysts were also prepared using non-porous MgO. Catalysts were characterized by XPS, SEM, TEM, FTIR, and TPD methods. Catalyst surface was characterized by its adsorption interaction with acidic and basic molecules, such as, $CDCl_3$ and pyridine (FTIR), as well as, CO_2 and NH_3 (TPD). The effect of surface properties on the BD yields will be discussed.

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Phase composition and activity of Zr-Zn-O catalysts in the reaction of conversion ethanol

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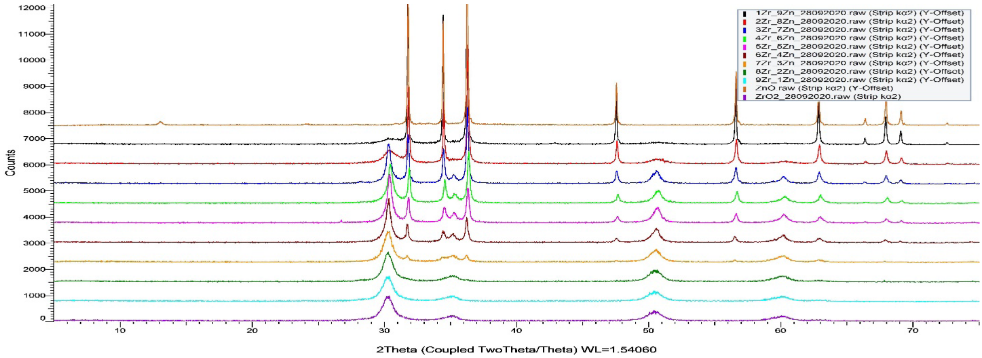
Keywords: ethanol conversion, binary catalysts, zinc oxide

Catalyst based on zinc oxide shows high activity in the reaction of conversion of ethanol to acetone [1]. Quite often, zirconium is added to complex dehydrogenation catalysts as promotor [2]. In this connection this work is devoted to studying the influence of zirconium oxide on activity of zinc oxide in the reaction of the conversion of ethanol.

Binary zirconium-zinc oxide catalysts of different compositions were prepared by co-precipitation method. The activity of the synthesized catalysts was studied on a flow-through installation unit with a quartz reactor in the temperature range of 250–600 °C. X-ray study of the prepared catalysts was carried out on an automated powder diffractometer (CuKα radiation, Ni filter, $3 \leq 2\theta \geq 80°$).

Figure 1 shows the diffraction patterns of all nine mZr/nZn ratios put together. At the beginning and at the end of these diffraction patterns, oxides ZrO_2 and ZnO are also presented. Interpretation of radiographs show that the formation of two phases is observed in the Zr-Zn-O catalytic system, namely zirconium oxide and zinc oxide. It is also found that the formation of chemical compounds between zirconium and zinc oxides is not observed.

Conducted research show that main product of ethanol conversion reaction over zirconium-zinc oxide catalysts is acetone and acetic aldehyde, ethylene and carbon dioxide are a by-product. Obtained results show that with increasing temperature, the yield of acetone passes through a maximum over all studied catalysts. Also, the yield of acetone with an increase in the content of zirconium oxide in the composition of the catalyst passes through two maxima at catalyst Zr-Zn = 3-7 and Zr-Zn = 8-2.



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The effect of particle size of Zeolitic Imidazolate Frameworks on its catalytic properties

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Keywords: Zeolitic Imidazolate Frameworks, size effect, textural and physicochemical properties, catalysis

The last decades, a novel class of materials, metal-organic frameworks (MOFs), has been received remarkable attention towards catalytic applications because of their high and tunable textural features, and in many cases easiness of separation form reaction mixture. One of MOFs' sub-class with similar zeolite's topologies, high chemical and thermal stability, as well as elevated textural features, are Zeolitic Imidazolate frameworks (ZIFs). ZIFs materials with tunable micro-/mesoporous structures and numerous active sites have proved to be excellent as efficient heterogeneous catalysts. Note that microporosity of ZIFs may lead to diffusion resistance of the reactants and products to and from the active sites inside the ZIF' particles and, therefore, severely limit their performance in catalysis. To overcome these limitations, we suggest to minimize the size of the ZIF's particles. Such approach allows shortening the diffusion path of reagents. Moreover, the decreasing of the particle size causes a strong increase of the surface to volume ratio and improves accessibility of active sites for reagents.

Herein, we demonstrate the effect of particle size of ZIFs in the range of 0.05-1.0 μm on their catalytic properties in three industrial important reactions, such as (1) synthesis of 1-methoxy-2-propanol (PGME) from methanol and propylene oxide, (2) synthesis of erythrulose (the monosaccharide) via aldol condensation of formaldehyde and dihydroxyacetone, and (3) synthesis of propylene carbonate from CO_2 and propylene oxide. ZIFs materials were formed by Zn(II) and 2-methylimidazole (ZIF-8) and 2-ethylimidazole (MAF-5(ZIF-14) and MAF-6(ZIF-71)) linkers. Crystal size of ZIFs was found to have a significant effect on its textural properties and acidity, and further on catalytic properties of ZIFs. In all cases activity of samples rises with decrease in particle size due to the increase in external surface area and decrease in ratio of V_{micro}/V_{total}. Other explanation was related to the increasing density of dislocations in the crystal that led the rising the number of acid and basic sites. Noteworthy, particle size of ZIFs can also affect the pathway and reaction selectivity. Thus, in the aldol condensation of formaldehyde and dihydroxyacetone in the presence of MAF-6 the selectivity towards erythrulose rises with increase in particle size. In general, our results suggest that effects of particle size must be accounted for when designing and synthesizing ZIFs materials for catalysis

T02: Catalytic solutions for energy-related challenges

Influence of the multifunctional mixed oxide-carbon composite support on the CO tolerance and stability of Pt electrocatalysts

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Keywords: $TiMoO_x$ mixed oxides, Composite materials, Pt electrocatalysts, CO-tolerance

CO tolerance of the Pt-based anode catalysts is highly important when feeding low temperature polymer electrolyte membrane (PEM) fuel cells with hydrogen from reformates. The way for improving the CO tolerance of the electrocatalyst by the bifunctional mechanism is to create interfaces between Pt particles and an oxide-containing support which is (i) stable under the reaction conditions, (ii) electroconductive, (iii) generates OH groups as oxidants at low potential and (iv) stabilizes the small size of the Pt particles. In our recent studies it has been demonstrated that the application of multifunctional mixed oxide-carbon composite supports is a promising step towards a novel class of fuel cell electrocatalysts [1,2].

Results on preparation and thorough characterization of 20 wt.% Pt electrocatalysts deposited onto $Ti_{0.8}Mo_{0.2}O_2$-C composites with different mixed oxide content ($Ti_{0.8}Mo_{0.2}O_2$/C mass ratio: 75/25, 50/50 and 25/75; where C= Black Pearls 2000 (Cabot)) are presented. The shift of the rutile TiO_2 diffraction peaks to lower angle observed by XRD confirms the incorporation of Mo into the TiO_2 lattice. According to the BET measurements the increase of the active carbon content in the composite materials results in pronounced increase of the surface area of the support (Table 1). According to CO_{ads} stripping voltammetry measurements, the oxidation of CO on the Pt/$Ti_{0.8}Mo_{0.2}O_2$-C catalysts commences at exceptionally low potential values (ca. 50 mV). Enhanced CO tolerance of the Pt electrocatalysts prepared by using the composite support materials was evidenced by the appearance of a CO-oxidation related "pre-peak" and by a shift of the maximum of the main CO oxidation peak towards less positive potential (see Table 1) compared to the reference commercial Pt/C (ca. 800 mV). On the Pt/25$Ti_{0.8}Mo_{0.2}O_2$-75C catalyst with highest value of the electrochemically active surface area (ECSA) the main CO_{ads} stripping peak is located at 775 mV (Table 1), while the corresponding peak in the case of the catalysts with higher mixed oxide content (25 and 50 %) is around 715 mV. Stability tests involving 500 polarization cycles demonstrated good corrosion resistance of all three composited supported Pt electrocatalysts.

Table 1. Influence of the $Ti_{0.8}Mo_{0.2}O_2$/C ratio on the electrochemical performance of the catalysts

Samples	**S_{BET}, m2/g** a)	**$E_{CO,max}$,**b) **mV**	**ECSA, m2/g_{Pt}**	**Δ ECSA,%** c)
Pt/75$Ti_{0.8}Mo_{0.2}O_2$-25C	289	715 (*sh*: 775)	123.0 ± 13.7	8.9 ± 0.5
Pt/50$Ti_{0.8}Mo_{0.2}O_2$-50C	562	715 (*sh*: 775)	122.2 ± 4.4	12.3 ± 0.6
Pt/25$Ti_{0.8}Mo_{0.2}O_2$-75C	930	775	130.3 ± 3.5	12.4 ± 0.5

a) surface area of support materials; b) the position of the main CO stripping peak determined from the CO_{ads}-stripping measurements; c) Δ ECSA= $\{1-(ECSA_{500}/ECSA_1)\}\times100\%$; sh= shoulder.

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Performance of mixed templates incorporated SAPO-34 for methanol to olefins reaction

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Keywords: methanol to olefins, morpholine, SAPO-34, tetraethylammonium hydroxide

Methanol to light olefins (MTO) stands out as a promising alternative for light olefins production in recent times. The present paper deals with the preparation of catalyst SAPO-34 by using dual templates, namely, tetraethylammonium hydroxide and morpholine, and it is utilized to convert methanol to olefins (ethylene and propylene). The two catalysts (S-1 and S-2) are prepared with different compositions, and their physicochemical properties have been characterized by several analytical techniques: XRD, BET, TGA, SEM, EDX, and FT-IR. It is noted that high moles of morpholine in S-1 lead to higher crystallinity, larger crystallite size, and smaller total acidity than S-2. The experiments have been conducted to evaluate the performance of catalysts at Weight hourly space velocity (WHSV) of 10 h^{-1} and at 450 ^{o}C. It has been found that the selectivities of ethylene and propylene, and the methanol conversion, catalyst S-2 has been found better than S-1.

Mesoporous catalysts for co-processing of biomass and petroleum

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Keywords: deoxygenation, hydrodesulfurization, hydrocracking, catalysts, mesoporous supports

The increasing demand for motor fuel and the environmental problems associated with the emission of greenhouse gases into the atmosphere require to replace fossil fuels with alternative, environmentally friendly energy resources, which include biomass. The existing liquid fuels from biomass (including bio-oil and biodiesel) do not always have good miscibility with petroleum fuels and require additional modification to meet fuel standards. This modification consists in the removal of oxygen and isomerization of the resulting hydrocarbons in the presence of hydrogen (the so-called hydrotreatment). Typically, the same conditions and catalysts are used in the hydrotreatment of fuel from biomass as in the hydrotreatment of oil fractions (hydrodesulfurization, hydrocracking, hydroisomerization). Therefore, the integration of biofuel hydrotreatment processes in the existing technology of hydrotreatment of oil fractions is one of the promising directions for the production of liquid motor fuel.

Existing techniques for co-processing of petroleum raw materials and biofuels are typically carried out without the use of solvents in the flow-mode with high consumption of gaseous hydrogen. Petroleum hydrocarbons, in this case, play the role of solvents. However, the high viscosity of petroleum hydrocarbons requires the use of high temperatures. The low solubility of hydrogen in such mixtures leads to the need for high gas pressures for the processes. This affects the efficiency and economy of the co-processing processes. The use of supercritical solvent, which can be easily separated from the final product (or included in the product), allows the temperature of the process to be decreased, and molecular hydrogen to be replaced with atomic, formed from the solvent molecules in the supercritical state.

At the moment, there are a large number of studies on the co-processing of oil fractions and biomass. The main areas of research are hydrotreatment of vegetable oils and diesel oil fraction, hydrotreatment of bio-oil and gasoline fraction, and catalytic cracking of bio-oil and vacuum gas oil. Hydrotreatment processes are usually carried out in a flow mode at a temperature of 280-420 °C at high pressures (50–90 bar) with a high ratio of hydrogen: raw materials. As catalysts, almost all studies use sulfide or phosphide CoMo and NiMo catalysts deposited on Al_2O_3. Several works investigate the effectiveness of Pt - and Rh- catalysts deposited on aluminum oxide or activated carbon.

In this work, we describe the use of novel mesoporous catalysts for the co-processing of oil fractions and biomass derivatives (bio-oil and fatty acids) in the medium of supercritical solvents.

Acknowledgments
The work was financially supported by the Russian Science Foundation (grant 19-79-10061) and the Russian Foundation for Basic Research (grants 19-08-00318, 20-08-00080).

Effect of metal-acid sites location and proximity in shaped catalyst on their catalytic behaviour in *n*-hexane hydroisomerization

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Keywords: shaped catalyst, metal location, *n*-hexane hydroisomerization, deactivation

Metal-acid bifunctional catalysts are widely used in many industrially significant chemical process because of their hydro/dehydrogenation and acid functions. In the current work, the effect of the metal-acid sites location and proximity in the shaped catalysts on their catalytic behaviour was investigated in *n*-hexane hydroisomerization. This reaction involves three steps, namely dehydrogenation of alkanes, skeletal isomerization of olefins and hydrogenation of the latter. Hydrogenation and dehydrogenation occur on the metallic sites, whereas isomerization or cracking require acid sites, therefore diffusion of the olefinic intermediates from the metallic sites to acidic ones and back is important. Generally, hydroisomerization of straight chain paraffinic hydrocarbons C_5-C_6 is one of the cheapest ways to increase production of high-octane gasoline components [1-2].

Four different types of shaped catalysts with Pt controlled location and the same composition were prepared by extrusion of H-Beta-25 zeolite agglomerated with bentonite or Bindzil as inorganic binders (Fig. 1). Experiments were performed in a fixed bed reactor (ID 12 mm) in a continuous mode with 3 g (7.3 cm^3) of Pt extrudates at 200-360 °C and 1-17 bar of H_2.

The results revealed that the metal location and the catalyst scale-up process had a significant effect on the physical-chemical properties of the final catalysts and their catalytic activity, stability and selectivity as will be discussed in detail in the lecture.

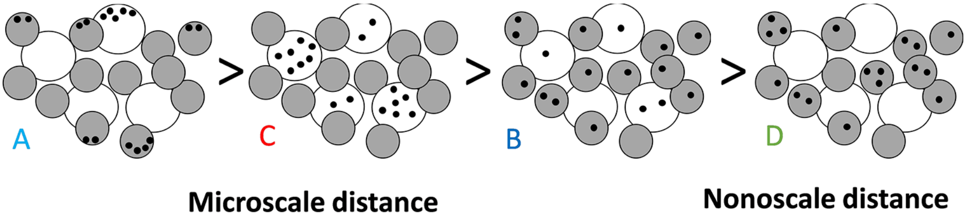

Fig. 1. Schematic picture of the catalysts employed in this study, showing Pt location and distance between the metal and acid sites. A: Pt/(H-Beta-25+binder), post synthesis; B: Pt/(H-Beta-25+binder), in-situ synthesis; C: (Pt/binder)+H-Beta-25; D: (Pt/H-Beta-25)+binder. Legend: H-Beta-25, zeolite (grey circle); bentonite or Bindzil-50/80, binder (white circle), Pt (black dots).

Acknowledgments

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T03: Nanoparticle catalysis

Synthesis and characterization of PdNi nanoparticles supported by carbon mixed transition metal oxides for applications in the electrochemical devices

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Keyword: catalysts, transfer phase, transition mixed oxides, cyclic voltammetry, electrochemical properties

PdNi 1:1 nanoparticles were synthesized through transfer phase method. The samples were then supported by carbon and carbon mixed with 30% transition mixed oxides (TMO). The prepared materials were analyzed by high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), and fourier transform infrared (FTIR) spectroscopy. The XRD data helped to conclude the alloy formation as no elemental species were present. The TEM images revealed the particle's size as of more than 4 nm. FTIR analyses surfaced the existence of transition in the oxides resonance regions. The preliminary electrochemical properties of the materials were examined by cyclic voltammetry (CV). The oxygen reduction reaction (ORR) voltammograms were obtained through the rotating ring disk electrode (RRDE) procedure. The electrocatalytic properties of carbon supported PdNi (1:1) were studied both in acidic and alkaline media. The carbon supported PdNi mixed with 30% WO_3 shows higher ORR specific and mass activities in both media especially in alkaline medium. PdNi 1:1 materials supported by carbon mixed with 30 % TMO also enhanced the stability properties.

Effect of Ag, Ca, and Fe on photocatalytic activity of ZnO nanoparticles to remove textile dyes under sunlight irradiation

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Keywords: photocatalyst, nanoparticles, doped ZnO, alkaline earth metals, transition metals, Industrial textile dye, photo degradation

The study provides the physical and chemical properties of the synthesized photocatalysts, and the doping ion influence on the photocatalytic reactions degradation of two textile dyes (direct dye DY86, and reactive dye RBY) under sun irradiation. The results show that the properties of doped ZnO were strongly influenced by the nature of dopant. This study shows that the photocatalytic activity of zinc oxide was improved by the doped treatment, the order for the catalyst photocatalytic activities is: ZnO/Fe>ZnO/Ag>ZnO/Ca>ZnO. ZnO doped with transition metal, revealed the highest photodegradation efficiency compared to alkaline earth metals. The dye's removal efficiency by nanoparticles of ZnO doped with Fe, Ag, and Ca is about 95%, 85%, and 81% respectively.

The use of polymeric Pd-containing catalysts for selective hydrogenation of phenylacetylene to styrene

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Keywords: phenylacetylene, styrene, hydrogenation, palladium, hyper-cross-linked polystyrene

Olefin polymerization is one of the most important processes in the modern petrochemical industry as it allows producing polyethylene and polystyrene, which are widely used in the production of plastics. Styrene is an important monomer for the production of polystyrene and other synthetic resins, such as acrylonitrile-butadiene-styrene resin. Currently, styrene is produced in industry by dehydrogenation of ethylbenzene. However, during this process phenylacetylene is formed as a side-product. Phenylacetylene must be removed from the resulting raw material since it poisons the polymerization catalysts, even in low concentrations. Separation of phenylacetylene from the feedstock is not economically feasible. Thus the development of methods for selective catalytic hydrogenation of phenylacetylene to styrene is highly demanded. It is noteworthy that among noble metals, palladium provides highly selective hydrogenation due to its higher adsorption affinity for triple bonds.

In this work, hydrogenation of phenylacetylene to styrene was studied in a batch mode at ambient hydrogen pressure in the presence of palladium-containing catalyst based on hyper-cross-linked polystyrene (HPS) bearing tertiary amino-groups (resin of MN100 type). The catalyst (1%-Pd/HPS) was synthesized by impregnation of the polymer MN100 with Pd acetate dissolved in tetrahydrofuran. Resulting sample 1%-Pd/HPS was used in hydrogenation reaction in both the initial (unreduced) and preliminarily activated in hydrogen flow at 300°C for 3 h forms. The catalyst 1%-Pd/HPS was also modified with aqueous solutions of alkali metal compounds (Na_2CO_3 and K_2CO_3, concentration of 0.0175 mol/L). During the hydrogenation process, the following parameters were varied: solvent nature (toluene, ethanol, 2-propanol), reaction temperature (90°C, 70°C, 65°C), catalyst loading (substrate-to-catalyst molar ratio was 5106 mol(phenylacetylene)/mol(Pd) or 10214 mol(phenylacetylene)/mol(Pd)).

As a result of the study, the following optimal conditions for hydrogenation of phenylacetylene were found: temperature of 90°C, solvent – toluene. Moreover, the use of unreduced catalyst at the substrate-to-catalyst molar ratio of 5106 mol/mol was preferable.

Modification of the catalyst 1%-Pd/HPS with alkali metal compounds was shown to have crutial effect on the selectivity with respect to styrene. In the presence of unreduced 1%-Pd/HPS selectivity reached 97.7% at 95% of phenylacetylene conversion, while modification of the catalyst with Na_2CO_3 and K_2CO_3 allowed increasing the selectivity up to 99.5% and 98.5%, respectively.

Acknowledgments
This work was supported by the Russian Science Foundation (project 20-19-00386).

T04: Combustion kinetics and catalysis

Determining the kinetic factors of combustion reactions, using the Reaction-Class Transition State Theory

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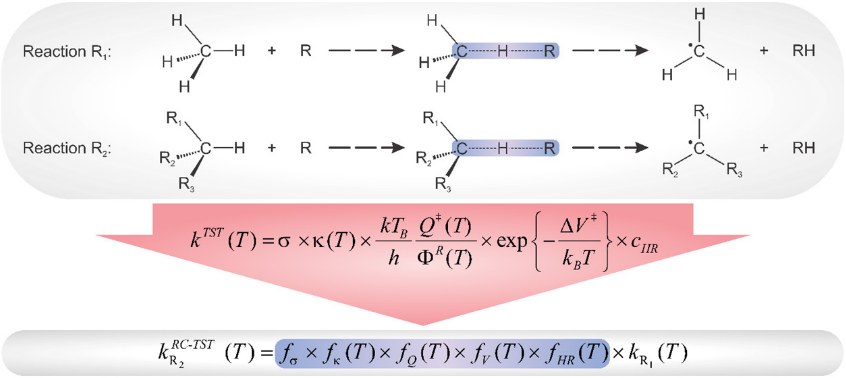
Keywords: combustion, kinetics, Reaction-Class Transition State Theory, RC-TST

An essential component for modeling complex reactions is the mechanism or kinetic model. The kinetic mechanism/model consists of all important reactions involving chemical species existing in the system with associated thermodynamic and kinetic parameters. The number of elementary reactions in such models may reach as much as tens of thousands. To meet this challenge, an automated method capable of generating reliable thermal rates of elementary steps is needed. A strict theoretical framework, relaying on an extrapolation of accurate rate constants of a chosen (reference) reaction to the whole family, is provided by the Reaction Class Transition State Theory (RC-TST).

The RC-TST method is taking advantage of the common structure denominator of all reactions in a given family to obtain rate expression of any reaction within a given class in a simple and cost-effective manner. All the necessary parameters are derived from Density Functional Theory calculations. The rate constants of the reference reaction are calculated at a high-level of theory or taken from experiment. The RC-TST method takes into account the quantum tunneling effect as well as the explicit treatment of anharmonicity of low-frequency inernal rotors. The results show that the RC-TST method utilizing either Linear Energy Relationship (LER), where only reaction energy is needed or Barrier Height Grouping (BHG), where no additional data is needed can predict the thermal rate constants with decent accuracy.

Figure



$$k^{TST}(T) = \sigma \times \kappa(T) \times \frac{kT_B}{h} \frac{Q^{\ddagger}(T)}{\Phi^R(T)} \times \exp\left\{-\frac{\Delta V^{\ddagger}}{k_B T}\right\} \times c_{IIR}$$

$$k_{R_2}^{RC\text{-}TST}(T) = f_\sigma \times f_\kappa(T) \times f_Q(T) \times f_V(T) \times f_{HR}(T) \times k_{R_1}(T)$$

The scheme of RC-TST method application. The rate constant $k_{RC\text{-}TST}$ is the product of factors, that represent the variable parameters within the classical Transition State Theory rate constant expression k_{TST}.

Kinetics of flax processing waste pyrolysis

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Keywords: kinetic, thermogravimetric analysis, flax waste, energy activation

Using of traditional fossil fuels results to restriction of its stocks and emission of carbon dioxide in the atmosphere. The plant biomasshasn't this disadvantage because it is «CO_2 neutral fuel», renewable and widespread raw material. The amount of crop waste in the Russian Federation that can be freely used without damage for agricultural purposes exceeds 50 million tons of fuel equivalent per year.

Flax production in the Russian Federation is about 80.000 tons/year. Flax shive is a waste of flax processing, the output of which exceeds 70%. This renewable resource can be used in the process of generating energy and energy carriers. The complex technology of biomass plant waste processing is more effective because apply to get higher level using of initial feedstocks energy. At the first stage the hydrolysis stage is spent with produce following products: furfural, vanillin, fuel additives and fuel components. The second stage is pyrolysis which is spent with producing: fuel gases, fuel additives and fuel components and carbon sorbents and fillers.

The article presents the results of studying the kinetics of the pyrolysis process. The results of investigation were obtained by thermogravimetric analysis of flax processing waste and their cellulose residues obtained by ethanolysis in a water-ethanol mixture (ethanol/water ratio 60/40) at a temperature of 185°C for 3 hours.

The samples of flax shive and it cellulose residue were used for investigation with using of thermogravimetricallyanalyzer NETZSCH Iris TG 201 F in temperature range at 30 by 1000□ in argon. The mass of selected samples were about 10 mg and the size distribution of samples particle was in interval 0.25-0.45mm. The kinetic study was performed using the NETZSCH Thermokinetik 4.1 software. The data on the activation energy of the pyrolysis process of the studied samples obtained using the model of independent methods showed values of 180 and 200 kJ / mol for the flax shive sample and its cellulose-containing residue, respectively.

The content of the main components of plant biomass was also determined thermogravimetrically using the NETZSCH program "Peak Separation" (version 2010.09). For this purpose, the main stages of thermal destruction of agricultural waste of plant origin were determined using standard substances - cellulose, hemicellulose and lignin and taking into account the content of moisture, ash and extractive substances. According to the data obtained, after ethanolysis of flax shive, the lignin content decreased from 29.6% to 15.4% (wt.). The content of hemicellulose and cellulose increased from 15.1 to 23.1% (wt.) and from 39.5 to 54.8% (wt.), respectively.

The rate of formation of volatiles in the case of the cellulose residue of the flax shive exceeded the maximum destruction rate of the flax shive by 1.75 times, which is associated with an increase in the concentration of cellulose in its composition.

In the course of thermogravimetric study of the samples, a mass spectrometric study of volatile products of thermal destruction in the mass range of 1-300 amu in the declared temperature range of 50-1000°C was also carried out. The analysis was carried out using an Aelos CSM 403 P mass spectrometric attachment to a NETZSCH TG IRIS thermal analyzer. According to the data obtained, the sample of the cellulose residue from the flax shive is distinguished by a narrower thermal region of the formation of volatile products in comparison with the flax shive, which is probably due to an increase in the proportion of cellulose in its composition.

Acknowledgments

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T05: Exploring reaction mechanisms

The kinetics of zeolitic imidazolate framework (ZIF-8) formation and synthesis in confined flow reactor

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Keywords: crystal growth, induction period, kinetics, metal-organic frameworks, synthesis

Metal organic frameworks (MOFs) are described as materials possessing extremely porous structure and thus huge specific surface. Due to these advantageous properties they are used in various fields of chemical technology, e.g., as catalysts or adsorbents [1, 2]. The fact that, the morphology of the forming crystals is depending on the applied synthesis method is widely known in the literature [3]. In this context, developing novel and carefully designed synthetic pathways gives us the opportunity of creating improved crystal structures.

As a model MOF system, the exploration of the kinetics of zinc(II)-ion and 2-methylimidazole precipitation reaction has crucial importance in understanding the crystal growth process. The nucleation and growth of such ZIF-8 crystals were examined by high-speed camera and UV-vis spectroscopy on short and longer time scales, respectively. In order to investigate the kinetic parameters of the system, the stochiometric ratio and reactant concentrations were systematically changed. We observed that, in the very short initial phase of the reaction (few seconds) a colloidal intermediate is formed. The recrystallization of this intermediate takes place on a longer time scale (hours) and further increases the turbidity in a second step. By applying 2-methylimidazole in stochiometric excess the recrystallization can be accelerated. The synthesis of ZIF-8 crystals was also carried out in confined Plexiglass flow reactor to shed light on what microstructure enhancement can be achieved by applying spatial gradients. We observed the macroscopic precipitate pattern formation with changing experimental parameters like volumetric flow rate, reactant concentration, and stochiometric ratio. Finally the microstructre of crystals, which were produced by the two separate synthetic techniques (well stirred and flow-driven) was examined by scanning electron microscopy and powder X-ray diffraction.

Acknowledgments

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Solving inverse problems of chemical kinetics by metaheuristic methods

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Keywords: mathematical modeling, inverse problem of chemical kinetics, gravitational search algorithm, harmony search, catalytic processes

Currently metaheuristic methods are successfully used to solve many problems of engineering optimization, such as multi-robot path planning, un-manned aerial vehicles navigation, the opinion leader detection in online social network, the identification of influential users in social network; the deployment of unmanned aerial vehicles, the data collection system of Internet of Things, the localization in wireless sensor network localization. In this article, we will consider the application of a metaheuristic algorithm, namely, the gravitational search algorithm, harmony search and particle swarm optimization methods to solve the inverse problem of chemical kinetics in application to heterogeneous catalysis. It is shown that metaheuristic algorithms have become more and more popular recently. In this regard, it is logical to apply these algorithms to various optimization problems. The optimization problem is formulated on the example of solving the inverse problem of chemical kinetics. The processes under study are the pre-reformation of propane into a methane-rich gas on a Ni-catalyst [1], process of mass and heat transfer in the reactor for the synthesis of methyl tert-butyl ether and the H_2SO_4-catalyzed alkylation of isobutane with olefins, which are an industrially important chemical processes.

We consider models that take into account changes in temperature and concentration profiles: ordinary differential equations, as well as second-order partial differential equations:

$$\varepsilon \frac{\partial C_i}{\partial t} + w \frac{\partial C_i}{\partial z} - D_{EZ} \frac{\partial^2 C_i}{\partial z^2} = -\sum_{j=1}^{N} \nu_{ji} \dot{\xi} v_j \left(C_i , T \right) \tag{1}$$

$$\overline{C_p \rho} \frac{\partial T}{\partial t} + w \sum_{i=1}^{N_I} C_i C_{pi} \frac{\partial T}{\partial z} - \lambda_{EZ} \frac{\partial^2 T}{\partial z^2} = \sum_{j=1}^{N_R} -\Delta_R H_j \dot{\xi} v_j \left(C_i , T \right) - \frac{4U_W}{d_R} \left(T - T_C \right) \tag{2}$$

Using these algorithms, the inverse problems of chemical kinetics were solved and the optimal values of the kinetic parameters of the reactions were found. It was proved that the models correctly described the available experimental data.

Acknowledgments

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Lyapunov stability of ring-like compartmental models

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Keywords: reaction kinetics, compartmental models, stability

It is known that kinetic systems defined by (abstract) complexes, reactions and reaction rate functions can be considered as universal descriptors of nonlinear dynamics in the sense that they can describe essentially any type of complex dynamical behaviour [1]. Therefore, a wide range of non-chemical processes in nature or technology can be formally modelled using kinetic systems. The main motivation for a kinetic representation is the availability of strong theoretical results on the relation between reaction network structure and fundamental dynamical properties in the theory of chemical reaction networks (CRNs) [2]. Compartmental models are used to study the flow of material, population, particles, vehicles, etc. between interconnected subsystems, and they can be easily represented in kinetic form [3]. In this contribution, we consider ring-like compartmental structures, where the compartments have known finite capacities, and the flow between them is driven by the concentration of material in the source compartment and the amount of available free space in the target compartment. Similar models with possibly different (e.g. pipe-like) topology can be used to model biochemical processes such as ribosome operation or even traffic flows [4]. It is important to note that the kinetic representation (i. e., the reaction graph) of the studied ring-like compartmental structure is not weakly reversible. But still, we start from the classical entropy-like logarithmic Lyapunov function known from the stability of weakly reversible deficiency zero CRNs. As a new result we show that for every ring-like compartmental model, with arbitrary finite capacities and arbitrary positive reaction rates for each transition, there exists a generalized logarithmic Lyapunov function which is suitable to prove stability.

Acknowledgments

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Multicriteria optimization of the catalytic reaction for the synthesis of benzyl butyl ether based on the kinetic model

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Keywords: reaction of benzyl butyl ether synthesis, kinetic model, multicriteria optimization

The work investigates the catalytic reaction of the benzyl butyl ether catalytic synthesis reaction by methods of mathematical modeling, based on experimental data [1]. A kinetic model of the process was developed according to a detailed scheme of chemical transformations [2]. Intermolecular dehydration of benzyl alcohol and n-butyl alcohol proceeds in three directions and leads to the formation of benzyl butyl, dibenzyl and dibutyl ethers. Benzyl butyl ether can be obtained from attacking n-butanol with benzyl cation that is generated from benzyl alcohol in reaction with $CuBr_2$ — $[PhCH_2]^+[CuBr_2(OH)]^-$ (E_1=5.37 kcal/mol) (fig. 1). At the same time, as a result of complex reaction of $[PhCH_2]^+[CuBr_2(OH)]^-$ with benzyl alcohol via an intermediate complex $[PhCH_2OHCH_2Ph]^+[CuBr_2(OH)]^-$ (E_4=14.00 kcal/mol) forms an accessory dibenzyl ether. The breakdown of the latter releases dibenzyl ether and water and completes the catalytic circuit (E_5=21.69 kcal/mol). The problem of multicriteria optimization is formulated based on the kinetic model. Variable parameters are temperature, molar ratio of starting reagents and reaction time. Optimality criteria are maximizing the yield of the target benzyl butyl ether and minimizing the yield of by-products. The solution of the multicriteria optimization problem was carried out by the NSGA-II Pareto-approximation algorithm. The results showed that an increase in the content of dibenzyl ether allows an increase in the yield of the target benzyl butyl ether. When the maximum permissible values of the molar ratio of the reactants, by-dibutyl ether increases yield while increasing the target output benzyl butyl.

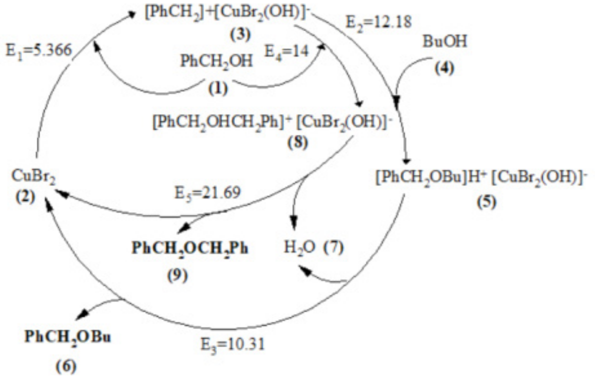

Fig. 1. Kinetic model of benzyl butyl ether catalytic synthesis – formation of benzyl butyl ether by benzyl cation

Acknowledgments

This research was performed due to the Russian Science Foundation grant (project No. 19-71-00006).

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Hydroisomerization of hexane over Pt-modified Beta-Bentonite extrudates shaped catalysts: synthesis, catalysis, reaction mechanism

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Keywords: extrudates, shaped catalysts, zeolite, hydroisomerization

Fundamental studies regarding the synthesis, physico-chemical characterization, reaction mechanism, catalysis and application of shaped extrudated catalysts have attracted attention of researchers working in academia and industry. Taking into consideration the depletion of fossil fuel resources, demand for the high quality environmental friendly fuel components, new stringent legislations regarding the exhaust emission control due to air pollution in big cities, these fundamental research studies in shaped extrudates catalysts will lead to synthesis of more efficient, cost effective catalysts.

In this research work we have focused on fundamental research regarding the synthesis, mechanism of shaping catalysts and physico-chemical properties of shaped extrudates using Bentonite aluminosilicate type of binder and powder H-Beta zeolite. Furthermore, these shaped extrudate catalysts were modified with Pt using different methods of modifications such as *in-situ* and post synthesis modifications. In-depth physico-chemical characterization of pristine and Pt-modified Beta-Bentonite extrudate catalysts were carried out using X-ray powder diffraction for structure and phase purity, scanning electron microscopy for morphological studies, metal contents were measured using energy dispersive X-ray micro analyses, Pt particle size, porosity and periodicity of pores were determined using transmission electron microscopy, surface area and pore volume was measured using nitrogen physisorption, Brønsted and Lewis acid sites were measured using FTIR-Pyridine, X-ray photo electron spectroscopy was used to measure the states of Pt in extrudate catalysts. The evaluation of the catalytic properties of pristine Beta-Bentonite extrudates and Pt-modified Beta-Bentonite was carried out in hydroisomerization of hexane using a fixed-bed reactor. It was observed that conversion of hexane and selectivity to branched chain isomers was higher for Pt-modified Beta-Bentonite than the pristine Beta-Bentonite extrudates. Detailed kinetic studies were performed with Pt-modified Beta-Bentonite extrudates synthesized using different methods of Pt introductions. Reaction mechanism of the hexane isomerization was proposed based on the product distributions of branched isomers, linear isomers and hexane conversion. Partial catalyst deactivation was observed during the hexane hydroisomerization which was attributed to the coke formation during the reaction. Detail correlations of catalytic activities, product distributions, types of products and conversion of hexane with catalyst characterization data will be performed during the presentation in the conference.

Investigation of the dynamical properties of the mechanism regulating the formation of reactive oxygen species in rhizosphere

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Numerous chemical and biochemical systems are known for their ability to self-organize under non-equilibrium thermodynamic conditions and produce diverse dynamics such as: bistability, oscillations, chaos etc. These dynamical states are especially important for normal functioning of biological systems where ability to exhibit various dynamics is essential for controlling biological processes. One example is the regulation of the formation of reactive oxygen species (ROS). They are formed as byproducts of various biochemical reactions which involve O_2, and they are involved in the processes which create energy vital for normal functioning of plants and other aerobic organisms. When ROS are present in low concentrations they have the role of signaling molecules but their high concentration can cause irreparable damage. Understanding mechanisms which regulate concentrations of ROS is of great importance.

Therefore, in this work detailed investigation of the mechanisms governing the dynamics of ROS formation in the rhizosphere, proposed by Taran et al[1] , was carried out with aim to determine its dynamical properties.

Acknowledgments

The financial support of the National Research, Development and Innovation Office (K119795) and GINOP-2.3.2-15-2016-00013 projects and by Ministry of Education, Sciences and Technology of Republic of Serbia (grant no. 172015 and contract number 451-03-9/2021-14/200146)

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Exploring the reaction mechanism of the direct synthesis of hydrogen peroxide with transient studies and FTIR-ATR

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Keywords: hydrogen peroxide, transient studies, FTIR-ATR

Hydrogen peroxide is frequently used as a green oxidizing agent because it is only producing water while applied as an oxidizing agent. However, it is currently mainly synthesized through the indirect multistep anthraquinone process in which large amounts of toxic organic waste are produced[1]. An alternative to the anthraquinone route is the direct synthesis from hydrogen and oxygen that has been successfully performed on lab scale[2]. Studies on solvent effects have shown that performing the reaction in organic protic solvents lead to higher yields than in water. Especially good is the performance in alcohols. Despite a seemingly purely inorganic reactions pathway of an Oxygen Reduction Reaction, further experiments demonstrated different dependencies in relation to hydrogen partial pressure in water and organic solvents which indicates the involvement of the organic solvent in the direct synthesis[3]. The role of the solvent and the mechanism was studied here with different transient methods and alcohols as model compounds. In addition, the reaction was performed in an FTIR-ATR system to study the reaction in-situ.

Three main observations were found from the gas and solvent step experiments. First it was observed that when switching from water to alcohol the system began to oscillate with declining amplitude regarding to hydrogen peroxide until reaching a steady state. During this period, the corresponding carbonyl of the alcohol was measured with a phase delay. In the FTIR-ATR experiments a similar oscillation was found after a switch from water to methanol took place. These oscillation could be attributed to a chain of reactions implying a hydrogen transfer from methanol to oxygen.

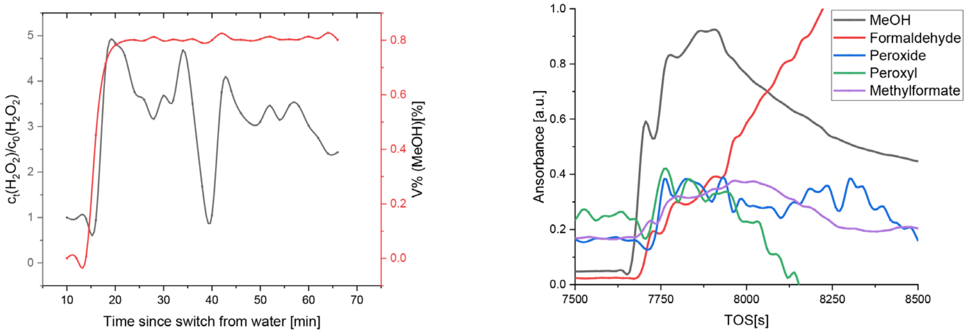

Figure 1. (left) Oscillation pattern after the switch to MeOH (right) development of hydrogen peroxide concentration after the switch H_2 to O_2 in MeOH.

Acknowledgments

This work is part of the activities financed by Academy of Finland, the Academy Professor grants 319002 (T. Salmi) and 320115 (Ole Reinsdorf). The economic support from Academy of Finland is gratefully acknowledged.

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Kinetics and mechanism of action of triterpenoids

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Keywords: inverse problems of chemical kinetics, optimization, harmony search algorithm

Triterpenoids have different types of biological activity. Interest in the pharmacological properties of lupan derivatives is caused by the discovery of antitumor and antiviral substances in this group. The antioxidant properties of biologically active substances are considered to be one of the most important characteristics of therapeutic activity [1]. In this regard, the kinetic regularities and mechanism of action as inhibitors of radical chain oxidation of organic compounds of two representatives of triterpenoids of the lupan series, which have polyfunctional fragments, are investigated in this work. The reaction proceeds through a number of stages, in which intermediate substances (radicals) and labile molecular products-participate. The concentration and lifetime of these substances are such that an experimental study of them is either extremely difficult or impossible. It is necessary to know not only the stages themselves that make up the reaction mechanism, but also the behavior of the intermediates over time. This information, together with the rate constants that characterize each stage quantitatively, makes up the mechanism of a complex reaction of organic matter oxidation in the presence of an inhibitor. An effective method for solving inverse problems of chemical kinetics using the conditional global optimization method is developed. The metaheuristic harmonic algorithm is used. A software package in the Python language was created, with the help of which mathematical modeling was carried out based on this algorithm. The result of this approach is to obtain a complete kinetic picture of the reaction, including a set of stages of the mechanism of this complex reaction, the kinetics of changes in the concentrations of the reaction participants, including labile intermediates, and the values of the rate constants of the stages. The calculation of the values of the concentrations of the observed substances was carried out by solving a direct kinetic problem based on an isothermal non-stationary model without changing the volume in a closed system based on the law of active masses. To solve the direct problem, the Radau2A method of the fifth order of accuracy is chosen. During mathematical modeling, the concentration of the observed substances in mol/l and the time in hours were set. The developed complex is used to develop the mechanism of the antioxidant action of aromatic amines, a number of uracil derivatives, fullerene C60, selenochromens, as well as to establish the mechanism of the molecular reaction of furan synthesis. The experimental results obtained can serve as a basis for the analysis of the reaction mechanism of the canonical scheme of radical chain oxidation of organic compounds in the presence of inhibitors. Using the method of mathematical modeling on the basis of experimental data, the mechanism of their antioxidant action is established and the rate constants of the stages included in it are determined.

Acknowledgments

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Catalytic chain termination by inhibitors in oxidation of unsaturated compounds in the liquid phase and microheterogeneous systems

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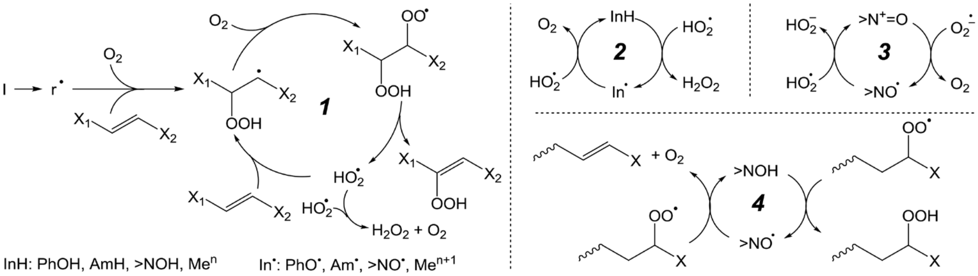
Keywords: antioxidant, catalytic chain termination, hydroperoxide radical, nitroxide radicals

A number of fundamentally new mechanisms of oxidation of unsaturated compounds in the liquid phase and in micelles in the presence of inhibitors (InH) of different classes have been discovered. In these cases the stoichiometry of chain termination becomes a variable value that depends not only on the type of antioxidant and the properties of the radical propagating the oxidation chain, but also on the properties of the medium. In liquid-phase oxidation $X_1CH{=}CHX_2$ (X_1, X_2 = –H, –R, –COOR, $–C_6H_5$, $–CH{=}CHX_2$), the chains are propagated by hydroperoxyl radicals $HO_2^{\bullet}$ (Scheme 1). In this case, phenols (PhOH), aromatic amines (AmH), nitroxyl radicals ($>NO^{\bullet}$) and transition metal compounds (Me^n) catalytically terminate the oxidation chain according to cycle 2 [1, 2]. The effective rate constant for the interaction of $>NO^{\bullet}$ with $HO_2^{\bullet}$ significantly depends on the polarity of the medium, which is explained by the specific solvation of the hydroperoxide radical. In a non-polar medium, the $>NO^{\bullet}$ reactivity is determined by the strength of the >NO–H bond formed [2]. During the oxidation of methyl linoleate in micelles $>NO^{\bullet}$ effectively dismute $HO_2^{\bullet}$ through cycles 2 (inside the micelle) and 3 (in an aqueous medium) [3]. In the liquid-phase oxidation of styrene and acrylates, multiple chain termination occurs by reactions of polyperoxide and nitroxyl radicals through cycle 4 [4]. The report presents a kinetic and quantum-chemical analysis of the detailed mechanism of the processes under consideration.

Scheme 1



Mechanisms of catalytic chain termination in oxidation of unsaturated compounds

Acknowledgments

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High-speed tracking of fast chemical precipitations

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Keywords: precipitation, induction period, fast kinetics, hydrodynamics

Heterogeneous reactions taking place in aqueous phase bear with significant importance both in applied and fundamental research. Among others, producing solid catalysts, crystallizing biomorphs or pharmaceutically relevant polymorphs, and yielding bottom-up made precipitate structures are prominent examples. To achieve a better control on product properties, reaction kinetics and mechanisms must be taken into account especially in dynamic systems where transport processes are coupled to chemistry. Since characteristic time scale of numerous precipitation reactions falls below 1 s within relevant concentration range, unique experimental protocols are needed. Inhere we present a high-speed camera supported experimental procedure capable to determine such characteristic time scales in the range of 10 ms to 1 s. The method is validated both experimentally and by performing 3D hydrodynamic simulations.

Acknowledgements

This work was supported by the National Research, Development and Innovation Office (K119795 and PD121010) and GINOP-2.3.2-15-2016-00013 and M-ERA.net MaSNEC projects.

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T06: Homogeneous and heterogeneous photocatalysis

Investigation of the efficiency of BiOI/BiOCl composite photocatalysts using UV, cool and warm white LED light sources – photon efficiency, toxicity, reusability, matrix effect, and energy consumption

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Keywords: BiOCl, BiOI, LED, heterogeneous photocatalysis, charge transfer, antibiotic

Semiconductor photocatalysis driven by visible light has become the world hot topic of intensive interest due to its potential applications in environmental purification and solar energy conversion. In the recent past, bismuth oxyhalides (BiOX, X=Cl, Br, I) have been widely used for the photocatalytic degradation of organic pollutants and other environmental remediation. Because of their advantageous properties, bismuth oxyhalides serve as potential alternatives for TiO_2, the most often used photocatalyst. The unique characteristic layered structure of BiOXs tends to inhibit the recombination of photogenerated electron-hole pairs and allow them to tune their light response from visible to UV light range. Benefitting from the unique properties, BiOXs have shown promising photocatalytic applications for the degradation of organic pollutants.

BiOCl, BiOI, and BiOI/BiOCl composite photocatalysts were prepared using solvothermal crystallization method and characterized by X-ray diffraction (XRD), the Brunauer-Emmett-Teller (BET) specific surface area, X-ray photoelectron spectroscopy (XPS), and the UV-Vis diffuse reflectance spectra (DRS).

Transformation of the methyl orange dye and sulphamethoxypyridazine antibiotic weres used to determine the photocatalytic activity of BiOI, BiOCl, and their composites. BiOI/BiOCl composite photocatalysts showed enhanced adsorption capacity and activity in decolorization and transformation of methyl orange and sulphamethoxypyridazine comparing to the BiOI and BiOCl. The composite having the highest activity contained 80% BiOI and 20% BiOCl.

The photocatalysts' efficiency and apparent quantum efficiency for transforming the target substances were determined under radiation with various LED light sources: UV (398 nm), cold white light, and warm white light. The apparent quantum yield for visible light was just slightly lower than for 398 nm UV radiation.

The relative contribution of radical-based reactions and direct charge transfer were investigated via the effect of dissolved oxygen, methanol, and 1,4-benzoquinone. Results of competing reactions proved that the main pathway for the transformation in both cases the direct charge transfer, which results in the demethylation of methyl orange, and a sulfur dioxide extrusion of sulphamethoxypyridazine.

The reusability of the composite photocatalyst was investigated during 3 cycles. The transformation rate slightly decreased, and the accumulation of toxic intermediates was observed. There was no significant change in the photocatalyst structure; the decrease of efficiency is mainly due to the adsorption and accumulation of hardly degradable intermediates on the surface.

Acknowledgments

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Methanol photocatalytic reforming reaction over alkali-doped graphitic carbon nitride

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Keywords: Pd co-catalyst, Li dopant, Na dopant, H_2 production, visible light

Photocatalytic hydrogen production is regarded as a promising approach for transforming solar energy into chemical energy. Many efforts have been made for photo-induced reforming of alcohols (involving methanol with the highest H/C ratio) in the presence of water providing H_2 and CO_2 (1).

$$CH_3OH + H_2O \xrightleftharpoons{\text{Photocatalyst, h}\nu} CO_2 + 3\,H_2 \tag{1}$$

Graphitic carbon nitride (g-C_3N_4) has a medium band gap (~ 2.7 eV) and possesses good thermal and chemical stability thus it emerges as one of the most promising photocatalytic materials[1]. Although its properties can be significantly tuned by doping[2], incorporation of alkali metals ions into the structure of g-C_3N_4 has been reported only in a few works. The aim of this work was to study the effect of Li and Na doping of g-C_3N_4 on the photocatalytic H_2 production in reaction (1). As the overvoltage of H_2 evolution and the recombination rate of electron-hole pairs can be lowered by depositing a metal co-catalyst onto the semiconductor, Pd/undoped- or doped g-C_3N_4 catalysts were prepared. Doped g-C_3N_4 was obtained by annealing of a mixture of cyanamide and the appropriate metal chloride at 550 °C for 3 h under Ar atmosphere. Pd co-catalyst was loaded from $PdCl_2$ by ascorbic acid reduction. Samples were characterized by UV-visible spectroscopy, XRD, TEM and XPS techniques. Photocatalytic hydrogen production rate was measured by using either a medium pressure Hg lamp (Osram HQL de luxe, 125W, $\lambda \geq 365$ nm) or a homemade LED light source providing four distinct wavelengths (400, 420, 440, 450 nm).

In the absence of Pd co-catalyst the rate of H_2 formation was under our detection limit. In accordance with our UV-visible spectroscopic results (Figure 1A) the Na dopant increased while the Li dopant decreased significantly the H_2 production rate under UV-visible irradiation (Figure 1B). The differences became even more apparent in the range of visible light (Figure 1C).

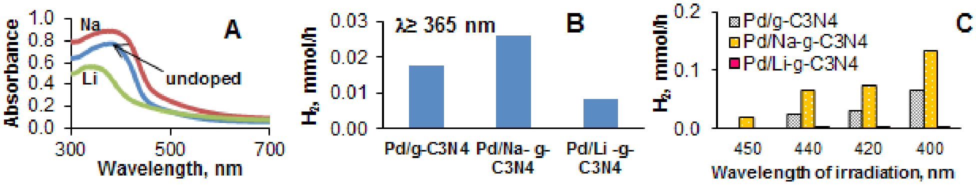

Figure 1. Comparison of doped and undoped g-C_3N_4 samples. A: UV-visible adsorption; B-C: Rate of H_2 formation

Acknowledgments

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T07: Hydrogen production and use

Mechanism and kinetics of platinum nanocatalyst degradation during the oxygen evolution reaction through *in situ* Transmission Electron Microscopy

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Keywords: *in situ*, electrocatalysis, water splitting, oxygen evolution, nanoscale

Molecular hydrogen is a pivotal compound for replacing fossil fuels as a global source of energy for transportation and energy storage. The most competitive way to produce hydrogen is through electrochemical water splitting, which is generally catalyzed by platinum nanocatalysts due to their high intrinsic activity. However, the productivity of this process decreases rapidly due to catalyst degradation. The overall process of water splitting is limited by the rate of the oxygen evolution reaction (OER) at the anode. For that reason, platinum catalysts at the anode are continuously subjected to electrochemical stress, which culminates with costly catalyst degradation. In this project we used *in situ* liquid-phase transmission electron microscopy (TEM) to evaluate what variables are responsible for the chemical and morphological changes of platinum nanocatalysts during the oxygen evolution reaction.

Our in situ TEM results showed that the observed catalyst degradation is a two-step process involving catalyst sintering followed by its dissolution into the electrolyte solution. Catalyst degradation is faster in polycrystalline platinum samples **(Figure 1)** and correlates with smaller grain size **(Figure 2)**, which suggests a central role of grain boundaries in the degradation process. Pulsed electrochemical stress induces different degradation kinetics compared to a continuous electrochemical stress, and the degradation kinetics depend on the pulse time and ON/OFF electrochemical potentials. We hypothesize that these results are explained by a recovery of the catalyst surface chemical properties during the resting (OFF) intervals thus avoiding the accumulation of electrochemical stress, while maintaining a high catalytic activity during the ON electrochemical pulses. Taken together our results suggest that the degradation of platinum during oxygen evolution conditions is mediated by mobile PtO_x species and when the accumulation of those species is prevented platinum degradation is inhibited. This new nanoscale understanding of platinum nanocatalysts during the oxygen evolution reaction opens the opportunity to produce hydrogen from water much more efficiently and enable many energy applications, such as storage of large energy quantities, and hydrogen fuel cells for production of electricity and power generation for transportation vehicles.

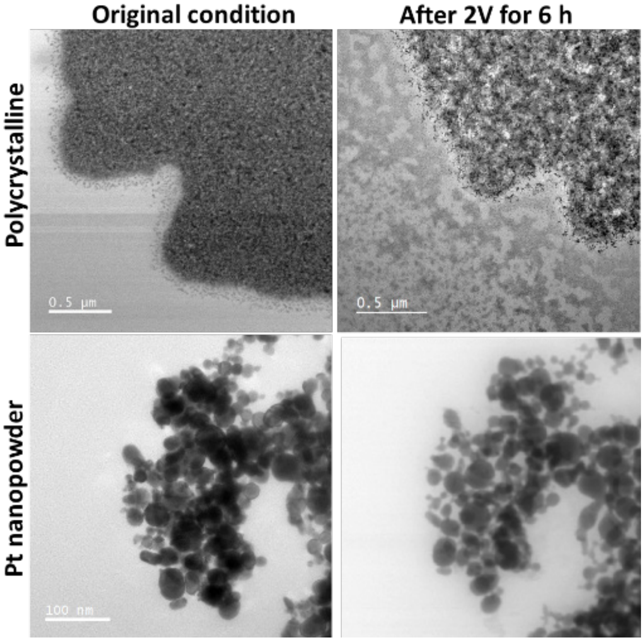

Figure 1. Degradation kinetics of polycrystalline Pt *vs.* Pt nanopowder

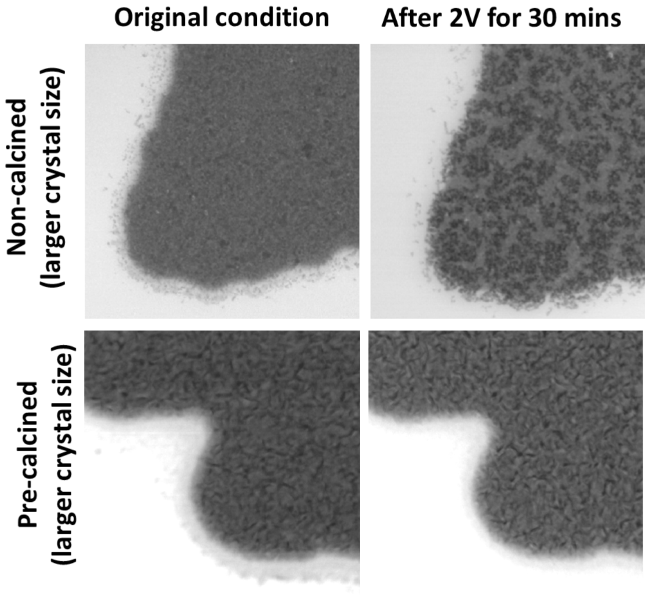

Figure 2. Effect of crystallite size on the Pt degradation kinetics during the OER

T08: Catalysis for biomass utilization

Comparison of hydrodeoxygenation of isoeugenol for production of jet fuels in batch and continuous reactors using Co- and Pt-catalysts

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Keywords: hydrodeoxygenation, batch reactor, trickle bed reactor, Co-catalyst, Pt-catalyst

Hydrodeoxygenation (HDO) of lignin derived model compounds has been intensively investigated. There is, however, a lack of information on continuous operation relevant for potential industrial implementation. In this work several mono- and bimetallic Co- and Pt-catalysts were tested in HDO of isoeugenol (Fig. 1a) both in batch and continuous reactors aiming at elucidation of especially mass transfer limitations, the effectiveness factor and catalyst deactivation.

Isoeugenol HDO was performed between 200–300 °C in dodecane and 1-decanol as solvents under 20 -30 bar hydrogen in the presence of different Co- and Pt-supported catalysts. Several powder and extrudate catalysts were prepared by impregnation. The catalysts were characterized by pyridine adsorption desorption, nitrogen adsorption and transmission electron microscopy. The initial concentration of isoeugenol was 0.013 mol/l and the catalyst mass was varied from 50 to 1000 mg. The liquid samples after certain time intervals were analyzed by a gas chromatograph. Comparative HDO studies were performed using both powder and extrudate catalysts.

10 wt% Co/SiO_2 pellets (Riogen, USA) gave high and relatively stable conversion after 120 time-on-stream in HDO of isoeugenol. Catalyst deactivation is visible, however, from the product distribution (Fig. 1b), i.e. formation of propylcyclohexane decreased with increasing time-on-stream, while propylbenzene and other unsaturated and even oxygenated products were generated in larger quantities. In the final work reaction rates and catalyst performance in batch and continuous reactors for isoeugenol HDO will be compared.

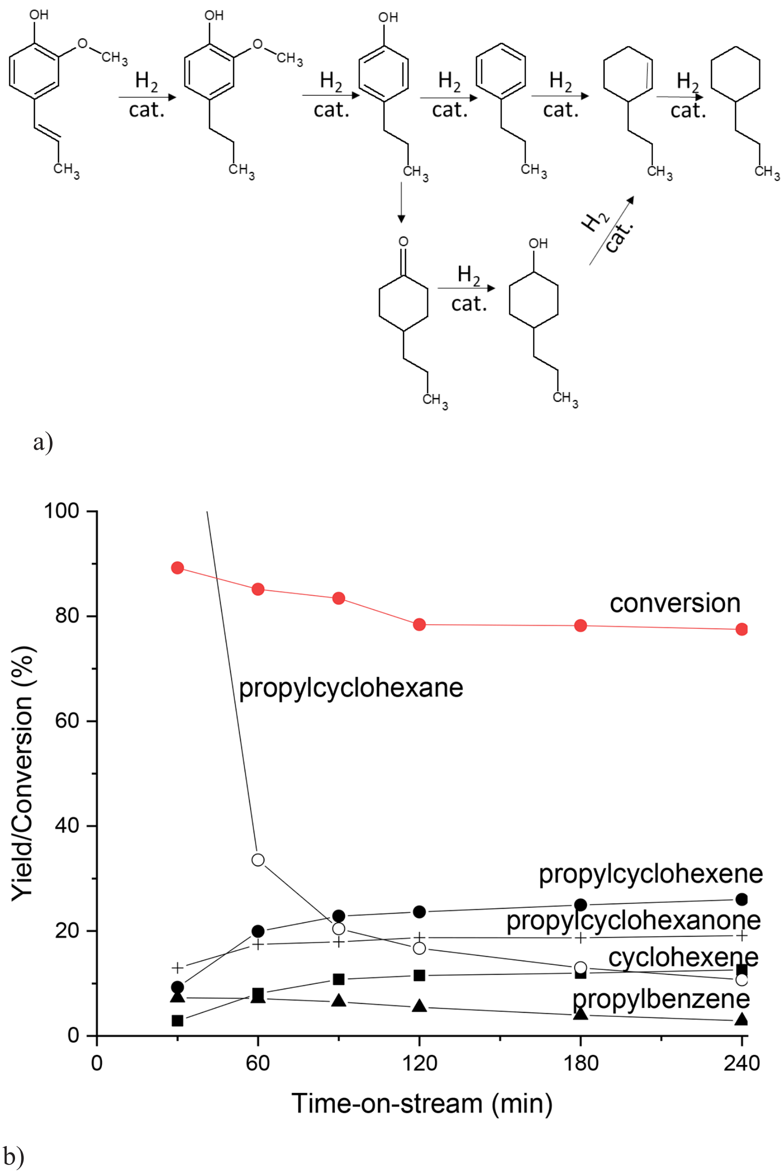

Fig. 1. a) A reaction scheme for HDO of isoeugenol and b) conversion and product yields of isoeugenol as a function of time-on-stream in hydrodeoxygenation of isoeugenol in a trickle bed reactor at 300 ^{o}C under 30 bar over 10 wt% Co/SiO_2 pellets extrudates in 1-decanol. Liquid and hydrogen flow rates were 0.1 ml/min and 50 ml/min, respectively.

Hydrolytic oxidation of cellobiose in the presence of a Pt-containing polymeric catalyst

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Keywords: cellobiose, oxidation, gluconic acid, glucaric acid, hypercrosslinked polystyrene

Studies of the processes of hydrolytic oxidation of disaccharides are the first step towards the development of technologies for the direct conversion of plant polysaccharides, primarily cellulose, into aldonic and aldaric acids, which are widely used in chemical synthesis and various industries. In particular, gluconic acid is used in the food, pharmaceutical, textile and metallurgical industries. Glucaric acid is also an important compound with broad prospects for use in the food industry, medicine, and the manufacture of detergents.

The aim of this work is to study the process of hydrolytic oxidation of cellobiose (4-(β-glucosido) -glucose) to gluconic and glucaric acids in the presence of a Pt-containing catalyst based on a mesoporous matrix of hypercrosslinked polystyrene (HPS) - 3% Pt / HPS MN270.

In the course of the work, the influence of the temperature of the process of hydrolytic oxidation of cellobiose on the degree of conversion of the substrate and the yield of reaction products was investigated. The experiments were carried out in the temperature range from 110 to 150 °C. Based on the obtained results of a qualitative and quantitative nature, a reaction scheme for the conversion of cellobiose into gluconic and glucaric acids was proposed under these conditions in the presence of a 3% Pt /HPS MN270 catalyst.

The study also optimized the process duration. It was shown that the maximum yield of gluconic acid is 21.6% with a reaction time of 1 hour. At the same time, if the target product is glucaric acid, then the optimal reaction time is 2 hours. The yield of acid in this case reaches 63.4%.

In the course of the work, the prospects of using Pt-containing catalytic systems based on a polymer matrix of hypercrosslinked polystyrene in the process of hydrolytic oxidation of cellobiose to gluconic and glucaric acids were shown. At a temperature of 145 °C, an O_2 pressure of 5 bar, a substrate/catalyst weight ratio of 4/1, the yield of gluconic and glucaric acids reaches 21.6 and 63.4%, respectively. The conversion of cellobiose is 100%.

The synthesized catalyst proved to be stable under the hydrothermal conditions of the process and was used for at least three successive cycles of use, without noticeable loss of activity.

The results obtained in the future can be used to create a technology for the catalytic conversion of plant polysaccharides, primarily cellulose, into aldonic and aldaric acids, which are widely used in chemical synthesis, food, pharmaceutical and other industries.

Acknowledgments

The work was financially supported by the Russian Science Foundation (grant 19-19-00490) and the Russian Foundation for Basic Research (grants 20-08-00079, 19-08-00414).

The use of zeolite-supported nanoparticles of ruthenium dioxide as catalyst of levulinic acid hydrogenation

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Keywords: levulinic acid, gamma-valerolactone, hydrogenation, ruthenium, zeolites

Intensive industrial development along with the growth of world population has led to excessive consumption of fossil fuels. Biomass is an alternative renewable source of energy and organic carbon. Valuable chemical compounds can be obtained as a result of lignocellulose processing: furfural, 5-hydroxymethylfurfural, valeric acid, levulinic acid (LA), etc. LA, obtained during acid hydrolysis of lignocellulosic biomass, can be converted into different chemical compounds, one of which is gamma-valerolactone (GVL). GVL is synthesized by selective catalytic hydrogenation of LA and can be used as a feedstock for production of valeric acid and its esters, 5-nonanone, 2-methyltetrahydrofuran and α-methylene-GVL. GVL can also serve as "green" solvent and fuel additive.

The development of new heterogeneous catalysts of LA hydrogenation to GVL involves the use of such supports as oxides, hydroxides and metal salts, carbon, zeolites, etc. Zeolites are widely used in organic syntheses both as individual catalysts and catalytic supports for metal nanoparticles. As supports, zeolites are able to provide high catalytic activity in hydrogenation reactions under relatively mild conditions. The strictly regular crystal structure of zeolites, hydrothermal stability and high porosity contribute to fairly uniform distribution of catalytically active metal and control to some extent the growth of nanoclusters, which increases the catalyst efficiency.

In the framework of this study, the following zeolite-based catalytic systems were synthesized by the wet impregration method: Ru/HZSM-5 with a silica module (SM) 23 and 40; Ru/H-β (SM 25), Ru/H-Y (SM 30) and Ru/H-Mordenite (SM 20). All the catalysts contained RuO_2 as catalytically active phase, ruthenium content determined by the XFA was about 4-5 wt.%. The catalytic properties of the synthesized systems were studied by the example of the reaction of LA hydrogenation to GVL in a batch mode (stainless steel ParrSeries 5000 Multiple Reactor System was used) in an aqueous medium.

While strudying catalytic properties of Ru/HZSM-5 (SM 40) optimal conditions were found (100°C, 1 Mpa of hydrogen, stirring rate 1000 rpm), which allowed achieving 98% of LA conversion for the reaction time 60 min. While testing a series of zeolite-based catalysts with close values of SM (about 20) under the specified optimal conditions, the highest LA conversion was found for Ru/H-Mordenite (76%) and Ru/HZSM-5 (69%). For other samples, the yield of GVL did not exceed 50%. It was shown that the rate of LA conversion is influenced by many factors: properties of zeolite and resulting catalyst (i.e. concentration of acid centers of different types); specific surface area of catalysts and the distribution of active phase (ruthenium dioxide).

Acknowledgments

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Microkinetics of butanol formation via ethanol coupling reactions over MgO-Al_2O_3 mixed oxide catalyst

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Keywords: Guerbet reaction, C-C coupling, butanol formation, kinetic modelling, reaction networks

The increasing demand for energy and the extensive use of fossil carbon resources, which is rapidly increasing the concentration of greenhouse gases in the atmosphere, initiated an intense research to establish the use of renewable carbon sources. As a renewable carbon source the lignocellulosic biomass has the largest potential. Its cellulose and hemicellulose components can be hydrolysed into sugars that can be converted to platform compounds by using various fermentation and chemical processes. The most important fermentation process produces bioethanol which is commonly used as a fuel additive and as a feedstock for the chemical industry. It is very important to mention ABE (Acetone, 1-Butanol, and Ethanol) fermentation, the best known biological source of 1-butanol, which is a better fuel than ethanol. Currently, biobutanol is much more expensive than gasoline, nevertheless, it is a very promising fuel candidate for the future. Catalytic conversion of bioethanol to butanol via Guerbet C-C coupling reaction is a more economical way to make butanol than the ABE fermentation [1]. However, the microkinetics of this reaction is not fully understood yet. Three different mechanisms have been proposed so far: (i) aldol-condensation of two acetaldehyde molecules obtained by ethanol dehydrogenation, (ii) acetaldehyde catalysed condensation of ethanol molecules, (iii) direct condensation of two ethanol molecules.

In the present work, the kinetics of butanol formation via ethanol coupling was studied over MgO-Al_2O_3 mixed oxide catalyst using a fixed-bed, flow-through reactor system. Dozens of experiments were carried out with He:EtOH=5:1 gas mixtures at 21 bar pressure, 275, 300 and 325 ^{o}C temperatures, and in the 0.25-2.50 $\mathrm{g}_{\mathrm{EtOH}}\,\mathrm{g}_{\mathrm{cat}}^{-1}\,\mathrm{h}^{-1}$ range of WHSV. Gas-phase products were observed only in trace amounts. The liquid-phase product mixture contained mainly water, butanol, hexanol, diethyl-ether, butyl-ethyl-ether, and acetaldehyde beside the unconverted ethanol.

For testing the proposed mechanisms, a general code was developed for the simulation of a 1+1D isothermal-isobaric model of the reactor describing catalytic reactions, adsorption/desorption, convection, mechanical dispersion and multicomponent molecular diffusion. Using chemical reaction network theory [2] a large number of candidate heterogeneous reaction mechanisms were generated based on the mechanisms proposed in the literature. The corresponding kinetic models were fitted to the experimental data in error-weighted least-squares sense (i.e. $w_i \sim \sigma_{\mathrm{exp}}^{-2}$) by optimizing their kinetic parameters while taking into account constraints based on physical considerations [2]. The best fitting models could reproduce the measured product distributions within experimental error and allowed us to determine the relative probability of the various reaction schemes for the C-C coupling reaction.

Acknowledgments

We acknowledge Dr. Hanna Solt, Dr. Ágnes Szegedi and Dr Miha Grilc for the help, grants 2018-2.1.11-TÉT-SI-2018-00011, NKFIH FK20 134332 for funding and KIFÜ for awarding us access to HPC resources.

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Electrocatalytic hydrogenation of glucose and xylose on highly dispersed carbon fiber supported Au nanocatalysts

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Keywords: Au nanocatalysts, carbon fiber, electrocatalytic, hydrogenation, xylose, glucose

Catalytic hydrogenation of monosaccharides has been conventionally carried out using H_2 gas under high temperature and pressure conditions. In this study, hydrogenation of glucose and xylose to form sorbitol and xylitol, respectively, was done electrochemically using highly dispersed Au nanoparticles (AuNPs) on activated carbon fiber (CF) support as catalyst. Glucose and xylose are two main components of cellulose and hemicellulose derived from wood biomass. The electrocatalytic process uses water as the source of hydrogen for the hydrogenation which was produced in-situ under ambient conditions. This eliminates the use of costly high purity H_2 for hydrogenation, thus providing a practical and environment friendly route for sugar alcohol production. CF supported AuNPs catalysts (CF/AuNPs) were synthesized using deposition-precipitation method. The physico-chemical characterization of the catalysts were carried out using SEM, TEM, N_2 physisorption, ICP-OES and electrochemical methods. The CF/AuNPs with the smallest Au cluster size (7.6 nm) and the highest dispersion gave twice the yield of sorbitol and three-times the yield of xylitol compared to a smooth Au metal electrocatalyst with comparable physical dimensions. This highlights the positive effect of using a highly dispersed metal nanocatalyst with a high surface area for electrocatalytic hydrogenation. Pretreatment of the CF support prior to Au deposition, either chemical or thermal, had a direct effect on the cluster size and dispersion of the Au nanocatalyst and in turn, the catalyst activity. This illustrates the influence of pretreatment on the surface functional groups of the activated carbon support and their role in obtaining a well-dispersed Au nanocatalyst.

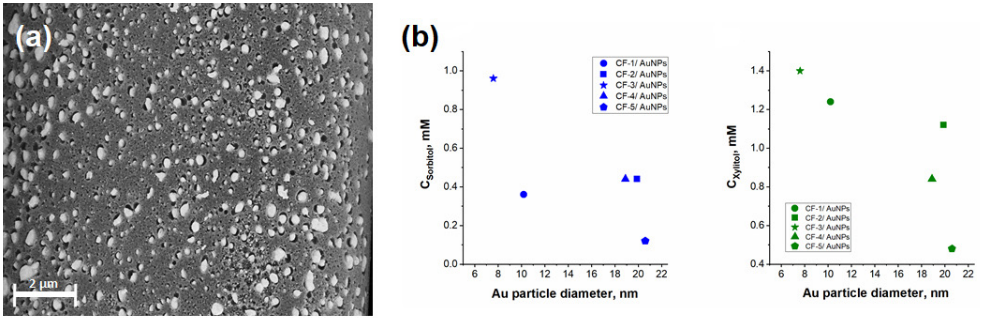

Figure 1. Scanning electron micrograph of a CF-supported AuNPs (CF/AuNPs) catalyst (a) and dependence of sorbitol and xylitol yields on the Au particle size of the CF/AuNPs catalysts with: untreated CF (CF-1/AuNPs), HCl-treated CF (CF-2/AuNPs), NaOH-treated CF (CF-3/AuNPs), CF calcined at 225 °C (CF-4/AuNPs), CF calcined at 325 °C (CF-5/AuNPs) (b).

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T09: Stochastic and deterministic reaction kinetics – theory and practice

Inference of RNA life-cycle kinetic rates and simultaneous gene clustering from sequencing data

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Keywords: statistical inference of kinetic rates, Bayesian inference, RNA life cycle, gene expression

We propose a hierarchical Bayesian approach to infer the RNA synthesis, processing, and degradation rates from sequencing data and to simultaneously clusterize genes whose rates have similar profiles. We apply our method to investigate transcriptional and post-transcriptional responses of murine fibroblasts to the activation of proto-oncogene MYC. We uncover a widespread choral regulation of the three rates, which was not previously observed in this biological system.

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Extensions of detailed balance for not necessarily reversible Markov chain models of reaction networks

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Keywords: stochastic reaction networks, stationary distributions, detail balance

We say that a measure π for a continuous-time Markov chain with transition rates q(x,y) is detailed balanced if for all states x,y we have π(x)q(x,y)=π(y)q(y,x). If this property holds for a stationary distribution π, then the stationary Markov chain is time reversible and π can be explicitly calculated (a notable example of where these properties are heavily used is the study of birth and death chains).

In the setting of stochastic reaction networks, the existence of a detailed balanced distribution and its connections with the detailed balanced steady states of the associated deterministic model have been extensively studied (see for example [1,3]). In this work, we extend the notion of detailed balanced distribution to cover not necessarily reversible Markov chain models of reaction networks (that is, we do not require that q(x,y)>0 whenever q(y,x)>0). While a generalization of the concept of time reversibility does not seem attainable, we fruitfully use this extension to explicitly calculate the stationary distribution of certain families of stochastic reaction networks. As a consequence, we are able to explicitly calculate the stationary distributions of generalizations of birth and death chains where the forward and backward jump sizes may not be equal to one another.

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Reaction extent (advancement of reaction): A new general definition

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Keywords: reaction extent, conversion, advancement of reaction, kinetic differential equation

Reaction coordinate is a routinely applied simple scalar measure for the advancement and the equilibrium of simple chemical reactions. Alternatively, the expressions: conversion and reaction extent are also used in the same context. One can often find general errors and useless approaches with these definitions and expressions both in textbooks and research papers in the field of formal reaction kinetics. Our aim is to pinpoint the typical errors in the application of these measures, and then to derive a new, more general definition for the reaction extent.

The common mistakes are as follows:

- It is quite common and unnecessary to use differentials when introducing the concept. There is nothing infinitesimal here.
- It is not exceptional to use the concept before defining it.
- Several authors provide an implicit definition (that does not really define the given quantity) and cannot get out from the trap built by themselves.
- No measurement protocol is given.
- It is only the case of a single reaction step that is treated.
- Nothing is stated about the (mathematical or chemical) properties of the reaction extent.
- Having introduced the concept this or that way in many works it will never ever be used any more.

The starting point of our concept is the derivation of a general definition for the reaction extent. It is based on the mere fact that in every simple elementary step – on the level of molecules – a known number of reactant species is converted into a known number of product species. We show that with the application of the stoichiometric matrix, the reaction extent can be precisely defined as a new vector valued function. Our goal is to apply this new definition to simple and complex reactions. We also search for and introduce new scaling rules that allow the unequivocal characterization and understanding the true meaning of the “final state” of chemical reactions. Our aim is to replace the previously applied *a priori* approach to the theory of detailed balance.

Acknowledgments

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Multicriteria optimization of gasoline catalytic reforming temperature regime based on a kinetic model with grouped hydrocarbons

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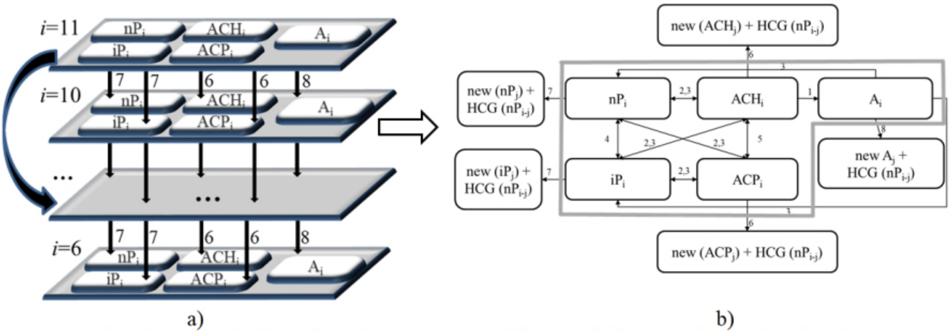
Keywords: mathematic modelling, gasoline catalytic reforming, kinetic model, multi criteria optimization, Pareto approximation, octane number

The authors elaborated a detailed kinetic model of gasoline catalytic reforming that accounts variation of temperature and the reaction mixture mole number. Particular components of the reaction mixture are grouped according to the hydrocarbon class: aromatic hydrocarbons; five-membered naphthenes; six-membered naphthenes; isoparaffins; and normal paraffins [1]. An industrial facility – a catalytic reforming unit L-35-11/300 – workflow data were used as experimental data. The schematic diagram of a reactor section and reformate stabilization section was examined. The inverse kinetic problem was resolved and kinetic parameters of the main stages were calculated. For resolving the issue of catalytic reforming restrictions for commercial Euro 6 Standard petrol (benzol and aromatic hydrocarbons content), the authors proposed to define and resolve the task of multicriteria optimization of conditions which would simultaneously account several criteria based on the kinetic model [2]. The optimality criteria are as follows: the yield and octane number of reformate, the octane number of the whole mixture, and content of benzol and aromatic hydrocarbons. Multicriteria optimization task resolution provided for defining the temperature mode in the reactor section, which allows one to lower the yield of benzol and aromatic hydrocarbons without any substantial reduction of octane number and increase in the reformate.



1 — reactions of naphthene dehydration (hydroforming process); 2 — dehydrocyclization of paraffins; 3 — hydrodecyclization;
4 — paraffins isomerization; 5 — naphthenes isomerization; 6 — naphthenes hydrocracking; 7 — paraffins hydrocracking;
8 — hydrocracking of aromatic hydrocarbons; i, j – number of carbon atoms (j < i).

Fig. 1. Scheme of the gasoline catalytic reforming transformations: a) schematic diagram; b) chemical transformations of groups with same number of carbon atoms

Acknowledgments

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Chemical reaction networks connected by diffusive and convective connections

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Chemical reactions are often taking place in different balance volumes that are connected by other physical mechanisms, such as convection and diffusive transfer. These physically meaningfull connections are linear and obey conservation laws.

It is shown that the overall model of above connected model is kinetic, i.e. it is also in mass action CRN form. Using passivity theory we show that the overall CRN model is stable if the constituting CRNs are complex balanced and Kirchhoff convection is assumed. The same statement remains true if one allows the presence of time-delays of the connections.

Static and dynamic Absolute Concentration Robustness

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Keywords: reaction networks, Absolute Concentration Robustness, ACR, robustness, empirical robustness, functional robustness, invariance, dynamics

Absolute Concentration Robustness (ACR) was introduced by Shinar and Feinberg as a way to define robustness in equilibrium species concentration in a mass action dynamical system. A dynamical system is ACR if all positive steady states are found in a hyperplane parallel to a coordinate hyperplane. This ensures that one of the variables, called the ACR variable, will always report the same value no matter which positive steady state the system finds itself in. The ACR definition was with a view to devise a mathematical condition that will ensure robustness in the function of the biological system being modeled. The robustness of function rests on what we refer to as *empirical robustness* – the concentration of a variable remains unvarying, when measured in the long run, across arbitrary initial conditions. While there is a positive correlation between ACR and empirical robustness, ACR is neither necessary nor sufficient for empirical robustness, a fact that can be noticed even in simple biochemical systems. To develop a stronger connection with empirical robustness, we define *dynamic ACR*, a property related to dynamics, rather than only to equilibrium behavior, and one that guarantees convergence to a robust value. Dynamic ACR provides the appropriate mathematical framework for empirical and functional robustness. We illustrate this with a rich body of examples of reaction networks, possessing various flavors of dynamic ACR properties.

Kinetic study of the oxidation of iodide ion by dicyanobis(phenanthroline)iron(III) in aqueous-organic solvent medium

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Keywords: iodide ion, dicyanobis(phenanthroline)iron(III), oxidation, aqueous-organic solvent, kinetics

This study surfaces the results of the kinetics of the electron transfer reaction between dicyanobis(phenanthroline)iron(III) and iodide ion in 85% aqueous-dioxane medium. Dicyanobis(phenanthroline)iron(III) oxidized iodide in two phases at 0.06 ionic strength and 285 ± 0.5 K. In the first phase of the reaction, the order of reaction with respect to the dicyanobis(phenanthroline)iron(III) was zero, and it was first with respect to the iodide ion. An overall first order was observed in the first phase of the reaction. An overall fractional (1.5) order was observed in the second phase of the reaction, which started soon after the first phase. In this phase, dicyanobis(phenanthroline)iron(III) and iodide ion followed the fractional (0.5) and first (1st) orders, respectively. The products of the reaction were characterized by UV-Visible spectra, and the reaction was followed spectrophotometrically at 518 nm by using kinetic mode of the UVProbe 2.42 under the fixed condition of pseudo-first order. The value of the overall rate constant $(k_1).(\varepsilon.b)$ in the first phase of the reaction was found to be 2.769 M^{-1} s^{-1}. However, the value of the overall rate constant $(k_2).(\varepsilon.b)^{0.5}$ has been determined and found 6.288 M^{-1} s^{-1} for the second phase of the reaction. The influence of ionic strength and protons (H^+) was also determined to draw a clear conclusion in the co-solvent mixture. The effect of ionic strength, as well as protons, showed that the values of the rate constants either zeroth "$\varepsilon.b.k_{obs}$" or fractional "$(\varepsilon.b)^{0.5}.k'_{obs}$" is decreasing with increasing the ionic strength, and the concentration of protons in the reaction mixture. The linear correlation between log $(\varepsilon.b.k_{obs})$ or log $\{(\varepsilon.b)^{0.5}.k'_{obs}\}$ versus $\sqrt{I}$ confirmed that the reacting entities in the rate-determining step(s) are opposite charge carriers. The values of $\varepsilon.b.k_{obs}$ and $(\varepsilon.b)^{0.5}.k'_{obs}$ showed a sine-wave pattern upon increasing the concentration of the acid or protons in the reaction mixture, which reveals complex kinetics. The thermodynamic parameters of activation were calculated for the second phase of the reaction. They were found as; $E_a = 51.7$ kJ mol^{-1}, $\Delta H^{\#} = 48.9$ kJ mol^{-1}, $\Delta S^{\#} = -128.09$ J K^{-1} mol^{-1}, $\Delta G^{\#} = 49.3$ kJ mol^{-1}, and $A = 3.3 \times 10^6$.

The theory of conjugate reactions in the context of modern ideas

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Keywords: conjugation, interference, determinant, initiation

Various types of possible interactions between reactions are discussed. Some of them are united by the general idea of chemical reaction interference. The ideas on conjugated reactions are broadened and the determinant formula is deduced; the coherence condition for chemical interference is formulated and associated phase shifts are determined. It is shown how interaction between reactions may be qualitatively and quantitatively assessed and kinetic analysis of complex reactions with under-researched mechanisms may be performed with simultaneous consideration of the stationary concentration method. Using particular examples, interference of hydrogen peroxide dissociation and oxidation of substrates is considered.

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Numerical modeling of precipitate formation in microfluidic system

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Keywords: modeling, precipitation, microfluidics, biomimetic

Microfluidic systems have become more and more popular in various chemical applications. By using the network of tiny tubes we are capable of creating biomimetic systems, with which we can study chemical processes under conditions similar to those occurring in living organisms [1]. The chemistry of kidney stone formation, which affects many people's lives, has been explored using these systems [2].

In our study we are investigating calcium oxalate formation in microchannels with numerical modeling. In this system fluid convection is coupled with a precipitation reaction which leads to the formation of solid particles. In order to describe the fluid motion, the Navier-Stokes equation is solved by using the PIMPLE method. Before the appearance of solid phase we consider a colloidal intermediate state from which precipitate is formed. Because of the density and the continuous growth of particles, the interaction between the fluid and the solid phase cannot be neglected. The trajectories of solid particles are followed by Lagrangian particle tracking. The calculations give us the opportunity to determine particle size distributions and to investigate the temporal and spatial changes in the flow and concentrations fields. With this model we are capable of not only reproducing experiments, but also calculating data which is experimentally difficult to measure [3].

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Algorithmic construction of reaction networks from delayed kinetic differential equations

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Keywords: reaction kinetics, reaction graph, time delay systems

It is known that general nonlinear dynamics can be formally described by chemical reaction networks (CRNs) which emerge from the abstraction of the laws of chemical kinetics [1]. The advantage of this graph-based description is that there exist powerful results on the relation between the network structure and the qualitative properties of the dynamics even if the parameters (i.e., the reaction rate coefficients) are not precisely known. This underlines the importance of the inverse problem, namely, how to construct a CRN that reproduces (or approximates) the dynamics of a given set of differential equations. This problem has been extensively studied for ordinary differential equations, and several methods have been developed for the computation of CRN structures with preferred properties [2].

Delayed reactions were introduced in the literature for the simplified representation of reaction cascades, or for describing explicit (e.g., transport) delays in compartmental models which are known to be representable by CRNs [3]. In this contribution we address the CRN construction problem for delayed differential equations (DDEs). We give necessary and sufficient conditions for the realizability of a DDE as a CRN. Moreover, we propose an efficient algorithm for the construction of a CRN that realizes a given DDE. We also show that this CRN realization is generally not unique and that the reaction graph having the maximum number of reactions contains all possible reaction graphs representing the same dynamics as sub-graphs. Finally, we generalize the results for simple model-transformations and uncertain models.

Acknowledgments

The authors acknowledge the support of the European Union, co-financed by the European Social Fund through the grant EFOP-3.6.3-VEKOP-16-2017-00002, and the support of the National Research, Development and Innovation Office (NKFIH) through grant no. 125739.

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T10: Miscellaneous

Silica coating for Pd/C catalysts: compromising active phase protection and accessibility

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Keywords: palladium, carbon, silica, protection, sintering, deactivation, hydrogenation, glucose oxidation

Carbon-supported palladium catalysts were covered by a siliceous layer to increase their sintering resistance. A commercial Pd/C catalyst was compared to catalysts prepared either by dry or wet impregnation on activated carbon or carbon black. In the case of dry impregnation, the Pd active phase was shown to be located within the micropores of the carbon support. The siliceous layer was evidenced by electron microscopy and XPS confirmed that Pd was indeed covered by Si. In all cases, the catalytic activity was lowered by the presence of the protecting layer, but thermal treatment allowed increasing the activity by creating some porosity within the layer, therefore allowing access to the underlying active phase, without deleterious sintering. Carbon black (CB) proved its superiority thanks to its non-microporous nature, which allowed the Pd nanoparticles to be located at the interface with the siliceous coating hence making them more accessible.

The Pd/CB catalyst was then encapsulated in a thin mesoporous silica layer (Figure). This was confirmed by XPS, TEM, electron tomography and nitrogen physisorption measurements. The covered catalyst was tested in the oxidative dehydrogenation of glucose into gluconic acid: the high catalytic activity was maintained in comparison with uncovered catalyst, indicating that the underlying active phase was easily reached by reactants. The silica pores sizes were varied by using different surfactant templating molecules and this was shown to affect selectivity.

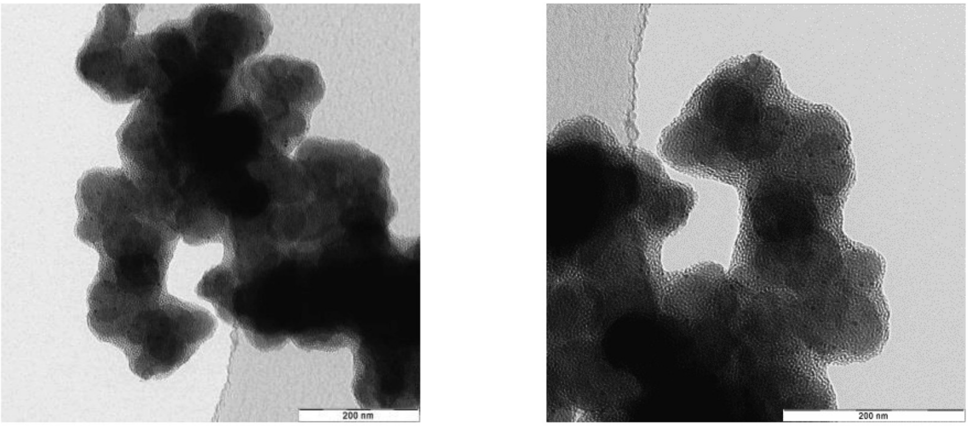

Figure: TEM micrographs of Pd/CB@SiO_2 catalyst covered by a mesoporous silica layer.

Acknowledgments

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Bio-inspired flow-driven chitosan pattern formations

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Keywords: self-organization, sol-gel transition, hydrogel, surface instabilities

Organic chemical gardens of chitosan hydrogel develop upon injecting an acidic chitosan solution into an alkaline solution. Besides complex and budding structures, tubular hydrogel formations develop that exhibit periodic surface patterns.[1] The underlying wrinkling and folding instability are identified by its characteristic wavelength dependence on the depth of the tubular elastic material formed.[1,2] The flow-driven conditions allow precise control over the structure that can help the design of soft bio-inspired materials.

Acknowledgments

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Over-equilibrium as a result of CPE

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Keywords: chemical equilibrium, conservative-perturbed equilibrium (CPE), PFR, CSTR, over-equilibrium

The effect of "over-equilibrium" is demonstrated both for two types of ideal chemical reactors, continuously stirred tank reactor (CSTR) and plug-flow reactor (PFR), respectively, under conditions of conservatively perturbed-equilibrium (CPE). Two types of complex chemical mechanisms are analyzed, acyclic and cyclic ones. Using computer experiments, it is shown that for the steady-state PFR this effect is more pronounced that for the steady-state CSTR, and it is true both for acyclic and cyclic reactions. The greater the difference between the initial concentrations of the two substances, the greater the "over equilibrium" concentration of the third substance, the initial concentration of which was equilibrium. At our values of kinetic parameters, the sensitivity of the time of occurrence of the extremum of the same reaction in different reactors (PFR and CSTR) is small, and at different reactions (acyclic and cyclic), but in one type of reactor (PFR or CSTR) – significant.

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Investigating corrosion reactions with Scanning Reference Electrode Technique

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Keywords: Scanning Reference Electrode Technique, galvanic corrosion, electric field, corrosion

Corrosion is a heterogeneous electrochemical reaction. Its rate is of special importance because generally corrosion is an undesirable process causing billions of dollars of loss anually. In order to alleviate this damage already available techniques must be employed and improved upon to study corrosion. One such method is the Scanning Reference Electrode Technique which is suitable for mapping the electric field generated between a galvanic pair.

In my work I will demonstrate what kind of information can we obtain with the help of this technique and how can we use it to better understand corrosion reaction and galvanic corrosion in particular.

Poster Presentations

T01: Catalysts in sustainable and green chemistry

Novel ceria and ceria-based nanocomposites as potential catalysts for environmental sustainability

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Keywords: novel ceria-carbon nanocomposites, methanol decomposition, ethyl acetate oxidation

The development of novel ceria based materials that can be successfully used as catalysts in various environmentally friendly processes due to a significant improvement of ceria intrinsic characteristics is the focus of our study. In particular, the combination of ceria with low-dimensional carbon materials such as graphene oxide (GO) and nanodiamond (ND) appears as a very promising approach. Actually, the decrease of ceria crystallite sizes deep in the nanoscale have been found to convert them into highly effective destructive adsorbent materials owing to their high surface area, strong adsorbability, and large number of highly reactive sites. Besides, the conductive robust structure of graphene often facilitates the charge transfer, redox reaction, as well as enforces the mechanical strengths of the resulting composites, while the presence of surface functional groups on the nanodiamond particles could play a supportive role in the catalytic activity of the obtained nanocomposites. The obtained samples were characterized with a complex of physicochemical techniques as X-ray diffraction, nitrogen physisorption, UV-Vis and Raman spectroscopies, and temperature-programmed reduction with hydrogen. The catalytic activity of the obtained nanostructured materials was followed in two environmentally friendly reactions – total oxidation of ethyl acetate as a representative of VOCs and methanol decomposition to hydrogen and CO as an alternative fuel source. The results show that the novel ceria and ceria based composite materials significantly outperform the hydrothermally obtained ceria catalyst used for comparison in both activity and selectivity to CO and hydrogen in the methanol decomposition reaction (Fig. 1), and in the selectivity to total oxidation of ethyl acetate. We assign these results to the significantly improved redox behavior and textural characteristics of the obtained novel ceria based materials.

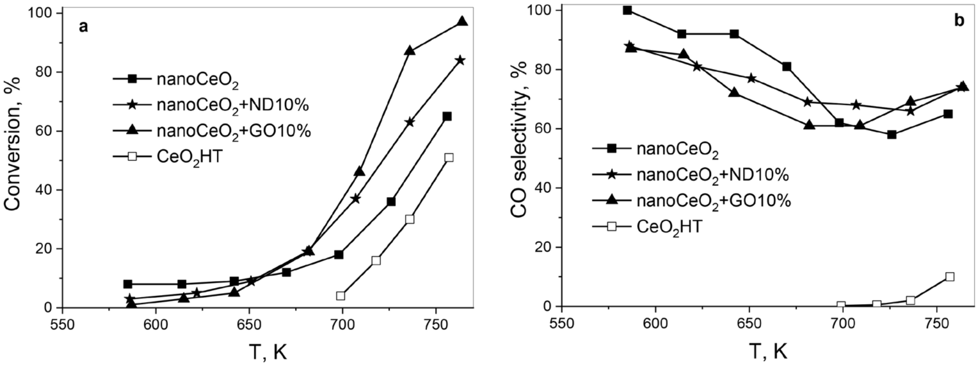

Figure 1. Conversion vs temperature (a) and selectivity to CO (b) in methanol decomposition reaction

Acknowledgments

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Novel nanosized mesoporous materials based on promoted with Ce and Ti manganese oxide systems as catalysts for total oxidation of ethyl acetate and methanol decomposition

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Keywords: binary Ti-Mn and Ce-Mn oxides, ethyl acetate oxidation, methanol decomposition

The advanced strategy for the sustainable environment protection envisages not only complete elimination of harmful pollutants but also a decrease of their emission. Volatile organic compounds (VOCs) represent a significant part of air pollutants and nowadays the catalytic total oxidation has been considered as the most effective approach for their elimination. On the other hand, the harmful emissions from the transport sector could be significantly reduced via replacement of the fossil fuels by clean and efficient alternative ones. In this aspect, hydrogen is considered as the most effective fuel, but its safety storage and transportation is still a significant problem. The application of various chemical compounds, which in case of need easily release hydrogen could be one reliable solution, but development of low-cost and highly active and selective catalysts under relatively low temperature are needed. Transition metal oxides have demonstrated many advantages for the production of cheap and environmentally friendly catalysts, but the problem with the improvement of their efficiency is still a matter of challenge. The development of nanostructured composites is well known strategy for the increase of the catalytic activity of the individual oxides via regulation of their structure, texture and appearance of synergetic effects. The aim of the current investigation is to develop novel nanosized mesoporous materials based on promoted with Ce or Ti manganese oxide systems and to test them as catalysts in various processes, such as total oxidation of ethyl acetate and methanol decomposition. The pure and binary oxide (1:1 mol ratio) materials were synthesized by a template-assisted hydrothermal technique using CTAB as a template. The obtained materials were characterized by low-temperature nitrogen physisorption, XRD, SEM, TEM, Raman, UV-Vis, XPS and temperature-programmed reduction with hydrogen. The role of structure, texture, and surface properties of the obtained materials on their catalytic properties under different catalytic reactions was in the focus of the study. All prepared materials exhibit high surface area and mesoporous volume with the exception of the pure manganese oxide. The binary oxides demonstrate improved textural characteristics in comparison with the single oxides. The XRD and Raman analyses showed co-existence of ceria, Mn_2O_3 and Mn_5O_8 for 5Ce5Mn, while only well crystallized anatase and rutile TiO_2 phases were found for 5Mn5Ti. The slight shifting in the anatase unit cell parameters found for the TiMn materials did not exclude partial isomorphous substitution of Ti^{4+} by Mn^{n+} ions.

The similarity in the ionic radius of Mn^{3+} and Ce^{4+} provides easier introduction of manganese species into the fluorite-like structure of CeO_2, modifying the crystallization of CeO_2, and forming $CeMnO_x$ solid solution. The XPS analyses showed stabilization of Ti, Ce and Mn ions in lower oxidative state in the obtained binary oxides. The additives of titania and ceria to managanese oxide promote their catalytic activity in total oxidation of ethyl acetate and methanol decomposition to syngas, but this effect is strongly influenced by type of additive.

Acknowledgments

Financial support from project № КП-06-ПМ39/1/2019 is gratefully acknowledged. European Regional Development Fund within the Operational Programme Science and Education for Smart Growth 2014 - 2020 under the Project Center of Exellence: National center of mechatronics and clean technologies - BG05M2OP001-1.001-0008 is also acknowledged.

First-principles investigation of structural and electronic properties of TiO_2 for photocatalytic reduction of CO_2

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Keywords: density functional theory, TiO_2, CO_2, hybrids, DFT+U

Titanium dioxide has in recent decades received significant attention due to its wide range of applications [1]. Rutile and anatase crystal phases have been particularly utilized as possible photocatalysts due to their photocatalytic activity. Nevertheless their activity is diminished by charge recombination and high band gaps, which can be overcome by means of doping, defects integration and the deposition of co-catalysts.

Density functional theory calculations were performed in GPAW [2] with the projector augmented wave method (PAW). Perdew Burke Ernzerhhof (PBE) functional was used, due to good agreement with experimental structural data, however it fails to properly describe the electronic structure, which is a known flaw of DFT [3]. The introduction of a Hubbard correction (DFT+U) on top of *d* and *f* orbitals, due to strong Coulomb interactions, is the simplest solution. Although the method is computationally on par with LDA and GGA, the U value has to be uniquely determined based on the desired property. Alternatively, hybrid functionals offer better electronic properties agreement with experiments, albeit at a much higher computational cost. Long range dispersion forces were also considered, thus Grimme D3 correction was employed over DFT+U calculations. Subsequently we studied the structural and electronic properties of rutile and anatase TiO_2 with PBE, PBE+U (U=4, 6 and 8 eV), PBE+U+D3 and benchmarked them to hybrids B3LYP, PBE0 and HSE06.

The results and efficiency of different methods on structural and electronic properties was discussed and benchmarked to hybrids HSE06, B3LYP and PBE0. We also obtained the optical properties of anatase and rutile within the random-phase approximation, which were compared to experimental data.

Finally the most prominent facets of rutile and anatase were constructed, which consist of rutile (001), (110), (101) and anatase (001), (011), (101) surfaces. Since the adsorption and subsequent activation of CO_2 molecule is of pivotal importance in the photoreduction, we investigated possible adsorption sites on all facets, employing PBE, PBE+U and PBE+U+D3 methodology. This study therefore provides significant insights into the structural, electronic and optical properties of rutile and anatase, in conjunction with adsorption and subsequent activation of CO_2.

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Hydrolysis-hydrogenolysis of cellulose to ethylene and 1,2-propylene glycols in the presence of catalysts based on tungsten (I) carbides

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Keywords: biomass, cellulose, hydrolysis-hydrogenolysis, ethylene glycol, 1,2-propylene glycol, tungsten

Ethylene and 1,2-propylene glycols (EG and PG) are widely used in industry as components of antifreezes and brake fluids, as well as for the synthesis of polyesters, solvents [1]. In industry, EG and PG are obtained from fossil sources of raw materials, the gradual depletion of which makes it necessary to search for alternative methods for the production of glycols. A promising field of research of EG and PG synthesis is the the direct one-pot production of glycols from plant biomass polysaccharides. As cellulose is the main component of plant materials (up to 70%), development of methods of the polysacchride transformations seems to be very perspective. The production of EG and PG from cellulose consists of two successive stages: 1) hydrolysis of the polysaccharide to glucose and 2) hydrogenolysis of glucose to EG and PG. One-pot application of these steps requires the use of bifunctional catalysts.

The aim of this work was the development of bifunctional catalysts for the hydrolysis-hydrogenolysis of cellulose in EG and PG based on nickel nanoparticles supported on tungsten (I) carbides (CW and Ni/CW). The obtained catalysts CW and Ni/CW samples were studied using a complex of physicochemical methods (XRD, TEM, nitrogen adsorption, pH_{ZERO}) [2].

It has been shown that the specific surface area for CW systems was in the range of 27-46 m^2/g. The introduction of Ni onto the CW samples led to an increase in the specific surface area. According to XRD data, the CW samples contained a W/W_2C mixture with small impurities of WC. Ni deposition did not change the phase state of the tungsten carbide support. The surface acidity of the CW samples measured by pH_{ZERO} was in the range of 4.1 - 4.9 and significuntely increased to 9.32 - 9.67 after Ni deposition.

The catalytic properties of CW catalysts were investigated in a high-pressure autoclave at 245 °C under H_2 atmosphere. The main reaction products were EG and PG, the by-product was glycerol. Total yield of EG and PG depended on W_2C/WC ratio. The maximum total yield of EG and PG reached 30% at $W_2C/WC = 30/1$. Ni deposition on CW led to an increase in the yields of both EG and PG to 45% [2].

Acknowledgments

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The influence of aluminium amount bond to SBA-15 on characteristics and performance of the synthesized catalyst

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Keywords: catalyst, wet impregnation, mesoporous silica, esterification

In reaction engineering, catalysts are important species which increase conversion rate. Reactions can be performed using homogeneous catalysts, but they are often corrosive and hazardous. There is a green alternative, using heterogeneous catalysts, which can be easily separated from the rection media and used several times consecutively. Active catalytic species are generally bonded to some kind of support. The supporting material is selected according to the application. All sorts of mesoporous silicas are widely used as supports for different types of catalysts. They have high surface areas, distinctive pore arrangement, and high thermal stability. With surface functionalization by active species the activity can be enhanced. There are two different techniques for surface functionalization: direct synthesis method and post synthesis method. According to active sites the catalysts are classified to acid and base catalysts. [1–3]

In the present study a series of solid acid catalysts were synthesized by wet impregnation with variable loadings of aluminium on mesoporous silica SBA-15. The selected mole ratios n_{Si}:n_{Al} were 1:0.056, 1:0.028 and 1:0.014. For the characterization of synthesized catalyst, the scanning electron microscopy (SEM), nitrogen adsorption-desorption (BET), dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FTIR), temperature programmed desorption (TPD), temperature programmed reduction (TPR) and thermogravimetric analysis (TGA) were used. A set of oleic acid esterification reactions with methanol were conducted to check the performance of the catalyst. The GC coupled with FID detector was applied for the determination of oleic acid and methyl oleate concentrations. The reactions were conducted in a laboratory batch reactor.

Acknowledgments

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Carbon foam supported Co-Zn ferrite nanoparticles as catalysts for methanol decomposition: Effect of Co/Zn ratio

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Keywords: carbon foam, composition effect, methanol decomposition, Co-Zn ferrite nanoparticles

Thanks to its particular intrinsic properties, high surface area and structural stability even at high temperatures. Carbon foams are materials particularly studied at the moment, for solving the problems related to thermal management, adsorption, energy storage, electromagnetic shielding, catalyst support, and sensors. In recent years, research has focused on the development of catalysts for the production of hydrogen, derived from poly-metallic oxides obtained from low-cost transition metals and low cost supports, in order to supplant the catalysts currently in use, produced with noble metals, substantially more expensive. The current investigation is focused on the synthesis of carbon foam (CF) from coal tar peach and furfural (1:1) as the main reagents, in which $xCoyZnFe_2O_4$ nanoparticles (mol ratio x:y = 2:8, 5:5, 8:2; total metal content of 8wt.%), are incorporated by incipient wetness impregnation under vacuum. The effect of the support on the formation of the phase composition was studied by Boehm method, XRD, nitrogen physisorption, FTIR, Moessbauer spectroscopy and TPR–TG. The catalytic properties of the obtained modification were tested in methanol decomposition with a potential for hydrogen production.

Table 1. Data for samples composition and dispersion (XRD, Moessbauer spectyroscopy), BET surface area (N_2 physisorption), initial temperature of reduction (TPR) and catalytic activity at 675 K.

Sample	Phase composition	Particle size nm	BET m^2/g	T_{ini} (K)	Conversion %
Co2Fe/CF	Spinel Fd-3m	28	995	515	84
Zn2Fe/CF	Spinel Fd-3m	43	746	513	87
2Co8Zn2Fe/CF	Spinel Fd-3m	18	702	530	71
5Co5Zn2Fe/CF	Spinel Fd-3m	14	558	508	84
8Co2Zn2Fe/CF	Spinel Fd-3m	18	604	507	77

Formation of spinel ferrite phase, which dispersion increases for the bimetallic materials is detected by XRD. The N_2 physisorption reveals more significant decrease in the BET surface area for the latter materials, probably due to the more intensive blocking of the micro/mesopores of the carbon support provoked by deposition of ferrite particles in them. The physicochemical study reveals that the catalytic behavior of the samples is in a complex relation to the Co/Zn ratio, location and dispersion of the loaded ferrite particles as well as to the phase transformations with them under the reaction medium.

Acknowledgements

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$(10\%Co+0.5\%Pd)/Al_2O_3$ catalyst examination in process of CO hydrogenation at low and high pressure

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Keywords: CO hydrogenation, low/high pressure, supported Co-Pd catalysts, in situ DRIFTS

Co-Pd catalysts are active in synthesis gas conversion. CH_4 and CO_2 as products are considered unwanted. Product distribution is influenced directly by thermodynamic parameters but other ones affect it indirectly. Process mechanism is complex and investigations at low and high pressure are necessary to achieve more information about the reasons and ways of selectivity change. Surface properties and selectivity of $(10\%Co+0.5\%Pd)/Al_2O_3$ system are presented. Chemisorption of H_2 and CO, *in situ* DRIFTS, catalytic measurements, *ex situ* XPS, TPR and TPD were carried out.

Preliminary study at 1 atm concerned samples pretreated up to 300 ºC and reduced at 300, 400, and 450 ºC in H_2. Sample of highest selectivity amongst all of them was $(10\%Co+0.5\%Pd)/Al_2O_3$ reduced successively 1 h at 300 and 400 °C. It demonstrated $CO_{conv.} = 8\%$, $CH_4/CO_2 = 160$, $H_{100C}/CO_s = 2.8$ at $T_{reac} = 300$ ºC in presence of Co^0 and Co^{n+}. This pretreatment mode resulted in: (i) a low level of unreduced metal; (ii) a great number of bimetallic particles; (iii) a low (if any) amount of pure Pd particles; (iv) low metal dispersion of 1%; (v) low amount of irreversibly adsorbed CO related to presence of stable H species ($T_{des} > 300$ ºC) that diminished contact of CO with catalytically active sites and provoked some increase of surface H/CO ratio favouring CH_4 formation (both factors influence selectivity); (vi) great portion of CO adsorption on metal particles in bridge form but domination of linear species; (vi) existence of sites for strong adsorption of formates and monodentate carbonates. Bidentate carbonate species desorbed within the interval 200–300 °C and such a decreased rate of their destruction was assigned to suppressed CO_2 formation, which in its turn diminished the WGSR rate and the adsorbed CO was spent mainly for CH_4 formation. Thus, the sample demonstrated better selectivity to hydrocarbons; (vii) stable metal particles surface with time at reaction temperatures T_{room}-250 ºC, and good activity in CO hydrogenation (including to C_{2+} products) even at $T_{reac} = 90$ ºC; (viii) increased CH_x bands intensity at reaction temperature over 175 ºC (especially that of CH_2 groups) revealed potential of the system to produce higher hydrocarbons; (ix) CO adsorption was characterized with low variety of species, same species alternating only their quota depending on T_{ads}. It can be considered that the studied catalyst possessed surface, which determined peculiar homogeneity of intermediates that approximates it to the Green chemistry idea for selective catalysts.

Catalytic test at 10.2 atm with a sample reduced at 260 ºC and $T_{reac} = T_{red} = 260$ ºC resulted in increased CO conversion (70-50% decreasing with time on stream), selectivity ratio $CH_4/CO_2 = 9.8$ and synthesis of C_{2+} hydrocarbons. Sample reduced at $T_{red} = 400$ ºC tested at same $T_{reac} = 260$ ºC demonstrated constant CO conversion (53-50% with time on stream), preserved selectivity to hydrocarbons at almost the same CO_2 production (2.2%), slight increase of CH_4 and $C_{2\text{-}4}$ at respective decrease of C_{5+} hydrocarbons. The tests of CO hydrogenation at increased pressure and decreased H_2/CO ratio in reaction flow revealed clear dependence of conversion and selectivity on T_{red}. Decrease in conversion after T_{red} = 260 ºC could be explained with metal particles agglomeration and high level of C_{5+} compounds formation, which limits surface diffusion of reagents/products. Stability of conversion and selectivity with time on stream after higher T_{red} results from stability in composition of supported phase(s) and decreased rate of agglomeration of metal particles.

Acknowledgements
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Unraveling the effect of well-dispersed nickel species in mesoporous KIT-6 for CO_2 reforming of CH_4 reaction

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Keywords: dry reforming of methane, nickel, synthesis, mesoporous silica

Nowadays, fossil fuels are used as the main energy sources. Coal, natural gas and oil combustion processes emit greenhouse gases, which released into the atmosphere cause hazards to human health and acceleration of global warming. Carbon dioxide is one of the components of exhaust gases which may be used in different chemical processes, such as dry reforming of methane (DRM).[1,2] The endothermic nature of DRM together with a lack of stable catalyst are major obstacles for commercialization and call for further catalyst development. Nickel-based catalysts have been extensively presented in the literature for such reactions. Although sintering of the active phase and coking are the main drawbacks of nickel catalysts, a choice of proper support may inhibit these processes by enhancing textural properties and dispersion of the active phase.[3] In principle, a proper carrier can positively affect catalytic activity, stability and selectivity of the prepared catalyst. Among different supports, mesoporous silicas e.g. SBA-15, MCM-41, KIT-6 are good candidates due their interesting structures that allow a good dispersion of the active phases. Only a few studies have dealt with Ni/KIT-6 catalysts for dry reforming of methane.[4–6] The synthesis of the catalyst, including the support and active phase addition, plays an important role in the catalytic activity. Therefore, in this study, a series of Ni-based KIT-6 materials were synthetized with nickel loadings varying from 2 to 8 wt.% by using a one-pot hydrothermal synthesis technique. The catalysts were characterized by SAXD, XRD, TEM/EDS, H_2-TPR, CO_2-TPD, H_2 chemisorption, TGA-MS, and tested in DRM assuming isothermal conditions at 750°C (under $CH_4/CO_2/Ar = 1/1/8$, and 100 ml/min total flow). The outlet gases were analyzed by a micro gas chromatograph (490 Varian Micro-GC). The studied samples revealed highly dispersed Ni species in the KIT-6 structure, leading to high activity in DRM at 750°C. On the contrary, when Ni is impregnated on KIT-6 samples, larger Ni^0 particles are observed which are prone to deactivation.

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RDF-waste-fuel-based catalysts for hydrogen production by methanol degradation

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Keywords: RDF fuel, nanoporous carbon, catalysts support

Every day large quantities of municipal and industrial waste are deposited in the landfills of Bulgaria. Meanwhile, cities continue to expand and often overload local waste management systems. In some European countries, landfilling has been reduced to zero, by using waste as an alternative fuel. RDF (Refuse Derived Fuel) is a mixture of industrial and municipal waste and usually contains highly flammable components (paper, plastic, etc.). The main characteristics of solid fuel derived from waste are the energy value, ash content and moisture content. Solid waste fuel is used dominantly in industrial and thermal power plants. RDF is mainly used within the European Union - in countries with high standard of waste recycling, such as Austria, Germany, Netherlands.

It is well known that the physico-chemical properties of supports affect significantly the activity of the catalysts obtained. The main objective of the present study is to utilize the RDF fuel obtained by processing it into liquid and gas products to be used as energy sources, and to produce solid product (porous carbon). The raw materials used were waste from roof-covering materials, made of polyvinyl chloride and polyolefins. The aim is to use the obtained porous carbon as a support for preparation of catalyst by applying a suitable active phase on its surface. The catalyst obtained is intended to be used for methanol decomposition, leading to production of hydrogen as a fuel. An additional contribution is the utilization of waste products from the industry and construction of buildings. The relationship between the physico-chemical properties of the porous carbons obtained and their applicability to be used as active phase supports for the preparation of high quality catalysts was studied. The investigations allow us to determine the treatment conditions for obtaining porous carbon with optimal characteristics for applications as catalyst support.

The most suitable raw materials have been found, and effective surface modification methods and treatment conditions have been devised to obtain effective porous carbons, that are used as appropriate supports for preparation of high effective catalyst in the process of methanol degradation for hydrogen production.

Acknowledgments

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Effect of MO_2 (M=Ce, Zr, Sn) doping in copper-titania composites on the formation of catalytic active sites for VOCs oxidation

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Keywords: copper-titania doped oxides, ethyl acetate oxidation, catalytic sites regulation

Transition metal oxide composites have a significant potential as catalysts due to their low cost, availability and possibility to increase the catalytic activity *via* improved dispersion, formation of solid solutions or generation of synergistic effects [1]. Copper oxide is generally reported as suitable catalyst for environmental remediation. Its dispersion and catalytic activity in total oxidation of VOCs could be strongly increased using TiO_2 as a support [2]. To avoid the main challenge of these catalysts related to the copper promoted sintering of TiO_2, doping with different metal oxides is suggested [3-5]. This study is focused at the effect of MO_2 (M=Ce, Zr, Sn) doping on the catalytic behaviour of CuO_2-TiO_2 in total oxidation of ethyl acetate (EA) as a representative VOCs. Binary mesoporous TiO_2-MO_2 (Ti:M=1:1) oxides were initially prepared by hydrothermal synthesis using CTAB as a template. Copper oxide (8wt.% Cu) was supported on them by incipient wetness impregnation with aqueous solution of $CuNO_3$ (WI) or by deposition of copper ammonia complex, followed by its hydrolysis (CH) and calcination at 773 K. The obtained materials were characterized by XRD, TEM, SEM, XPS, UV-Vis, FTIR and TPR.

It was assumed that the catalytic behaviour of CuTiM oxide composites in total oxidation of EA is determined by the formation of interface layer and the stabilization of small CuO crystallites on it. Their formation is regulated by the mechanism of copper precursor interaction with the TiO_2-MO_2 matrix. The electronegativity and the metal ionic radius of dopant provide variations in the active redox pairs in the interface layer.

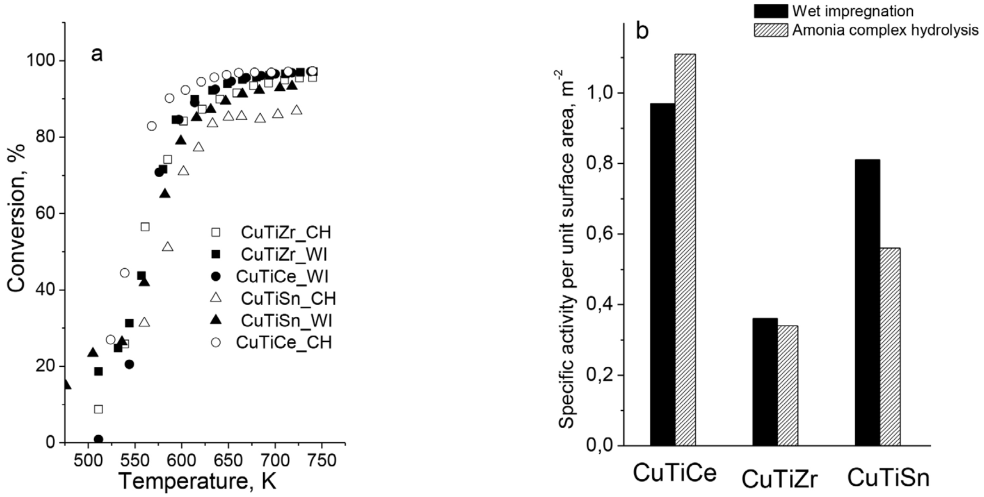

Figure 1. Conversion (a) and specific activity (b) on various catalysts

Acknowledgments

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Biomass based nanoporous carbon as catalyst support for hydrogen production

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Keywords: biomass, hydrogen, methanol, decomposition, catalysts

Hydrogen is considered as the fuel of the future, however there are some problems connected with storage of this highly flammable gas. Hydrogen is light and extremely powerful rocket propellant, with low molecular weight and burns with extreme intensity. Today, liquid hydrogen is the signature fuel of the American space program and is used by other countries for launching satellites. Hydrogen is also intended to be used for fuel for cars and boats, for the energy needs of buildings, and as an energy storage medium. Hydrogen can be produced by steam reforming of hydrocarbons, water electrolysis or by other methods. Catalytic methanol decomposition is promising method for steam reforming. Decomposition of methanol is reliable way to produce high purity hydrogen. Porous carbons are appropriate to be used in heterogeneous catalysis because they satisfy most of the support properties required. Advantages of the porous carbons is their stability and the possibility to control the pore structure, particle size [1].

The aim of the present investigation is preparation on the base of agricultural waste /grape seeds/ of nanoporous carbon with texture and chemical surface properties, suitable for catalyst support for methanol degradation.

Grape seeds based activated carbon is produced by carbonization at 450 ºC for 1 h and hydropyrolysis at 750 ºC for 45 min. The obtained carbon is modified with manganese and tested as catalysts in methanol decomposition for hydrogen production. Various physicochemical techniques, such as XRD, N_2 physisorption, FTIR, UV-Vis and TPR are used for characterization of the samples.

The nanoporous carbons from grape seeds possess moderate surface area and well-developed porous structure, with considerably high amount of micro- and mesopores. The modification treatment reduces micro- and mesopore volumes due to the formation of Mn into the pores. The catalyst based on biomass carbon exhibits high catalytic activity and selectivity. The state of manganese phase and its catalytic behaviour is related to carbon structure and surface functionality. Mn catalyst represent catalytic activity above 400 ºC with a steep increase in the conversion up to 35% at 460 ºC. Data show that catalytic activity is favored by the location of manganese species into the mesopores of carbon support. Catalytic activity of the obtained catalyst is strongly suppressed by the location of the active phase in the less accessible for the reactant micropores. It appears that catalytic selectivity is also influenced by the Mn oxidative state, as Mn^{3+}/Mn^{4+} ions increase the ability for methanol decomposition to CO.

Acknowledgments

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Subnanometer cluster-based catalysts for highly selective oxidative dehydrogenation of cycloalkanes

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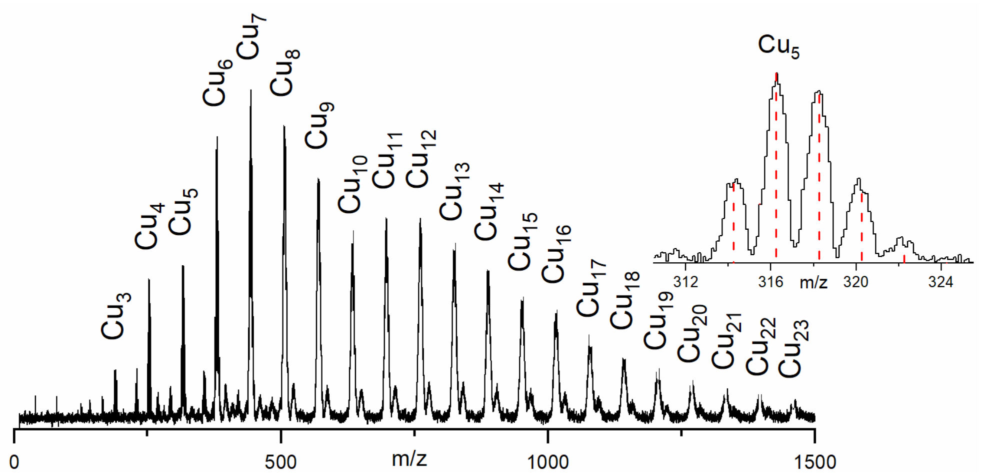
Keywords: metal cluster, copper, dehydrogenation, cyclohexene

The design and understanding of highly selective catalysts, which play an important role in industrial processes and environmental protection, remains a steady challenge in current research and applications. The aim of the present study is to identify highly active and selective catalysts for the industry central dehydrogenation reactions. On this path, we use catalysts made of well-defined subnanometer size metal clusters made of a handful of atoms. For the preparation and the characterization of such catalysts, we employ mass spectrometry methods. In this study, the catalysts are produced in a gas aggregation source by magnetron sputtering of a copper target, where clusters of various sizes (from a single atom up to several tens of atoms) and charge form a molecular beam. The beam of clusters is then guided by two linear octupoles towards a quadrupole mass selector, where the desired cluster with single atomicity is extracted from the beam. Next, these clusters of single size are deposited on the catalyst substrate. The amount of catalyst applied on the support is controlled and a metal loading of the equivalent of 5 and 10 % of an atomic monolayer equivalent surface coverage is applied to avoid the aggregation of cluster upon their landing on the support. As a prototype reaction, the gas-phase catalytic oxidative dehydrogenation of cyclohexene is chosen, performed at a pressure of 800 Torr in the temperature range of 50-400 °C. The reaction products are analyzed by real-time mass spectrometry in a custom test equipment. The results demonstrate the atomic efficiency and performance control by the size of copper clusters, by changing the size of the catalytic moiety in an atom-by-atom fashion.



Left: Mass spectrum of positively charged copper clusters produced in the cluster source, optimized for Cu_3-Cu_{23} clusters. Right: Resolved isotopic distribution of the copper pentamer (dashed line - calculated intensities according to isotopic composition)

Acknowledgments

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T02: Catalytic solutions for energy-related challenges

Pre-treatment in water fluid as an approach to the synthesis of highly active OCM catalyst

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Keywords: oxidative coupling of methane, catalyst synthesis, water fluid, silica gel

Oxidative coupling of methane (OCM) is an attractive one-step method to produce ethane and ethylene from the natural gas. Among catalysts tested in this reaction, NaWMn/SiO_2, which is conventionally prepared by wetness impregnation of a silica gel as a support, demonstrates the best performance. However, despite a nearly 30-year history of this system, its operation mechanism remains disputable.[1] It is generally accepted that the phase composition of as-prepared catalyst includes Na_2WO_4, Mn_xO_y (mainly Mn_2O_3) and SiO_2 in the form of tobalite. The formation of the latter in the course of the catalyst preparation that includes a high-temperature treatment (>650°C) is considered as essential for a high efficiency of the resulting catalyst. However, it is not known whether the catalytic performance can be fully assigned to the components present in the system as individual phases, or to metal ions which could modify the bulk of the silica support on some stage of the catalyst preparation. To shed light on the origin of the NaWMn/SiO_2 catalyst activity, we prepared the series of catalysts of the same chemical composition supported on various crystalline and amorphous forms of silica.

Water fluids at temperatures approaching the critical point (374°C) are known to increase the lattice mobility which results in structuring and crystallization of amorphous silica.[2] In this work we varied the parameters of the silica treatment in water fluids (temperature, fluid density, time of processing) to obtain catalyst supports using a granular silica gel (Davisil grade 646, Aldrich, 0.2-0.5 mm particle size) as a precursor. The morphology and phase composition of resulting materials were characterized using X-ray powder diffraction, scanning electron microscopy and specific surface area measurements.

It was found that material treatment with liquid water and water fluid above the critical point destroys the silica granules that is unfavourable in terms of the further utilization of the material as a catalyst support. On the contrary, the treatment in the water vapour under certain conditions made it possible to obtain granular silica samples with various texture, degree of crystallinity and phase composition, based on which NaWMn/SiO_2 catalysts were prepared.

No clear correlation of the performance of the catalysts obtained after the deposition of active components (Na, W, Mn) with the crystalline structure of the support was observed, whereas a strong effect of textural characteristics of the latter was revealed. It was concluded that the OCM catalytic activity can be assigned solely to the components deposited on the surface of the silica support. The effcharachiency of the catalysts depends on the intensity of the interaction of the support with molten sodium tungstate and on the rate of redox processes in which this melt and manganese oxide are involved.

Acknowledgments

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Mesoporous Beta zeolite catalysts for of 2-methylthiophene cracking: Effect of mesoporosity and acidity

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Keywords: Beta zeolite, desilication, desulfurization, cracking

The ever-growing worldwide focus on environmental pollution has led numerous countries to create laws and regulations to restrict gasoline sulfur content [1]. *Circa* 90% of the total sulfur present in gasoline comes from the Fluidized Cracking unit (FCC) [2]. An alternative for the desulfurization of these streams is incorporating an additive to the FCC catalyst to reduce the in situ sulfur content in gasoline by transforming organosulfurized compounds to lighter sulfur products (H_2S and thiols), and heavier compounds (dibenzothiophenes and bulkier molecules). This should shift lighter compounds to the LPG range, whereas heavier ones turn to the LCO range. Thus, the purification process would not decrease quality in these fractions. The current study has evaluated how changes in acidic and textural properties provoked by mesoporosity generation in the Beta zeolite affect activity and yield in the formation of H_2S in the transformation of 2-methylthiophene in an n-hexane stream. For this to be assessed, an n-hexane stream containing 100 ppm sulfur (2-methylthiophene – 2MT, used as a gasoline-range sulfurized model molecule) was used as a model molecule of gasoline. The reactional tests were conducted at 500 ^{o}C, 1 atm, and 0.83 s^{-1}. The mesoporous Beta zeolite (HB_{meso}) was obtained from the desilication of a commercial Beta zeolite (HB) according to De Oliveira *et al* [3] using a 0.3 mol/L NaOH solution at 75 °C for 15 min. The HB_{meso} and HB catalysts were characterized using the following techniques: N_2 physisorption, XRF, XRD, NH_4-TPD, pyridine FTIR, TG in oxidative atmosphere, and α-test. The desilication promoted the generation of intracrystalline mesoporosity, with a relative crystallinity loss of 29%, SAR reduction from 18 to 12, and total acidity preservation. FTIR demonstrated an increase in the number of Si-OH-Al, Al-OH, and Si-OH groups in HB_{meso} when compared to HB. Pyridine FTIR showed that mesoporosity generation promoted a reduction in Brønsted and Lewis acid sites concentration ratio (B/L) from 5.8 (HB) to 3.7 (HB_{meso}). However, the number of strong Brønsted acid sites of HB_{meso} estimated by the α-test was 38% larger than that of HB, which favored cracking and hydrogen transfer reactions. HB_{meso} demonstrated to be more active for cracking reactions than HB. Mesoporosity generation promoted higher accessibility of strong Brønsted acid sites, increasing the H_2S yield from 35% (HB) to 71% (HB_{meso}), and decreased 3-methylthiophene (3MT) formation from 39% (HB) to 12% (HB_{meso}) in the transformation of 2-MT.

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T04: Combustion kinetics and catalysis

Kinetics of homogeneous pyrolysis of *n*-butane in the medium- and high-temperature region

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Keywords: kinetics, pyrolysis, adiabatic compression, *n*-butane

The experimental results on the kinetics of gas-phase reactions obtained in a free-piston adiabatic compression reactor are of great interest due to the fundamental possibility of determining the kinetic parameters of reactions under homogeneous conditions without heterogeneous complications and in a wide temperature range from 900-1000 K to 1500 K and above [1, 2]. Pyrolysis of normal and isoalkanes C_4-C_6 was studied by this method [3]. For *n*-butane (mixture *n*-C_4H_{10} 2.0 vol.%, Ar – balance), the experimental data [4] were processed using an improved version of the kinetic treatment technique [1]. The values of the total rate of the decomposition of *n*-butane, the rate constant of this reaction (shown in the figure in comparison with the literature data) and the rate constants of the formation of products are obtained. In the temperature range of 990-1160 K, the rate constant satisfactorily coincides with the values obtained using a flow reactor (Shevel'kova et al.). In the high temperature range, the rate constant are close to the values obtained by the shock tube method (Wittig).

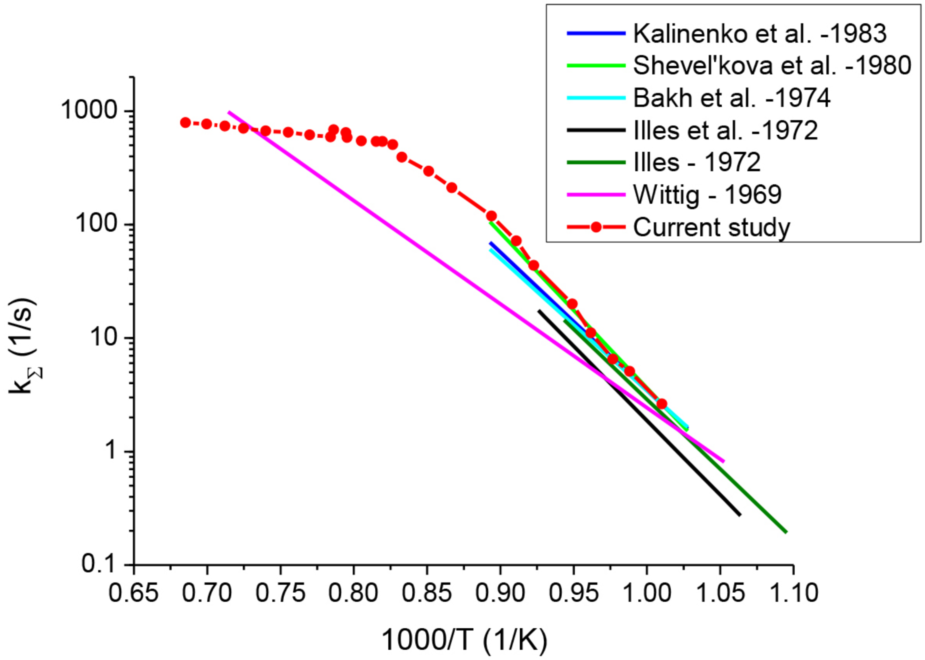

Fig. 1. Arrhenius plot comparing our result for k with previous study (data from NIST Chemical Kinetics Database).

Acknowledgments

This work was carried out within the State Program of TIPS RAS.

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MnOx-CeO$_2$ oxides supported on SBA-15 for VOCs oxidation

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Keywords: SBA-15, Mn-Ce-SBA-15, *n*-hexane combustion, toluene oxidation, propane oxidation

The design of a catalytic system for complete oxidation of hydrocarbons is an important problem of the environmental catalysis. Manganese oxide is reported to be quite promising among the metal oxides used for preparation of supported catalysts for the removal of VOC. Cerium has high oxygen storage capacity, associated with fast Ce^{4+}/Ce^{3+} redox process, making more oxygen available for the oxidation process. Mesoporous silica materials have attracted much attention because of their large surface area, uniform pore-size distribution, large pore size, and wide potential applications in the fields of separation, adsorption, and catalysis. Among the different types of mesoporous silicas, SBA-15 has attracted much interest because of its thicker pore walls and higher hydrothermal stability. This work is focused on the investigation of the structural and catalytic properties of series of mono component manganese and bi-component Mn-Ce catalysts supported on SBA-15.

Single component (Mn) and bi-component Mn-Ce samples with different Mn:Ce ratio were prepared on SBA-15 according to the ‘‘two-solvent’’ technique. The obtained materials were characterized by SAXS, N_2 adsorption-desorption, XRD, SEM and TEM microscopy, XPS, H_2-TPR, propane-TPR and O_2-TPD. The catalytic properties were tested in the complete oxidation of *n*-hexane, toluene and propane.

The modification of SBA-15 with Mn leads to the decrease of the specific BET surface area, pore volume and modification of the adsorption-desorption curve shape. This might be due to the partial pore blocking by Mn or Mn-Ce particles which is confirmed by TEM images revealing the location of Mn and Ce clusters inside the channels of SBA-15. According to the XRD data the formation of MnO_2 (pyrolusite) and Mn_2O_3 (bixbyite) is visible from the XRD patterns for a single component Mn catalyst supported on the SBA-15. No crystalline phase detected in the case of bi-component Mn-Ce on SBA-15, owing to high dispersion of the manganese and cerium oxides. This could be explained as a result of mixed Mn-Ce oxide formation, which is confirmed by EDX-TEM analysis. The predominant species on the surface of all catalyst is Mn^{3+}.The highest activity of the mono-component manganese sample in all studied reaction is explained by its higher reducibility as a result of lower interaction of the manganese oxide with the SBA-15. The fine dispersion of manganese and cerium oxide and their strong interaction in the channels of the SBA-15 molecular sieve, leads to the formation of difficult-to-reduce oxide phases and, consequently, to lower catalytic activity compared to nanocomponent manganese oxide catalyst. The mesoporous structure can prevent the agglomeration of the oxide particles, thus leading to the successful development of a new and stable catalyst for decreasing greenhouse gas emissions.

Acknowledgments

The authors express their gratitude to the National Science Fund of Bulgaria for the financial support under the Contract КП-06-Н49/4.

Reaction kinetics and mechanism of catalytic oxidation of propane on Co–ZSM-5 zeolites

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Keywords: reaction kinetics, mechanism, zeolites, catalytic combustion, propane

In recent years, the attention of scientists has focused on the use of zeolites as catalysts supports due to their thermal and acid stability and moisture resistance. They have high specific surface area which is a prerequisite for the creation of active catalytic systems. One of the best adsorbents and supports for catalytic systems used for the degradation of VOCs are zeolite aluminosilicates, thanks to their adjustable surface properties, their controllable hydrophobicity and the ability to deposit metals and metal oxides. The starting ZSM-5 materials with different Si/Al were used for the present study. Cobalt was incorporated from $Co(CH_3OO)_2.4H_2O$ by incipient wetness impregnation technique followed by drying and calcination in air 2 h at 450 ºC. The obtained materials were characterized by XRD, N_2 adsorption-desorption, TPR, TPO and XPS. The formation of different cobalt oxide species would be suggested from TPR data: extra framework Co_3O_4; CoO strongly interacting with zeolite framework and framework cobalt or some other types of cobalt silicate. XPS data show that Co^{2+} predominate on the surface.

The catalysts performance has been evaluated by tests on combustion of propane. In order to extend further the analysis of the different behaviour of the studied catalyst samples, an investigation on the kinetics and mechanism of the reaction has been carried out. The kinetic parameters were calculated by applying the method, consisting of a direct integration of the reaction rate based on data from light-off curves. As a first step a power law kinetic model has been fitted to the experimental data. In order to account for the inhibiting effect of the water vapour (both produced by the reaction or additionally added to the gas feed), the mechanistic models are modified, thus containing an additional term in the denominator, in order to take into account, the adsorption of water. Based on the values of the observed reaction orders, established by power – law kinetics model, the following mechanistic models are proposed for checking their consistence with the obtained experimental results: Mars‒van Krevelen, water molecules compete with the propane molecules for the oxidized and reduced adsorption sites; effect of slow desorption of the products is included; Langmuir‒Hinshelwood, adsorption of propane and oxygen on different types of sites, dissociative adsorption of oxygen, water molecules compete with the methane and oxygen molecules for the corresponding type of adsorption sites; Eley‒Rideal mechanism, propane molecules are impinging directly from gas phase, water molecules compete with the oxygen molecules for one and the same type of adsorption sites. It was concluded that the high catalytic activity of cobalt modified zeolites is explained by the high reducibility as result of lower interaction of the cobalt oxide with the supports. The observed insignificant changes in the zeolite structure, morphology, oxide particle size and oxide phases after reaction reveal that the zeolite structure can prevents the agglomeration of the oxide particles, thus giving new opportunities for development of stable catalyst for prevention of greenhouse gas emissions.

Acknowledgments

The authors express their gratitude to the National Science Fund of Bulgaria for the financial support under the Contract КП-06-Н49/4.

T05: Exploring reaction mechanisms

Nucleation and growth kinetics of lithium phosphate precipitation

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Keywords: microfludics, well-stirred, homogeneous, heterogeneous, nucleation

Microfluidics offers a great opportunity to study crystallization. By simultaneously injecting lithium chloride and sodium phosphate at equal flow rates into a Y-shaped microchannel, the growth of individual polycrystalline lithium phosphate particles was investigated along and transverse to the flow. [1] Constant growth is observed parallel to the flow because of the stationary concentration field, while, apart from diffusion, advective forces contribute to the growth transverse to the direction of flow.

A well-stirred system was also employed to study the mechanism of nucleation by measuring turbidity with a uv-vis spectrophotometer at various temperatures. The reaction rate scales with the reactant concentration according to a power law. At high supersaturation, the mechanism is mostly dominated by homogeneous nucleation and at low supersaturation, heterogeneous nucleation is the dominant mechanism. The microstructure of the particles have been characterized by SEM and XRD for both scenarios.

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The kinetic characteristic of the vacuum gas oil's oxycracking

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Keywords: kinetics, oxygen-containing compounds, oxycracking, vacuum gas oil

In the course of this study was conducted of the oxygen effect on the kinetics of the formation of oxygen-containing compounds (OCC) in the process of catalytic cracking in the presence of oxygen – oxidative catalytic cracking (oxycracking) vacuum gas oil (VGO).
Considering the complexity of the component composition of the raw materials and oxycracking products, all hydrocarbons during the analysis were divided into 8 narrow fractions in accordance with the number of carbon atoms: C_1-C_4, C_5-C_9, C_{10}-C_{12}, C_{13}-C_{16}, C_{17}-C_{21}, C_{22} -C_{30}, C_{31}-C_{35} and C_{36}-C_{40}. Taking into account that the fractions from C_1 to C_{26} are part of the target light oil products, then the main attention was directed precisely at them.

The kinetics of the formation of oxygen-containing compounds (OCC) during oxycracking of vacuum gas oil was experimentally studied. The kinetic parameters of the process of formation of oxygen-containing compounds in five target fractions under oxycracking conditions are established:

1. the average reaction rate of the formation of OCC in oxycracking products in the first 600 seconds is limited by the oxidation rate of the C_{10}-C_{12} fraction, up to 900 seconds the oxidation of the C_5-C_9 fraction (during this period, the direction/mechanism of the formation of OCC in this fraction changes), and then the fraction C_1-C_4. The presence of the induction period indicates that the formation of OCC in the C_1-C_4 and C_5-C_9 fraction occurs according to the unbranched chain mechanism, and C_{10}-C_{30} – through the chain with degenerate branching;
2. C_{17}-C_{21} shows the highes t true rate of formation of OCC among the target fractions (with the exception of the initial period from 0 to 300 seconds, when it is C_1-C_4); in the period from 1800 to 2700 seconds, the true rate of formation of OCC in the C_{22}-C_{30} fraction is higher than in the target C_1-C_{21} fraction, which is associated with an intensification of the formation of OSPs with an increase in the duration of the process;
3. the values of the activation energy made it possible to establish the region of location of the processes of formation of OCC:
   - at 500°C the formation of OCC in C_5-C_9, C_{13}-C_{16} and C_{17}-C_{21} is realized in the external transition region; the formation of OCC in C_1-C_4 occurs at the boundary between the diffusion and kinetic, in C_{10}-C_{12} - in the purely kinetic region;
   - at 550°C, a decrease up to negative values of the activation energy of the process of formation of OCC for all studied fractions is associated with the transition of the formation of OCC in the external kinetic region.

Can the results of a chemical process be beneficial to a purpose of clinical medicine?

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Keywords: H_2O_2 cleavage, free radicals, oxidation process, oxidative stress

Pursuing the impact of glyoxal (GL) and oxalic acid (OA) on the $VO(acac)_2$-catalyzed cyclohexane oxidation by H_2O_2 has revealed the noticeable acceleration of the process in presence of these reducing agents (Fig. 1) [1]. On the other hand, the impressive pH decrease of the $VO(acac)_2$ solutions induced by H_2O_2 was detected. Presence of e.g. OA sufficiently modified the response of pH, profiles of voltammograms, UV-vis and NMR spectra to H_2O_2 additives. Further study exhibited that micro-doses (below 4 μM) of H_2O_2 already caused a similar effect, particularly on pH (Fig. 2).

We speculate that the species generated in the course of interaction between H_2O_2 and catalyst (free radicals, mainly HO•) may be responsible for the above phenomena. For example, hydroxyl radicals, due to their extremely high activity and acidity can noteworthy affect the electrochemical and electronic spectra of reaction systems. Presence of reducing agents also modifies such spectra. The acquired data led us to assume that the revealed effect may be profitable to the elaboration of a swift-tracking method (e.g. by simple pH measuring) of oxidative stress caused by free radicals. Such approach may complement the current indirect and complicated biomarkers-based techniques.

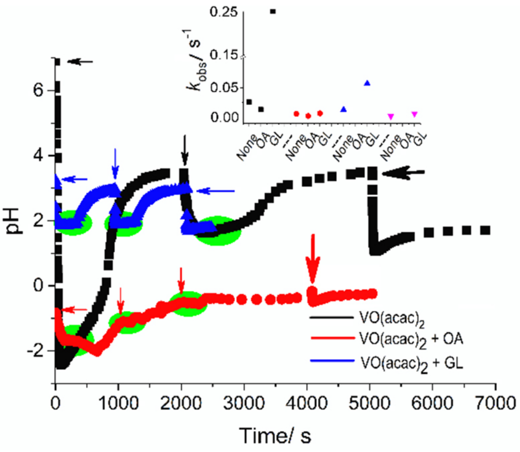

Figure 1. Yield of products (*1*), initial rate of products accumulation (*2*) and H_2O_2 consumption (*3*) in dependence on oxalic acid content. $VO(acac)_2$ = 0.06 mM, MeCN, 40 °C.

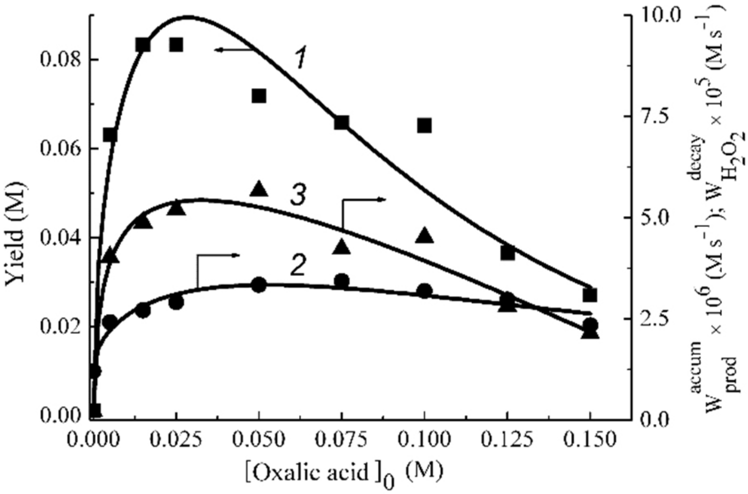

Figure 2. Kinetics of pH level altering caused by H_2O_2 addition into VO(acac)$_2$ solutions. *Inset*: the squares, circles, triangles and inverted triangles represent the impact of reducing agents on the rates (k_{obs}) of oxidation (squares) and reduction (circles) counterparts on the graph. MeCN, 20 °C.

The authors thank Prof. Andrzej Sobkowiak for numerous valuable advices.

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Investigation of the antioxidative mechanisms of ellagic acid – computational study

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Although there are numerous studies devoted to the investigation of antioxidative action of ellagic acid (**EA**) in scientific literature, the mechanisms of its activity have not yet been fully elucidated. The quantum mechanics–based test for overall free-radical scavenging activity was utilized for the investigation of antioxidative capacity of **EA** toward the HO and CCl_3OO radicals at physiological conditions. With HO·, **EA** reacts via hydrogen atom transfer and radical adduct formation mechanisms, whereas sequential proton loss electron transfer mechanism is responsible for scavenging CCl_3OO· radical. In addition, in comparison to trolox, **EA** is more reactive toward HO·, but less reactive toward CCl_3OO. The obtained rate constants for overall reaction of **EA** with both selected free radicals are in a very good agreement with the corresponding experimental values. All calculations were carried out using the M06-2X/6-311++G(d,p) theoretical model in combination with the CPCM solvation model.

Kinetic and mechanistic investigation for the ceric sulfate–oxalic acid redox reaction as an integral part of the cerium-catalyzed BZ reaction

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Keywords: kinetics, reaction mechanism, thermodynamics, cerium, oxalic acid

We present an approach for investigating kinetics and mechanism of a wide class of the redox reactions for which the rate-determining step is the decay of an intermediate complex. This approach allows one: (i) to establish experimentally the algebraic and differential process models for such a reaction based on a generalized technique for determining the stoichiometry of variable-valence metal complexes, (ii) compute the unknown thermodynamic and kinetic model parameters by means of the extended thermodynamic methods for solving the generalized inverse problem of complexation equilibria and their modelling, (iii) create the final quantitative model that covers a combined algebraic and differential process model with the computed model parameters, (iv) derive the overall rate law on the basis of all the chemical, algebraic, and differential equations that describe the rapid pre-equilibria and subsequent non-equilibrium processes within this investigated system, and also (v) draw a conclusion on the corresponding reaction mechanism using the information on the identified intermediates and the pathways of this redox reaction under study.

We also report results of applying this experimental, mathematical, and computational technique to investigate the kinetics and mechanism of the oxalic acid oxidation by cerium(IV) in sulfuric acid medium, which is an integral part of the cerium-catalyzed oscillatory Belousov–Zhabotinsky (BZ) reaction. A model of the process under study involving three parallel reaction pathways is experimentally established. For two of these pathways, the two different intermediate complexes are identified and characterized. The unknown thermodynamic and kinetic parameters are calculated for this established process model by means of the above mentioned technique. A detailed mechanism for the initial stages of this reaction is also considered, and the corresponding overall rate law is derived on the basis of all the equations that describe the rapid pre-equilibria and way out of these pre-equilibria within this investigated system. The quantitative process model is created that covers the set of the above equations with the obtained model parameters. On the basis of this model, the distribution diagrams are also constructed for the computed fractions of all the detectable cerium(IV) species in the conditions of the BZ reaction.

We show that generally the investigated redox process proceeds along the three reaction channels, i.e. the two parallel unimolecular pathways with an initial formation of the two identified intermediate complexes and a bimolecular path of the direct oxidation of oxalic acid by cerium(IV). However, under the BZ reaction conditions, the contribution of the bimolecular path becomes negligibly small, and the main reaction pathway in the oxidation of oxalic acid by cerium(IV) is realized through an intermediate mechanism with one predominating intermediate complex under study. Our results can be used for a more detailed describing the organic subset in the mechanism of the BZ reaction involving the oxalic acid and the further development of its modelling.

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T06: Homogeneous and heterogeneous photocatalysis

Redox and photochemical properties of 1,4-benzoquinone derivatives

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Keywords: 1,4-benzoquinone derivatives, quinone oxidation, photochemistry

The aim of this research was to investigate the photochemical properties and redox reactions of various substituted 1,4-benzoquinone derivatives. The kinetics of these reactions was investigated primarily by spectrophotometry. With the help of the known reaction properties (*e.g.* rate equation, acid-base properties, redox potentials), as a result of complex research, we can presumably obtain a renewable, environmentally friendly energy source, such as *e.g.* a redox flow battery.[1]

Using spectrophotometry, the photochemical stability of a 1,4-benzoquinone derivative (2-tert-butyl-1,4-benzoquinone) was determined along with the rate equation of its reaction with hydrogen peroxide. The acid dissociation constant of the hydroxyquinone formed in the photoreaction and in the reaction with hydrogen peroxide was measured. Furthermore, the rate equation of its irreversible polymerization to humic acid in an alkaline medium or by a strong oxidizing agent was investigated.

Cyclic voltammetry (CV) measurements were also performed on some other derivatives as a link between the photoreaction results and the battery. Both the electrochemical and photochemical properties are highly dependent on the identity of the quinone substituent.

Acknowledgments

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Photocatalytic degradation of carbamazepine by SBA-15 type nanoporous silica immobilized TiO_2 catalysts

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Keywords: titania, SBA-15, carbamazepine, photocatalysis

Biologically treated wastewater contain organic micropollutants, such as pharmaceutical residues. An effective and inexpensive elimination method is their photocatalytic degradation. Titania is the most active semiconductor photocatalyst under UV radiation, however its nanosized crystals have tendency to agglomerate, resulting in difficult recovery from the reaction media. Titania can be easily immobilized on nanoporous silica supports creating high surface area composites. SBA-15 type silica is a promising candidate as a support for nanosized titania particles because of its high surface area and hexagonally ordered, 5-10 nm sized, uniform pore structure.

TiO_2/SBA-15 catalysts are usually prepared by the well-known Ti-alkoxide hydrolysis method. In contrast, we have applied post synthesis incipient wetness impregnation with $TiOSO_4$. Titanium(IV) oxysulfate is a low cost byproduct of white pigment manufacturing. SBA-15 support was of commercial origin (XF-Nano) with 8 nm pore size and 523 m^2/g surface area. Titania was loaded in 17 and 23 and 40 wt. % on silica and heat treated at 550 °C. Some impregnated samples were subjected to internal hydrolysis by keeping them above ammonia/water vapor at 60 °C, followed by the same heat treatment. Textural investigations (XRD, TEM, N_2 physisorption) evidenced that finely dispersed crystalline anatase phase was formed on impregnated samples. On hydrothermally treated ones titania was amorphous, or at least the particle size was lower than 5 nm. Impregnation did not result in pore blocking of SBA-15, titania was found to homogeneously distributed in the channels and on the external surface of silica. FT-IR spectroscopic investigations revealed the incorporation of a part of titania into the silica matrix, resulting in formation of Lewis acid sites on the catalyst. The presence of sulfate species were also detected on titania.

Catalytic activity of TiO_2/SBA-15 composites were tested in photocatalytic degradation of $5 \cdot 10^{-6}$ M carbamazepine (CARB) water solutions, and was compared to commercial P25 titania. Catalytic tests were carried out in a self-developed cylindrical, batch photo-reactor with oxygen bubbling, applying 361 nm (UV-A) or 254 (UV-C) wavelength low-pressure Hg lamps, products of LightTech Co., Hungary. Catalytic results showed that by photolysis or photooxidation low drug conversion could be detected. By means of P25 catalyst CARB was eliminated in shorter than 5 minutes. TiO_2/SBA-15 catalysts are also of high activity, decomposing CARB in 10-40 min. Titania/silica catalysts with low and high amount of titania (17/40 wt.%) showed better catalytic performance, than the intermediate values, probably due to more easy accessibility of the active sites. As could be expected by the amorphous character of titania, the activity of hydrothermally treated samples were inferior to simple impregnated ones.

Decomposition intermediates of Carb was investigated by UHPLC-MS system, after preconcentration with off-line solid-phase extraction. Degradation pathways were mapped and 13 different intermediate compounds, still containing the heterocyclic structure of CARB, could be identified. Similarities and differences in reaction mechanism in comparison with different irradiation energies will be discussed.

Acknowledgments

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T07: Hydrogen production and use

Selective oxidation of CO in H_2-rich gases over supported Ag and Ag-Ce catalysts

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Keywords: Ag-Ce catalysts, preferentional CO oxidation in hydrogen rich gases

The preferentional CO oxidation in hydrogen rich gases (PROX) has been studied for application in polymer electrolyte membrane fuel cells (PEMFCs) to reduce CO in the fuel gases below 10 ppm. Very promising catalytic system that received great attention during the last years is the Co-Ce mixed oxide and Au catalysts. Silver, another member of group IB, has been scarcely investigated as a PROX catalyst in spite of its high activity in low temperature CO oxidation in absence of hydrogen. The main objective of our investigation is to establish the influence of support, silver loading and addition of CeO2 on the actyvity of Ag-based catalysts in PROX process.

The silver was loaded on different supports (SiO_2, CeO_2 and MnO_2) by impregnation with aqueous solution of $AgNO_3$. The Ag-Ce catalysts were obtained from a mixed aqueous solution of $AgNO_3$ and $Ce(NO_3)_2.6H_2O$. The prepared catalysts were characterized by XRD, TPR, high resolution SEM, O_2-TPD, XPS, EPR. All samples were calcined and pre-treated in pure O_2 2h at 450°C before the catalytic test.

The catalytic tests show that the 5% Ag/SiO_2 and 5% Ag/CeO_2 samples reach maximum activity in the temperature interval 60–100°C and at higher temperatures – 120–140°C for Ag/MnO_2. Obviously, the activity should be related to the interaction between Ag particles and the support. Since the catalyst with better performance was Ag/SiO_2, SiO_2 was chosen as a support in order to investigate the influence of Ag loading and modification with CeO_2. According to XRD data, Ag presents as metal in Ag/SiO2 samples. The formation of silver metal particles covered by Ag^{1+}, Ag_2O and $Ag_n^{\delta+}$ clusters are established after pretreatment in O_2 in $AgCeO_2/SiO_2$ catalyst by the applied physicochemical methods. SEM images show homogeneous distribution of silver and CeO_2 particles on silica support. The mean particle diameter of Ag slightly increases with increasing silver content. O_2-TPD spectra of the monometallic Ag catalysts show availability of surface and bulk oxygen species. Addition of CeO_2 increases the amount of both of them. The CO conversion curves are “volcano-shaped” and maximum is reached in the temperature interval 70–100°C. Activity increases with Ag loading. Ceria modified sample show better performance than the monometallic silver one, most probably because CeO_2 provides more surface oxygen species to Ag. The selectivity for CO oxidation increases after cerium addition. For all samples selectivity to CO_2 decreases with temperature increase. This means that at low temperature oxygen preferentially interacts with CO, but at higher – with hydrogen.

According to these preliminary results, we can conclude that silica supported silver catalysts are promising systems for selective oxidation of CO at low temperatures. Samples promoted with cerium oxide show better performance, most probably because more surface oxygen species are provided to the Ag.

Acknowledgments

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T08: Catalysis for biomass utilization

Preparation of biomass driven phenol on bifunctional hierarchical Beta zeolite

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Keywords: hierarchical Beta zeolite, bifunctional catalysts, phenol production, gas phase reaction

Over the last few years, the significant development of industrial activities has caused environmental hazards with irreparable damages to the ecosystems plus harmful consequences on human health. The replacement of fossil fuels with alternative energy sources could address this problem. Lignocellulosic biomass is a promising inexpensive renewable material that could satisfy society's requirements for chemicals and fuels. Lignin is one of the major components of lignocellulosic biomass, which is composed of methoxylated alkylphenol moieties. The conversion of methoxyalkylphenols to phenol is a promising alternative process for its preparation.

In this study, we developed hierarchical Beta zeolites modified with Pt, Ni and/or Ru, and they were investigated in a gas-phase phenol preparation from methoxyalkylphenols or ethylphenol.

The initial zeolite Beta was synthesized without template and was treated with a solution of HF and NH_4F. The monocomponent Pt (1 wt. %), Ni (10 wt. %) and Ru (5 wt. %) and bicomponent Ni (10 wt. %)-Pt (1 wt. %) and Ru (5 wt. %)-Pt (1 wt. %) hierarchical Beta zeolites were prepared by impregnation. Functionalization with Ni and Pt or Ru and Pt was done in a two-step procedure, in which first, the zeolite was modified with Pt and then the second metal (Ni or Ru) was loaded. The obtained catalysts were characterized by XRD, nitrogen physisorption, temperature-programmed reduction, UV Vis spectroscopy and solid state NMR spectroscopy. The catalysts show high catalytic activity and selectivity in a gas-phase conversion of methoxyalkylphenols or etylphenol to phenol. Among them the bicomponet hierarchical beta zeolites show higher conversion of etylphenol or methoxyalkylphenols to phenol than their monocomponent analogues. The bicomponent hierarchy Beta zeolite catalysts were examined in three consecutive reaction cycles and a slight decrease in activity was observed. Carrying out the reaction in a gas-phase phenol preparation from methoxyalkylphenols or ethylphenol and in the presence of a highly active heterogeneous catalyst is an environmental approach for phenol production.

Acknowledgements

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Nanostructured Ru-containing catalyst based on a new dendrimer of the 2nd generation: comparison with polymer catalysts in oxidative transformation of betulin

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Keywords: dendrimer based catalyst, polymer based catalyst, nanoparticles, betulin oxidation

Industrial synthesis of biologically active substances from natural compounds often requires catalyst application. Nowadays one of the research tasks in heterogeneous catalysis is to find supports for which better fixation of the catalytically active nanoparticles (NP) would be ensured without any leaching, and which will also provide stable catalyst operation under repeated use. Dendrimers belonging to a group of highly branched polymers can have a strong potential of their utilization as catalyst supports. They were previously demonstrated to be effective stabilizing agents in the synthesis of NP of various types [1, 2]. Another stabilizing polymer system widely investigated in catalysis is hypercrosslinked polystyrene (HPS) [3, 4]. Supported platinum, palladium and ruthenium find their applications for example in the aerobic oxidation of carbohydrates to carboxylic acids [5]. In this work, synthesis of catalysts based on a new pyridyl-phenylene dendrimer of the 2nd generation and a polymer, which structure is based on the same monomer AB2 as applied in dendrimer synthesis, is reported. The catalysts, containing both Ru and magnetic Fe_3O_4 NP, were evaluated in aerobic oxidation of betulin, which is naturally occurring triterpene of lupane structure. As a comparison HPS based Ru NP were also studied. The products of oxidation, namely betulinal and betulonal, are of great interest, because of their biological activity e.g. antitumor, anti-inflammatory, antiparasitic, anticancer and anti-HIV properties. Formation of NP was provided by the interactions of a metal compound with coordinating pyridine groups in pyridylphenylene dendrimer and polymer, and by sorption of the precursor into HPS followed by reduction step. Some results on betulin oxidation are given in Table 1. In the final work the catalyst properties will be correlated with their performance.

Table 1 Results on betulin oxidation

Catalyst	Mass of the catalyst, mg	Conversion, %	Catalyst/Substrate ratio	Yield of betulinal, %	Yield of betulonal, %
3 wt.% Ru-HPS	600	28	3/1	6.6	-
0.8 wt.% Ru-dendrimer	400	53	2/1	4.8	4.9
1.5 wt.% Ru-polymer	150	18	1/1	4.2	2.1

Reaction conditions: C_0(betulin)=0.045 mol/L, solvent mesitylene, 140°C, 6 h, oxidant synthetic air

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Biogas reforming and bi-reforming of methane over composite materials prepared by combustion synthesis

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Keywords: methane, biogas, synthesis-gas, combustion synthesis

Self-propagating high-temperature synthesis (SHS) method is used worldwide for the low-cost production of engineering and functional materials such as advanced ceramics, intermetallics, catalysts and magnetic materials. The method exploits self-sustaining solid-flame combustion reactions for the internal development of very high temperatures over very short periods. It therefore offers many advantages over traditional methods such as much lower energy costs, ease of manufacture and capability for producing materials with unique properties and characteristics. It was found, that method offers a good possibility for the preparation of new, active ceramic catalysts and carriers with compositions, structure and properties, which satisfy the stringent requirements of many applications. Very high interest to SHS catalyst can be explained by high activity of catalysts prepared by this methods and advantages of SHS method in comparison with traditional methods of preparation.

Resistant to temperature extremes and thermal shocks is one of the most important requirements for catalysts. Works on research of intermetallic compounds as a contact mass for conversion of methane were carried out. Method of self-propagating high temperature synthesis was used for synthesis of catalysts. Investigation of the activity of catalysts based on the initial mixture of metal oxides produced in the solution combustion synthesis process was carried out in the reaction of carbon dioxide conversion and partial oxidation of methane. The catalysts were prepared by SHS and incipient wetness supporting methods based on Al – NiO - Al_2O_3 and Al – NiO - Al_2O_3 -M systems. The analyses of Al – NiO - Al_2O_3 catalyst using XRD, SEM and BET methods provided useful information in understanding the catalytic activity of catalysts at the conversion of methane. It was found causes of optimal catalyst activity. The increase of NiO concentration and decrease of the Al concentration in the initial charge increases combustion velocity. It is connected with approach the stoichiometric composition, and therefore a greater heat generation affects the increase in the reaction rate. High temperatures (when there is more than 27% NiO and lower than 55% Al in the initial batch) affect the stabilization of the crystal lattice. The change of crystal lattice parameters influences the catalytic activity. 100% methane conversion at 750°C was carried out on the catalyst, whereas the conversion of CO_2 reached 81.7% at 900^{o}C. H_2 yield reached 99.2%, yield of CO - 99.1% in the ratio of $H_2/CO = 1.2$. Thus, effective catalysts for the production of synthesis gas from methane have been developed. These data indicate a significant advantage of the new composite materials produced by combustion synthesis process.

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Fuel production by bioethanol coupling over magnesia-alumina mixed oxide catalysts

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Keywords: Guerbet reaction, butanol fuel, ethanol coupling

Conversion of bioethanol to 1-butanol is of significant interest because 1-butanol can be renewable blending component of gasoline or precursor of a number of valuable chemicals. The alcohol coupling reaction, known as Guerbet alkylation, proceeds as direct catalytic α-alkylation, involving hydrogen autotransfer.

Different pathways were proposed for the ethanol coupling reaction over catalysts having acid-basic properties. According to the most accepted mechanism the C-C coupling occurs via the consecutive steps of (i) alcohol dehydrogenation to aldehyde, (ii) coupling of the carbonyl compounds by aldol addition, (iii) dehydration of the aldol product to get unsaturated aldehyde, and (iv) the hydrogenation of the obtained unsaturated aldehyde to saturated alcohol by the hydrogen formed in step (i) [1]. It is hardly understood how the hydrogen, formed in step (i) is preserved and used in step (iv). If the catalyst contains metal component, active in hydrogenation and dehydrogenation, it can be believed that the metal promotes the hydrogen transfer reactions from the beginning till the end of transformation series. However, because the reaction proceeds also in the absence of active metal component, an alternative mechanism had to be rationalized. An acetaldehyde catalyzed ethanol condensation mechanism was suggested, where ethanol would be the hydrogen donor.

For the complexity of the process, the catalyst must contain optimal balance of acid-base and hydrogenation-dehydrogenation functions. In the present work MgO-Al_2O_3 mixed oxide catalyst was prepared using Al-Mg hydrotalcite as precursor. The precursor of the catalyst was synthetized by co-precipitation. Metal containing derivatives were prepared by impregnating the hydrotalcite precursor with the aqueous solution of Pd, Pt, Ru, or Ni salts. The catalyst precursors were calcined at 550 °C to get the mixed oxide or its metal containing derivative. The physical-chemical properties of the catalysts were widely characterized in order to establish structure-activity relationships. The catalytic measurements were carried out in a high-pressure, fixed bed, flow-through reactor system [2] at 21 bar total pressure using H_2 or He carrier gas in the temperature range of 250-350 °C and at WHSV = 1 $g \cdot g_{cat.}^{-1} \cdot h^{-1}$. Catalysts, containing metal component, were pre-reduced in H_2 flow at 450 °C.

The MgO-Al_2O_3 mixed oxide catalyst showed moderate activity (4-30 % ethanol conversion), high liquid product yields (>95%) and high selectivity for alcohols (70-90%). Under the same reaction conditions, a metal modifier significantly improved the activity (14-65% ethanol conversion) and the alcohol yield; however, the selectivity towards alcohols decreased due to hydrodeoxygenation side reactions, especially at higher reaction temperatures (>250 °C). Relationship between the catalytic properties and the physical-chemical properties of the catalysts will be discussed.

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T09: Stochastic and deterministic reaction kinetics – theory and practice

Use of the Taylor theorem to predict kinetic curves in an arbitrary mechanism

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Keywords: numerical integration, complex reaction mechanisms, analytical solutions

The Taylor theorem is a central results in mathematical analysis, which is directly applicable in the interpretation of kinetic curves in complex mechanisms [1-2].

A kinetic model kinetic model describes the concentrations of species A_1, A_2, …, A_n through a set of ordinary differential equations:

$$\frac{\mathrm{d}[\mathrm{A}_i]}{\mathrm{d}t} = f_i\left([\mathrm{A}_1],[\mathrm{A}_2],\ldots,[\mathrm{A}_n]\right) \qquad i=1,\ldots,n$$

If the model is kinetic mass action type model, all of the functions f_i are polynomials in all of their concentration variables. The constants appearing in these functions are rate constants. Consider an arbitrary constant λ with dimension inverse time and two transformations of the time variable to dimensionless variable τ such that:

$$\tau = 1-\mathrm{e}^{-\lambda t} \quad \text{or} \quad \tau = 1-\frac{1}{1+\lambda t}$$

Consider the concentrations as a function of τ instead of *t*. The derivatives of the concentrations with respect to τ are:

$$\frac{\mathrm{d}[\mathrm{A}_i]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{A}_i]}{\mathrm{d}\tau}\lambda(1-\tau) \text{ or } \frac{\mathrm{d}[\mathrm{A}_i]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{A}_i]}{\mathrm{d}\tau}\lambda(1-\tau)^2$$

Rewrite the differential equations with τ as the independent variable:

$$\frac{\mathrm{d}[\mathrm{A}_i]}{\mathrm{d}\tau} = \frac{1}{\lambda(1-\tau)} f_i\left([\mathrm{A}_1](\tau),[\mathrm{A}_2](\tau),\ldots,[\mathrm{A}_n](\tau)\right) \qquad i=1,\ldots,n \qquad \text{or}$$

$$\frac{\mathrm{d}[\mathrm{A}_i]}{\mathrm{d}\tau} = \frac{1}{\lambda(1-\tau)^2} f_i\left([\mathrm{A}_1](\tau),[\mathrm{A}_2](\tau),\ldots,[\mathrm{A}_n](\tau)\right) \qquad i=1,\ldots,n$$

The poster will discuss how this transformed equation can be used to predict kinetic curves from an arbitrary mechanism using the Taylor theorem.

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Urea-urease clocktime-reaction in presence of zinc-cation and 2-methyl-imidazole

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Keywords: clock reaction, inhibition, pH-controlled precipitation

The main aim of our study is to realize precipitation of different compounds and the aggregation of particles (e.g., nanoparticles) in a pH clock reaction, in which the pH increases in time. To use a clock reaction in these processes, the effect of the components on the kinetics of a known clock reaction should be investigated first.

The enzymatic decomposition of urea with urease is a well-known reaction in the literature.[1] The increase of the pH is very fast after the injection of the enzyme solution. (**Fig 1)**

The activity of the enzyme can be influenced by d-group metal ions such as zinc and cobalt.[2] These metal cations are coordinated to the active part of the enzyme and slowed down the enzymatic decomposition of urea. At same time zinc cations also produce a precipitate with the enzyme around a pH of 5.70.

On the other hand, basic organic compounds, such as heterocyclic compounds can also inhibit the reaction, when it is coordinated to the nickel-part of the enzyme.[3]

The reaction mixture was placed in a 100 mL cuvette in a thermostated block and stirred with magnetic stirrer, pH was measured with an electrode and the turbidity change was followed by using an UV-Vis spectrophotometer. The pH is set with a solution of acetic acid. The investigation is essential to start the concept of the synthesis of the metal-organic framework using enzymatic reactions.

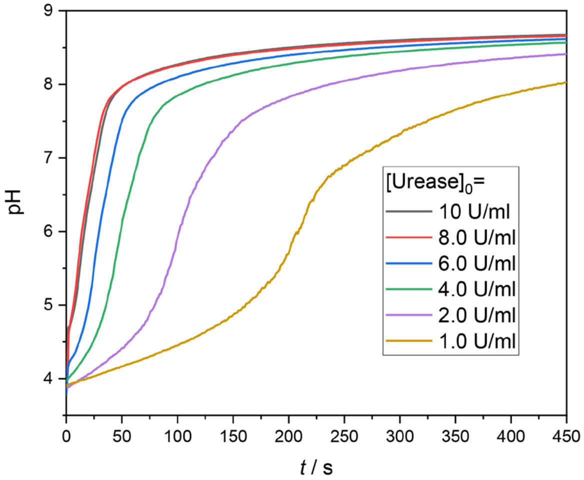

Fig 1. Urea-urease reactions with different enzyme amounts

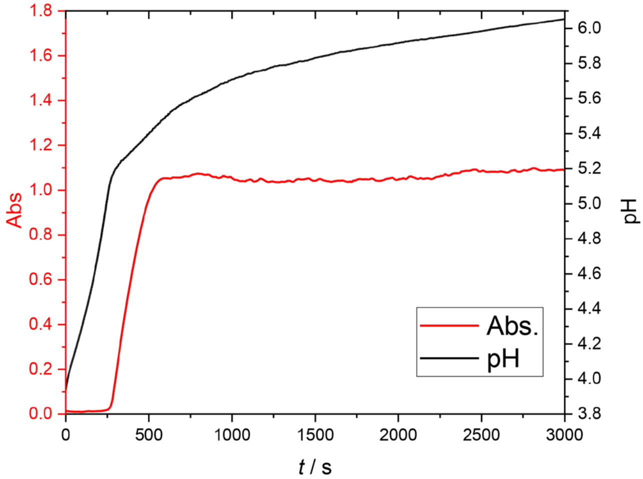

Fig 2. Urea-urease reaction in the presence of zinc and 2-methyl-imidazole

Acknowledgments

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How substituents affect the activation parameters of the reaction between 1,4-benzoquinones and hydrogen peroxide

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Keywords: quinone oxidation, Hammett substituent constants, activation parameters

The reaction between benzoquinone derivatives (QR, where R = H, Cl, Me, *tert*-Bu and 2,6-di-Cl) and hydrogen peroxide was measured for different substituted benzoquinones. The reaction itself together with the mechanisms is well-known.[1,2] The rate equation is explained by the following three-step mechanism:

$H_2O_2 \rightleftharpoons H^+ + HO_2^-$ fast pre-equilibrium, $K_a(H_2O_2)$
$QR + HO_2^- \rightarrow QR\text{-}O^- + H_2O$ rate determining step, k_b

Kinetic measurements in the 10-40 °C temperature range have been performed and the temperature dependent k_b values for the different derivatives were determined. The activation parameters (activation energy, activation enthalpy, activation entropy, activation Gibbs free energy) for the rate determining step were calculates from the Eyring- and Arrhenius-plots of the temperature dependent k_b values.

It was found the activation entropy depends on the number of substituents on the 1,4-benzoquinone ring (*approx.* -128 J mol^{-1} K^{-1} for mono- and -142 J mol^{-1} K^{-1} for disubstituted derivatives). The other activation parameters, however, depend on the electron donating or withdrawing effects of the substituents. When these parameters are plotted against Hammett substituent constants, a linear correlation can be seen with E_a and $\Delta H^‡$.

The experimentally determined activation parameter values were compared with the results of the quantum chemistry calculations at the M06L/6-311+G(d,p) level of theory employing the SMD solvation model. In line with the kinetic measurements, the oxirane ring opening step was found to be rate determining regardless of the substituents on the benzoquinone.

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A comparison of the stochastic and deterministic approach in a nucleation-growth type model of nanoparticle formation

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Keywords: kinetic differential equations, analytical solution, Gillespie algorithm, mass kernel, diffusion kernel

A kinetic model describing nanoparticle formation is presented here using both the deterministic and stochastic approaches. The model starts from a monomer unit, two of which combine in a slow second-order seed formation reaction. The other process is second-order particle growth between a particle and a monomer unit, the rate constant of which is proportional to the mass of the growing nanoparticle. Exact analytical solutions are derived for the time dependence of the concentrations [1] of all different kinds of nanoparticles. These are compared with the results of simulations using the Gillespie algorithm [2]. An interesting aspect of this system is that the very high number of different species guarantees that the individual concentrations or particle numbers are extremely low, yet the deterministic approach still gives a description that seems acceptable for interpreting experimental results.

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T10: Miscellaneous

Out-of-equilibrium synthesis of metal–organic frameworks at antagonistic concentration gradients

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Keywords: reaction-diffusion, out-of-equilibrium, cross-gradients, metal–organic framework, gels, crystallization

Metal‒organic frameworks (MOFs) are unique materials consisting of metal ions and organic linkers, having a characteristic porous structure and exceptional chemical stability. MOFs are used in gas storage, separation, heterogeneous catalysis, targeted drug delivery, electronics, etc. The design of the chemical and physical properties of these materials (i.e., morphology, average size, and polydispersity) can be achieved by controlling the fluxes of the reagents through diffusion, e.g., by using hydrogels [1]. In these methods, temporary nonequilibrium processes are necessarily occurred and affected the forming product, but finally, the systems reached their thermodynamic equilibrium. Our goal is to investigate what happens if the system is permanently kept out of equilibrium during the whole synthesis. Such conditions can be maintained by the continuous two-side feed of the gel matrix with fresh reactants.

Here we use a home-made two-channel open gel reactor [2] to synthesize zeolitic imidazolate framework-8 (ZIF-8) particles in an out-of-equilibrium reaction-diffusion (RD) process at fixed cross-gradients of reactants; these are $Zn(NO_3)_2$ and 2-Methylimidazole. The reactor is a cuboid piece of 2 m/V% agarose hydrogel, pierced with two parallel, cylindrical fluidic channels (channel distance 10 mm). The agarose gel body serves as the RD medium, where the convection and sedimentation are prevented; the channels are for the continuously renewed flows of the separated reagent solutions. In our setup, the gel is reagent-free (‘empty’) at the beginning. As we start the reagent flows, the ZIF-8 formation happens at the meeting of two counter-propagating diffusive fronts, creating a localized precipitate band. The band is sampled and then analyzed by scanning electron microscopy (SEM). We investigate how the initial concentrations, the synthesis time, and the spatial position along the concentration gradients affect the average size and polydispersity of the forming product. We compare the tendencies resulting from our out-of-equilibrium synthesis with the classical bulk synthesis and previous hydrogel-assisted methods. Our experimental findings are supported by numerical simulations with an RD model incorporating diffusion, nucleation, and crystal growth.

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Effects of Sn/Pt ratio on activity for dehydrogenation of *n*-butane over PtSn/$MgAl_2O_4$ catalyst in the presence of steam

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Keywords: butenes, 1,3-butadiene, SnPt bimetallic catalyst

1. Introduction

Dehydrogenation (DH) of *n*-butane to form butenes and 1,3-butadiene over supported Pt-Sn catalysts is a significant theme in a chemical industry. Alkane DH was usually performed with H_2 using Pt-based supported catalysts to prevent coke formation[1], however this condition is unfavorable for equilibrium of the alkene and alkadiene formation. We are inverstigating the *n*-butane DH over PtSn/$MgAl_2O_4$ in the presence of steam to remove coke on the catalyst[2]. In this presentation, we report the effects of Sn/Pt ratio on the catalytic activity and selectivity to butenes and 1,3-butadiene during the DH with stram.

2. Experimental

$MgAl_2O_4$ (spinel, surface area = 100 m^2/g) was prepared by an impregnation method using γ-Al_2O_3 and $Mg(NO_3)_2$ aqueous solution. A support precursor was calcined at 550 °C for 2 h under air flow and at 800 °C for 4 h in a muffle furnace. The PtSn/$MgAl_2O_4$ (Sn/Pt molar ratio = 2.0, 4.5, and 6.5) catalysts were prepared by a stepwise impregnation method using the prepared $MgAl_2O_4$, $Pt(NH_3)_2(NO_3)_2$, and Na_2SnO_3. After the impregnation, the catalyst was prepared by calcination at 550 °C for 3 h and followed by reduction at 550 °C for 3 h. Sodium ions remaining in the catalyst was removed by washing the catalysts precursor before the calcination. The loadings of Pt were adjusted to 1.0 wt%.

The DH was typically performed at 550 °C for 6 h using a fixed-bed continuous flow reactor (cat. weight = 0.50 g, *n*-butane/He/H_2O = 1/4/3, total flow rate = 99 ml/min).

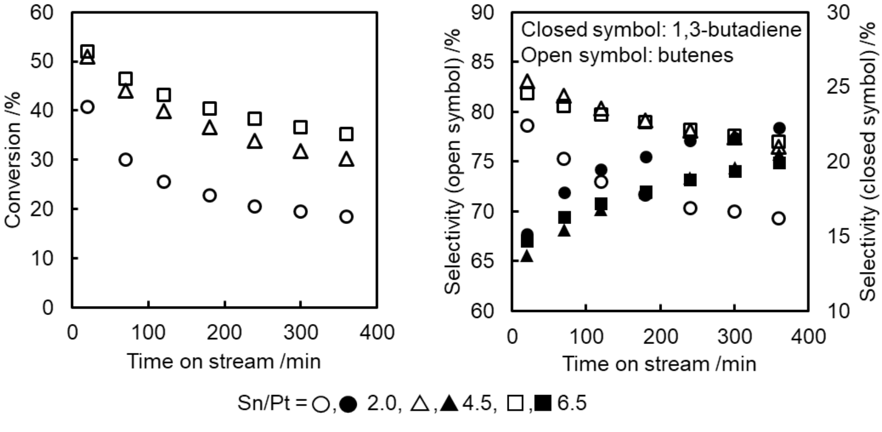

Fig. 1.

3. Results and discussion

The conversion and selectivity to butenes and butadiene were summarized in Fig.1. The initial conversion obtained by the Sn/Pt = 2.0 catalyst was lower than these obtained by the Sn/Pt = 4.5 and 6.5 catalysts. With increasing the Sn/Pt ratio, the deactivation during the reaction was improved. The selectivities to 1,3-butadiene increased with the decreasing selectivities to butenes, indicating that highly active species for alkane DH decreased due to coke formation. The degree of the deactivation with the reaction time corresponded to Sn/Pt ratio, and the catalyst having Sn/Pt = 6.5 was the most stable among the tested catalyst. In the presentation, we discuss the relationship between the Sn/Pt ratios and the active species on these catalysts based on the performance of the catalysts.

References

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